

NGAIZA'S SERIES OF ADVANCED CHEMISTRY

PHYSICAL CHEMISTRY **New edition**

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NGAIZA EDUCATION HUB ORGANISATION (NEH)

Ngaiza education hub organisation

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PREFACE

An introduction of 2009 syllabus for advanced level of Tanzania secondary education and 2019 new NECTA format have increased the demand of books which build students' competency on various concepts. For science subjects like advanced chemistry, the demand is even higher for obvious reasons.

This book is a part of an effort to fulfill the demand for chemistry subject. It is the result of having strong desire to build students' competency in advanced chemistry. This is sweet news to hear because the book discuss intensively all matters related to physical chemistry as required by the syllabus.

Organisation

The book is organised into seven parts; **part 1** up to **7**. Each part discusses intensively particular topic(s) in the syllabus: **part 1** discusses **gases**, **part 2** discusses **solutions**, **part 3** discusses **chemical kinetics** and **part 4** discusses **chemical equilibrium**. Also **part 5** discusses **ionic equilibria**, **part 6** discusses **electrochemistry** and finally **part 7** discusses **thermochemistry**.

Each part is divided into number of chapters which discuss several matters of a particular sub-topic in accordance with the syllabus.

At the end of each chapter there is an exercise which is termed as **digging deeper exercise** reflecting its impact of digging deeper various matters discussed in the respective chapter. In this new edition, digging deeper exercises have been divided into three categories: **BINDER questions**, **REAL questions** and **HOT questions**. **BINDER** questions comprises of questions which deepen **basic understanding** of various concept discussed in a particular chapter; they act as concepts' binder! **REAL** questions comprises of questions which cover variety of **real** life scenarios. And finally **HOT** questions comprises of **higher order thinking** questions to sharpen students' critical thinking ability. Both students and teachers will find these exercises very useful.

At the end of each part there are **competency examination questions** which are very useful to students who wish to examine themselves on their understanding capacity of matters discussed in the respective part. The questions cover knowledge of all sub-topics discussed in the respective part; therefore, students are advised to attempt answering them after completing the study of all sub-topics in the chapters of the respective part. Also teachers will find questions useful in assessing students' competency on a particular topic.

Near the end of the book, there are **answers and solutions for digging deeper exercises and examination questions** for providing a guide to students on answering questions relating to different topics of physical chemistry. Students are recommended to check these solutions after an attempt of answering questions through writing down and not just through mind imagination of answers.

I hope both teachers and students will find this book helpful and interesting.

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Ngaiza Lusima.

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PART ONE

GASES

Chapter 1

GAS LAWS

INTRODUCTION

States of matter is the function of strength of intermolecular forces. If the intermolecular forces present in a substance are so weak that room temperature is enough to break them, then that substance is referred as a gaseous substance. If the intermolecular forces are slightly strong, then the room temperature will just be enough to weaken them and the substance will be referred as a liquid substance. And if the intermolecular forces are too strong for room temperature to break or even to weaken them, the substance is referred as solid substance.

So there are three common states of matter which are gaseous state, liquid state and solid state. There is a fourth state of matter which is obtained when a substance is heated to very high temperature (above 5000°C), so that the substance become the mixture of positively charged ions and electrons (after complete ionisation of the substance) and the state is known as **plasma** which is common on the sun.

It should be understood that:

The three states of matter are interchangeable; for example, gases can be converted to liquids by compressing the gas at a suitable temperature.

Gases become more difficult to liquefy as the temperature increases because the kinetic energies of the particles that make up the gas also increases.

The **critical temperature** of a substance *is the temperature at and above which vapour of the substance cannot be liquefied, no matter how much pressure is applied*. It is the minimum temperature at which gas liquefaction becomes impossible. Keeping in mind that, temperature is continuous data, critical temperature can also be stated as the maximum temperature at which gas liquefaction is possible.

Gas can be liquefied at critical temperature by applying external pressure through compression which is known as critical pressure. The **critical pressure** of a substance is therefore *the pressure required to liquefy a gas at its critical temperature*.

*Critical temperature and critical pressure of a substance are collectively known as **critical state** of the substance. The volume occupied by one mole of a gas at its critical state is known as **critical volume**.*

Variables of gaseous state

Physical condition of a gas is described by four properties which are pressure, volume, temperature and amount (number of moles) of the gas. The four properties are known as **variables of gaseous state** which may simply be defined as *basic properties which describe the entire condition of the gas*.

1. Pressure (P)

Gas exerts pressure due to collision between gas particles (molecules like oxygen gas or atoms like helium gas) and the walls of the container. The amount of pressure is therefore expected to depend on two things, namely:

- Collision frequency and
- Collision energy

Collision frequency: This is the number of collision of gas particles (hitting container's walls) per unit time. Greater collision frequency means higher pressure.

Collision energy: This is determined by kinetic energy which in turn depends on the speed of gas particles hitting the container's walls. Greater collision energy means higher pressure.

The pressure exerted by gas is actually the force exerted by gas particles hitting the wall of the container per unit area (of the wall). It is commonly expressed in millimetres of mercury (mmHg), atmosphere (atm), torr, Pascal (Pa) or kilopascal (kPa) such that:

- $1\text{atm} = 760\text{mmHg} = 101.325\text{kPa}$
- $1\text{mmHg} = 1\text{torr}$ and $1\text{kPa} = 1000\text{Pa}$

2. Volume (V)

Gas occupies the volume of the container in which it is enclosed. The volume is commonly expressed in litres (L), millilitres (mL), cm^3 , dm^3 or m^3 such that:

- $1\text{L} = 1\text{dm}^3$ and $1\text{dm}^3 = 1000\text{cm}^3$
- $1\text{L} = 1000\text{mL}$ and $1\text{mL} = 1\text{cm}^3$
- $1\text{m}^3 = 10^6\text{cm}^3$ and $1\text{L (or } 1\text{dm}^3) = 10^{-3}\text{m}^3$

Volume of the container affects the frequency of collision between gas particles and container's wall and hence it also affects the amount of pressure exerted by the gas in the container. Larger container means that each individual gas particle has to move greater distance before hitting the container's wall leading to smaller collision frequency and hence lower pressure.

3. Temperature (T)

Gases have temperature which is usually measured in degree of Celsius ($^{\circ}\text{C}$) or Kelvin scale such that; Kelvin (K) = Celsius($^{\circ}\text{C}$) + 273.

Temperature affects both the collision frequency and the collision energy and therefore affecting amount of pressure exerted by the gas. When the temperature is increased, speed and thus kinetic energy is increased too which in turn makes collision between gas particles and container's walls more energetic and more frequent as well; leading to higher pressure.

4. Amount of the gas (n)

The amount of the gas present is the number of gas particles which is given as the number of moles of gas particles. The number of moles of the gas is usually calculated from measured mass of the gas by using the following formula: $n = \frac{m}{M_r}$; where m is the mass of the gas and M_r is its molar mass.

When mass the gas is increased, the number of moles of gas particles is increased too leading to more frequent collisions between gas particles and container's walls and hence pressure of the gas is increased.

MAIN GAS LAWS

Gas laws *describe the relationship between the four variables of gaseous state*. They demonstrate properties and behaviour of gases in different conditions of temperature, pressure and volume. These laws have played a crucial role in predicting the behaviour of gases in different environments, designing and optimizing chemical reactions, developing and improving technologies, and understanding the properties of gases.

There are six main gas laws which are:

- Boyle's law
- Charles's law
- Gay-Lussac's law (also known as Amontons's law)
- Avogadro's law
- Combined gas law
- Ideal gas law

Among the six laws, Boyle's law, Charles's law and Avogadro's law are fundamental from which other three gas laws can be derived.

Also the first four gas laws (Boyle's law, Charles's law, Amontons's law and Avogadro's law) are known as **specific gas laws** or **individual gas laws**. The **individual gas laws** describe the relationship between two of the four variables of gaseous state while keeping the remaining two variables constant. This is different to the combined gas law which connects three variables and ideal gas law which connects all four variables.

Combined gas law and ideal gas law are **merger gas laws** as they are formed by combining (merging) two or more individual gas laws. As we are going to witness soon, the former is the merger of two gas laws (Boyle's and Charles's law) while the latter is the merger of three gas laws (Boyle's, Charles's and Avogadro's law).

BOYLE'S LAW

Boyle's law is the individual gas law which describes the relationship between volume and pressure of the gas when its amount and temperature are kept constant.

The law states that, "Volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature"

Thus according to Boyle's law: $V \propto \frac{1}{P}$ or $V = \frac{k}{P}$ or $PV = k$

Thus $P_1V_1 = P_2V_2 = P_3V_3 = \dots = P_nV_n$

Note:

Since $n = \frac{m}{M_r}$ and M_r is constant, if mass of the gas is fixed (constant), number of moles of the gas (n) must be constant too.

So Boyle's law is applicable when there are constant number of moles of the gas and temperature.

Qualitative explanation to justify Boyle's law

If the gas volume of a given amount of gas at a given temperature is decreased (that is, if the volume of the gas container is decreased), the gas particles will have to move shorter distance before making collision with container's wall leading to increase in collision frequency and hence pressure of the gas will increase as suggested by Boyle's law.

Real life example of Boyle's law

Breathing: As the lungs expand, the volume inside the lungs increases and the pressure inside decreases in accordance with Boyle's law (this leads to the inhalation). During the exhalation, the volume inside the lungs decreases and the pressure increases (also in accordance with Boyle's law).

Example 1

A 120cm^3 gas syringe containing 100cm^3 of gas that was compressed to certain volume. After the compression, the pressure of the gas in the syringe changed to 144.75kPa . If the atmospheric pressure is 101.325kPa , and the temperature remains unchanged, what is the new volume of the gas after compression?

Solution

Since temperature is kept constant (remains unchanged), Boyle's law is applicable.

That is $P_1V_1 = P_2V_2$ or $V_2 = \frac{P_1V_1}{P_2}$

Where $P_1 = 101.325\text{kPa}$; $V_1 = 100\text{cm}^3$, $P_2 = 144.75\text{kPa}$

Substituting $V_2 = \frac{101.325\text{kPa} \times 100\text{cm}^3}{144.75\text{kPa}} = 70\text{cm}^3$

The volume is 70cm^3 .

Example 2

In hospital, the gas pressure in a 100L cylinder of oxygen is 405.3kPa. What volume of gas can be released slowly to a patient on releasing it to an atmospheric pressure of 1atm?

Solution

$$P_1 = 405.3\text{kPa} = \frac{405.3\text{kPa}}{101.325\text{kPa/atm}} = 4\text{atm (Recall: } 1\text{atm} = 101.325\text{kPa)}$$

$$P_2 = 1\text{atm and } V_1 = 100\text{L}$$

Then by using Boyle's law:

$$P_1 V_1 = P_2 V_2 \text{ or } V_2 = \frac{P_1 V_1}{P_2} = \frac{4\text{atm} \times 100\text{L}}{1\text{atm}} = 400\text{L}$$

The volume is 400L.

CHARLES'S LAW

This is the individual gas law which describes the relationship between volume and temperature of the gas when its amount and pressure are kept constant.

The law state that, *"The volume of fixed mass of a gas varies directly proportional to its absolute temperature at constant pressure."*

Thus according to Charles' law: $V \propto T$ or $V = kT$ or $\frac{V}{T} = k$

$$\text{Thus } \frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = \dots \dots \dots \frac{V_n}{T_n}$$

Experimentally it was found that the volume of the gas increase by $\frac{1}{273}$ of its original volume for every increase of 1°C and will decrease by the same factor for every decrease of 1°C from 0°C .

- Thus if V_o is initial volume of the gas at 0°C , then volume of the gas at 273°C we would expect to be: $V_f = V_o + \frac{273}{273}V_o = 2V_o$
- So the volume of the gas will be doubled at $+273^\circ\text{C}$.
- Also the volume of the gas at -273°C we would expect to be:

$$V_f = V_o - \frac{273}{273}V_o = 0$$

So the volume of the gas is expected to be zero at -273°C . -273°C is known as **absolute zero temperature**.

This can be verified graphically as follows:

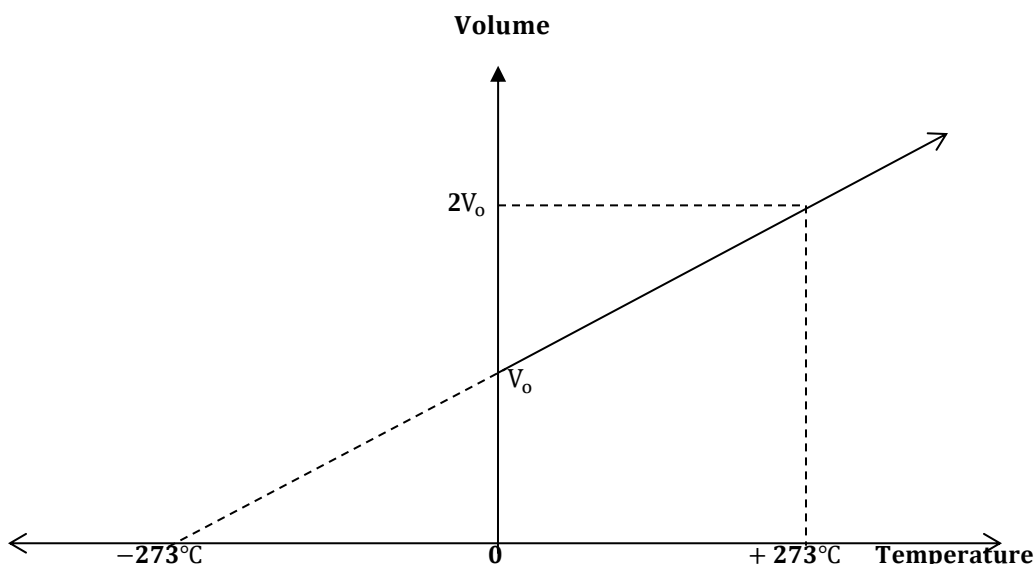


Figure 1.1 Graph for illustrating Charles's law

Definition of absolute zero temperature

This is the hypothetical temperature where by all gases were supposed to have zero volume.

It is hypothetical because all gases become liquefied before reaching -273°C (0K).

Qualitative explanation to justify Charles's law

The basic suggests that an increase in temperature would lead to an increase in pressure of the gas by increasing both collision frequency and collision energy. The only way to stop pressure from increasing under such conditions is to increase volume, which will decrease collision frequency despite the increase of collision energy and therefore keeping pressure constant. Hence for the pressure to remain constant, the increase in temperature of given amount of the gas must be accompanied with the increase in volume as suggested by Charles's law.

Real life example of Charles's law

Floating of hot-air balloon: According to Charles's law, the air inside the balloon being hotter than the air outside, has larger volume. Larger volume implies that the air inside has smaller density and hence the balloon floats.

Example 3

What change in temperature (in Celsius) required to decrease 5L of a gas at 27°C to 3L at the same pressure.

Solution

Since pressure was the same (constant), Charles's law is applicable.

From Charles's law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ or $T_2 = \frac{V_2 \times T_1}{V_1}$

Where: $V_1 = 5\text{L}$, $V_2 = 3\text{L}$ and $T_1 = 27^{\circ}\text{C} = (273 + 27)\text{K} = 300\text{K}$

Substituting $T_2 = \frac{3\text{L} \times 300\text{K}}{5\text{L}} = 180\text{K} = (180 - 273)^{\circ}\text{C} = -93^{\circ}\text{C}$

The change required is decrease in temperature from 27°C to -93°C .

COMBINED GAS LAW

Combined gas law describes the relationship between volume, pressure and temperature of fixed amount of the gas.

It can be stated as, "Volume of fixed mass of a gas varies directly proportional to absolute temperature and inversely proportional to its pressure."

That is $V \propto \frac{T}{P}$ or $\frac{PV}{T} = k$

The law can be obtained by combining Boyle's law and Charles's law as shown below:

From Boyles' law: $V \propto \frac{1}{P}$ (i)

From Charles's law: $V \propto T$ (ii)

Combining (i) and (ii) gives: $V \propto \frac{T}{P}$ or $\frac{PV}{T} = k$ (Combined gas law)

Hence $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \frac{P_3 V_3}{T_3} = \dots = \frac{P_n V_n}{T_n}$

The above final result which is also known as **general gas equation** is more useful in understanding volume of the gas when both pressure and temperature are changing while mass of the gas is kept constant.

It should be noted that:

Boyle's and Charles's law may be deduced from general gas equation.

Boyle's law can be deduced as follows:

From $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$; when temperature is constant, $T_1 = T_2 = T$

Then $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ or $P_1 V_1 = P_2 V_2$ which is Boyle's law.

Charles's law can be deduced as follows:

From $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$; When pressure is constant, $P_1 = P_2 = P$

Then $\frac{PV_1}{T_1} = \frac{PV_2}{T_2}$ or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ which is equivalent to Charles' law

Real life example of combined gas law

Helium balloon: On the surface of the earth, the balloon filled with helium will have a specific pressure, temperature and volume. If you let go of the balloon, it will fly. The temperature and air pressure start to decrease as you get higher in the air and therefore keeping $\frac{PV}{T}$ constant in accordance with combined gas law.

Example 4

50cm³ of a gas at 1atm and 27°C was compressed to 40cm³ at 37°C. Calculate the final pressure of the gas in torr.

Solution

Using combined gas law; $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

Where: $V_1 = 50\text{cm}^3$, $V_2 = 40\text{cm}^3$, $T_1 = 27^\circ\text{C} = (273 + 27)\text{K} = 300\text{K}$,

$T_2 = 37^\circ\text{C} = (273 + 37)\text{K} = 310\text{K}$ and $P_1 = 1\text{atm} = 760\text{torr}$

$$\text{Substituting } \frac{760\text{torr} \times 50\text{cm}^3}{300\text{K}} = \frac{P_2 \times 40\text{cm}^3}{310\text{K}}$$

From which $P_2 = 981.7\text{torr}$

The final pressure is approximately 982torr

GAY-LUSSAC'S LAW

Gay-Lussac's law (also known as **Amontons's law**) is the individual gas law which describes the relationship between pressure and temperature of the gas when its amount and volume are kept constant.

The law states that, "Pressure of given mass of a gas varies directly proportional to its absolute temperature provided that the volume of the gas is constant". The law is also simply known as **pressure law** of gases.

Thus according to pressure law:

$$P \propto T \text{ or } P = kT \text{ or } \frac{P}{T} = k \text{ where } k \text{ is the constant for proportionality}$$

$$\text{Hence } \frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{P_3}{T_3} = \dots = \frac{P_n}{T_n}$$

Gay-Lussac's law can also be deduced from general gas equation as follows:

$$\text{From } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}; \text{ When volume is constant, } V_1 = V_2 = V$$

$$\text{Then } \frac{P_1 V}{T_1} = \frac{P_2 V}{T_2} \text{ or } \frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which is equivalent to Pressure law}$$

Qualitative explanation to justify Gay-Lussac's law

When the temperature of given amount of a gas in a certain container is increased, speed and thus kinetic energy is increased too which in turn increases both collision frequency and collision energy. The increase in collision frequency and collision energy as consequence of temperature rise, makes the pressure to raise as suggested by Gay-Lussac's law.

Real life example of Gay-Lussac's law

Reading of pressure gauge of the tyre: The pressure reading of the car tyre is higher when the car is travelling over hot region than it was when the car was in the garage due to the increase in pressure as per Gay-Lussac's law.

Example 5

A cylinder of propane gas at 22°C exerted a pressure of 9 atm. When exposed to sunlight it warmed up to 32°C. What is the new pressure in the container?

Solution

Given that:

$$P_1 = 9 \text{ atm}, T_1 = 22^\circ\text{C} = 295\text{K}, T_2 = 32^\circ\text{C} = 305\text{K}$$

Then by using Gay-Lussac's law;

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ or } P_2 = \frac{T_2}{T_1} \times P_1 = \frac{305\text{K}}{295\text{K}} \times 9\text{atm} = 9.3\text{atm}$$

The new pressure is 9.3atm.

AVOGADRO'S LAW

This is the individual gas law which describes the relationship between volume and amount (number of moles) of the gas when its pressure and temperature are kept constant.

The law states, "Volume of all gases varies directly proportional to their number of moles at constant temperature and pressure."

Thus according to Avogadro's law:

$V \propto n$, or $V = kn$ or $\frac{V}{n} = k$ where k is the proportionality constant

$$\text{Thus } \frac{V_1}{n_1} = \frac{V_2}{n_2} = \frac{V_3}{n_3} = \dots = \frac{V_n}{n_n}$$

If $V_1 = V_2 = V$ (Equal volume)

Then the equation $\frac{V_1}{n_1} = \frac{V_2}{n_2}$ becomes;

$\frac{V}{n_1} = \frac{V}{n_2}$ or $n_1 = n_2$ and hence Avogadro's law can alternatively be stated as follows:

"Equal volume of different gases at constant conditions of temperature and pressure contain the same number moles (or molecules)."

Qualitative explanation to justify Avogadro's law

Here the basic suggests that an increase in the number of gas particles (at constant temperature) would lead to an increase in pressure of the gas by increasing collision frequency. The only way to stop pressure from increasing under such conditions is to increase volume, which will decrease collision frequency despite the increase of amount of the gas and therefore keeping pressure constant. Hence for the pressure to remain constant, the increase in number of moles of the gas at given temperature and pressure must be accompanied with the increase in volume as suggested by Avogadro's law.

Real life example of Avogadro's law

A balloon filled with helium weighs much less than an identical balloon filled with air: Avogadro's law implies that equal volumes contain equal numbers of molecules, when pressure and temperature are held constant. Since both balloons contain the same number of molecules, and since helium atoms have lower mass than either oxygen molecules or nitrogen molecules in air, the helium balloon is lighter.

Example 6

A cylinder with a movable piston contains 4g of helium at room temperature. More helium was added to the cylinder and the volume was adjusted so that the gas pressure remained the same. How many grams of helium were added to the cylinder (kept at the same room temperature) if the volume was changed from 5L to 8L?

Solution

Since both temperature and pressure were kept constant, Avogadro's law is applicable.

$$\text{Thus } \frac{V_1}{n_1} = \frac{V_2}{n_2} \text{ or } n_2 = \frac{V_2}{V_1} \times n_1$$

$$n_1 = \frac{4\text{g}}{4\text{g/mol}} = 1\text{mol}, V_1 = 5\text{L and } V_2 = 8\text{L}$$

$$\text{Substituting } n_2 = \frac{8\text{L}}{5\text{L}} \times 1\text{mol} = 1.6\text{mol}$$

$$\text{Thus number of moles to be added} = n_2 - n_1 = (1.6 - 1)\text{mol} = 0.6\text{mol}$$

$$\text{Hence the mass of helium added is } 0.6\text{mol} \times 4\text{g/mol} = 2.4\text{g}$$

IDEAL GAS LAW

Ideal gas law describes the relationship between all four variables (volume, pressure, temperature and number of moles) of gaseous state.

It can be stated as, "Volume of all gases varies directly proportional to their number of moles and absolute temperature and inversely proportional to their pressure."

Ideal gas law can be obtained by combining the three fundamental gas laws which are Boyle's law, Charles's law and Avogadro's law as shown below:

From Boyle's law: $V \propto \frac{1}{P}$; constants: n and T

From Charles's law: $V \propto T$; constants: n and P

Avogadro's law: $V \propto n$; constants: P and T

Combining the three laws: $V \propto \frac{nT}{P}$ or $V = \frac{nRT}{P}$ (All four variables of the gaseous state are changing).

Where **R** is the proportionality constant and the constant is known as **universal gas constant** or **molar gas constant**.

Hence **PV = nRT** and the result is known as **ideal gas law**. It is also more famously known as **ideal gas equation**. It is actually **the equation of state** for ideal gases because it relates all variables of gaseous state which are temperature (T), pressure (P), volume (V) and number of moles (n).

Also from the ideal gas question, $PV = nRT$; $\frac{PV}{nT} = R$

Thus; $\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$

The value of universal gas constant, R

When $n = 1$ at s.t.p, $V = 22.4 \text{ dm}^3$ (or $22.4 \times 10^{-3} \text{ m}^3$), $T = 273 \text{ K}$,

$P = 1 \text{ atm}$ (or 101325 N/m^2)

Then from $PV = nRT$ or $R = \frac{PV}{nT}$

Substituting $P = 1 \text{ atm}$, $V = 22.4 \text{ dm}^3$ (22.4L), $T = 273 \text{ K}$, $n = 1 \text{ mol}$

Thus $R = \frac{1 \text{ atm} \times 22.4 \text{ L}}{1 \text{ mol} \times 273 \text{ K}} = 0.082 \text{ atm L mol}^{-1} \text{ K}^{-1}$ or $0.082 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$

Hence the value of $R = 0.082$ must be used when:

- Volume is in litres or dm^3
- Pressure is in atmospheres

Substituting $P = 101325 \text{ N/m}^2$, $V = 22.4 \times 10^{-3} \text{ m}^3$, $T = 273 \text{ K}$, $n = 1 \text{ mol}$

Then $R = \frac{101325 \text{ N m}^{-2} \times 22.4 \times 10^{-3} \text{ m}^3}{1 \text{ mol} \times 273 \text{ K}} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

Hence the value of $R = 8.314$ must be used when:

- Given volume is in m^3
- Pressure is in Pascal (Pa) or N/m^2

Remember:

$1 \text{ atm} = 760 \text{ mmHg}$; $1 \text{ torr} = 1 \text{ mmHg}$; So $1 \text{ atm} = 760 \text{ torr}$

Applications of ideal gas law

Ideal gas law describes the behaviour of an ideal gas under any condition of pressure, volume, and temperature. This makes it more useful than any form of gas law we have discussed so far. The law is useful in different ways including:

1. Determination of molar mass of a gas

From ideal gas equation; $PV = nRT$

But $n = \frac{m}{M_r}$ then $PV = \frac{m}{M_r} \times RT$

From which: $M_r = \frac{mRT}{PV}$

Where m is the given mass of the gas in grams, g

T is the absolute temperature in Kelvin, K

P is the pressure exerted by the gas

V is the volume of the gas = volume of the container

R is the universal molar gas constant

And M_r is the molar mass of the gas in g/mol.

2. Determination of the density of the gas

Density of the gas can be expressed in two different ways, namely:

- Normal density.
- Relative density (commonly is termed as vapour density)

Normal density of a gas is the mass per unit volume of the gas at given conditions of temperature and pressure.

That is; Normal density (ρ) = $\frac{m}{V}$

Where m is the mass of the gas

V is the volume of the gas = volume of the container.

Relative density (or vapour density) of a gas is the ratio of the normal density of the gas to the normal density of hydrogen gas at the given conditions of temperature and pressure.

That is, relative density = $\frac{\rho_g}{\rho_{H_2}}$

Where ρ_g is the normal density of the gas

ρ_{H_2} is the normal density of the hydrogen gas.

From ideal gas equation; $PV = nRT$ but $n = \frac{m}{M_r}$

Then $PV = \frac{m}{M_r} \times RT$ or $PM_r = \left(\frac{m}{V}\right) \times RT$ but $\frac{m}{V}$ = Normal density, ρ

Hence $\rho = \frac{PM_r}{RT}$

If M_{H_2} and M_g are molar masses of hydrogen gas and another gas respectively

And ρ_{H_2} and ρ_g are normal densities of hydrogen gas and the another gas respectively

Then $\frac{\rho_g}{\rho_{H_2}} = \frac{PM_g}{RT} \div \frac{P \times M_{H_2}}{RT} = \frac{M_g}{M_{H_2}}$

But $\frac{\rho_g}{\rho_{H_2}} = \text{Relative density (vapour density) of the gas}$

And molar mass of hydrogen gas is 2g/mol

Hence **Relative density** = $\frac{M_g}{2g/mol}$

3. Determination of molar concentration of the gas

From ideal gas equation: $PV = nRT$ or $P = \left(\frac{n}{V}\right)RT$

But $\frac{n}{V} = \text{concentration of the gas in } \text{mol dm}^{-3}$ which is denoted as []

Then $P = []RT$

Hence [] = $\frac{P}{RT}$

4. Derivation of relationship between pressure and number of moles of gas

From ideal gas equation, $PV = nRT$ or $P = \frac{nRT}{V}$

If the volume of the container, V , is fixed at given temperature; that is V and T are constants;

Then $\frac{RT}{V} = \text{constant}$

Thus $P = \text{constant} \times n$ or $P \propto n$

Hence we can conclude that: For fixed volume of a gas at constant temperature, pressure of the gas varies directly proportional to the number of moles (or molecules) of the gas.

Since $n = \frac{m}{M_r}$; and for the given gas, M_r is constant; number of moles of the gas (n) varies directly proportional to the mass of the gas (m). And therefore it can also be said that: the pressure of the given volume of gas at given temperature increases as the mass of the gas increases.

Example 7

Calculate the molecular weight of the gas if 1.82g of the gas occupies volume of 2L at 25°C and 737mmHg. Assume the gas behaves ideally.

Solution

From ideal gas equation: $PV = \frac{m}{M_r}RT$

From which: $M_r = \frac{mRT}{PV}$

Where $m = 1.82g$, $R = 0.082$, $T = 25^\circ\text{C} = (25 + 273)K = 298K$

$P = 737\text{mmHg} = \frac{737}{760} \text{ atm}$

$M_r = \frac{1.82 \times 0.082 \times 298 \times 760}{737 \times 2} \text{ g/mol} = 23\text{g/mol}$

Hence molecular mass of the compound is 23g/mol

Example 8

A 1000cm³ bulb contains 1.197g of gas at standard pressure and temperature at 20°C. Assume the gas behaves ideally. Calculate its:

- (i) Relative density
- (ii) Normal density

Solution

$$(i) \text{ Relative density} = \frac{M_g}{2g/mol}$$

Where M_g is the molar mass of the gas

$$\text{But from } PV = nRT$$

$$\text{Where } n = \frac{m_g}{M_g}$$

$$\text{So } PV = \frac{m_g}{M_g} RT \text{ or } M_g = \frac{m_g RT}{PV}$$

Where: m_g is the given mass of the gas = 1.197g

P = standard pressure = 1atm

$$V = 1000\text{cm}^3 = 1\text{L}$$

$$T = 20^\circ\text{C} = 293\text{K}$$

$$R = 0.082$$

$$\text{Then } M_g = \frac{1.197 \times 0.082 \times 293}{1 \times 1} \text{ g/mol} = 28.76 \text{ g/mol}$$

$$\text{So relative density} = \frac{28.76 \text{ g/mol}}{2 \text{ g/mol}} = 14.38$$

Hence relative density is 14.38

$$(ii) \text{ Normal density} = \frac{m}{V} = \frac{1.197\text{g}}{1 \text{ litre}} = 1.197 \text{ g/L}$$

Hence normal density of the gas is 1.197g/L

Example 9

If 6.4g of CH_4 has pressure of 0.5atm and volume of 2 litres. Find pressure of 9g of C_2H_6 having 1litre volume under constant temperature.

Solution

$$\text{Using } n = \frac{m}{M_r}$$

$$\text{Number of moles of } \text{CH}_4 = \frac{6.4}{16} \text{ mol} = 0.4 \text{ mol}$$

$$\text{Number of moles of } \text{C}_2\text{H}_6 = \frac{9}{30} \text{ mol} = 0.3 \text{ mol}$$

$$\text{From ideal gas equation: } \frac{PV}{nT} = R = \text{constant}$$

$$\text{Then } \frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

$$\text{But } T_1 = T_2 = T (\text{temperature is constant})$$

$$\text{It follows that: } \frac{P_1 V_1}{n_1} = \frac{P_2 V_2}{n_2}$$

$$\text{Substituting } \frac{0.5 \text{ atm} \times 2 \text{ L}}{0.4 \text{ mol}} = \frac{P_2 \times 1 \text{ L}}{0.3 \text{ mol}}$$

$$\text{From which } P_2 = 0.75 \text{ atm}$$

Hence the pressure is 0.75 atm

OTHER GAS LAWS

Gas laws which are going to be discussed under this heading are Dalton's law of partial pressure and Graham's law of diffusion.

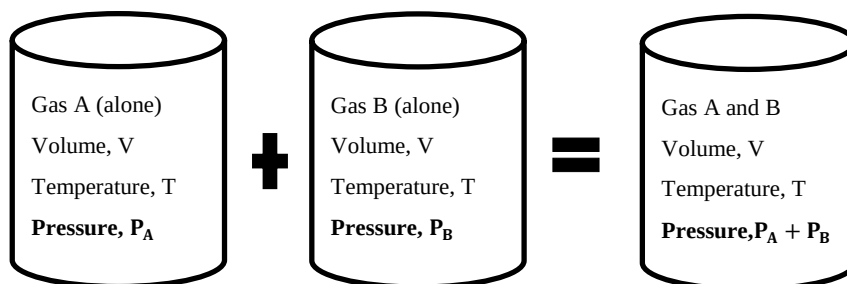
DALTON'S LAW OF PARTIAL PRESSURE

Dalton's law of partial pressure *describes the relationship between the total pressure of a mixture of non-reacting ideal gases and the partial pressures of each individual component.* Whereas, **partial pressure** is the pressure which would be exerted by a particular gas constituent in the gaseous mixture if the gas would be alone in the container at the same temperature.

Dalton's law of partial pressure state that: "The total pressure exerted in the container of the mixture of two or more gases is equal to the summation of their partial pressures provided that the gases do not react." The law implies that the pressure depends on the total number of gas particles, not on the types of particles.

Thus if the container, have two gases say A and B with their respective partial pressures, P_A and P_B

Then by Dalton's law of partial pressure: $P_T = P_A + P_B$



Qualitative explanation to justify Dalton's law of partial pressure

Gas particles are very far apart in the container. Due to this large distances between them, the particles of one gas in a mixture hit the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture is therefore becoming equals to the sum of the (partial) pressures of the individual gases as suggested by Dalton's law.

Theoretical applications of Dalton's law of partial pressure

1. Determining total pressure exerted by gaseous mixture

This can simply be done directly from the law if the partial pressures of the components are known. For example, if the mixture consist of two gases; A and B, then $P_T = P_A + P_B$

2. Determining mole fraction of an individual gas in the gaseous mixture

This can be done if partial pressure of the gas and total pressure are known. To understand this, again consider the same mixture of two gases; A and B.

From the Dalton's law of partial pressure; $P_T = P_A + P_B$

But from ideal gas equation: $PV = nRT$ or $P = \frac{nRT}{V}$

$$\text{Then } P_A = \frac{n_A RT}{V}, P_B = \frac{n_B RT}{V}$$

$$\text{Thus } P_T = \frac{n_A RT}{V} + \frac{n_B RT}{V}$$

$$P_T = \frac{RT}{V} (n_A + n_B)$$

$$\text{Then } \frac{P_A}{P_T} = \frac{n_A RT}{V} \div \frac{RT}{V} (n_A + n_B)$$

$$\frac{P_A}{P_T} = \frac{n_A}{(n_A + n_B)}$$

$$\text{But } \frac{n_A}{(n_A + n_B)} = X_A$$

Where X_A is the mole fraction of A

$$\text{Hence } X_A = \frac{P_A}{P_T}$$

3. Determining partial pressure of a gas in the gaseous mixture from its mole composition

This can be done if the mole fraction of the gas and the total pressure are known as shown below.

$$\text{From (2) above; } X_A = \frac{P_A}{P_T}$$

$$\text{Then } P_A = X_A P_T$$

Be aware of this fact!

Introducing new gas in the container with gases, does not change the partial pressures of the gases in the container because **it does both increases the total pressure in the container and decreases the mole fraction of the gases by the same proportion.**

- To understand this considers gas C is introduced in the container of volume, V, with two gases, say A and B at temperature T.

Before addition of gas C in the container:

$$P_A = X_A P_T = \left(\frac{n_A}{n_A + n_B} \right) P_T = \left(\frac{n_A}{n_A + n_B} \right) \frac{(n_A + n_B) RT}{V} = \frac{n_A RT}{V}$$

$$\text{And } P_B = X_B P_T = \left(\frac{n_B}{n_A + n_B} \right) P_T = \left(\frac{n_B}{n_A + n_B} \right) \frac{(n_A + n_B) RT}{V} = \frac{n_B RT}{V}$$

After addition of gas C in the container:

Total pressure in the container will change, say from P_T to P_{T2}

And total number of moles of gases will change from $(n_A + n_B)$ to $(n_A + n_B + n_C)$

$$P_A = X_A P_{T2} = \left(\frac{n_A}{n_A + n_B + n_C} \right) P_{T2} = \left(\frac{n_A}{n_A + n_B + n_C} \right) \frac{(n_A + n_B + n_C) RT}{V} = \frac{n_A RT}{V}$$

$$P_B = X_B P_{T2} = \left(\frac{n_B}{n_A + n_B + n_C} \right) P_{T2} = \left(\frac{n_B}{n_A + n_B + n_C} \right) \frac{(n_A + n_B + n_C) RT}{V} = \frac{n_B RT}{V}$$

Hence partial pressure of A and B remain unchanged even after addition of C in the container (provided that the gas has no reaction with A or B present in the container).

Real life example of Dalton's law of partial pressure

Breathing problem for mountain climbers: Percentage of oxygen in air is 21% by moles (or more commonly noted as by volume which does not change the meaning as long as you are familiar with Avogadro's law). Thus according to Dalton's law of partial pressure, oxygen also accounts for 21 percent of the atmosphere's total pressure. As one ascend to higher altitude, atmospheric pressure

tends to decrease which in turn decreases partial pressure of oxygen in accordance with the Dalton's law. It is difficult for oxygen to go into the bloodstream when its partial pressure decreases. So people who climb to high altitudes experience difficulty in breathing and may experience hypoxia which is life threatening medical problem.

Example 10

Nitrogen gas is collected over water at 22°C, and the volume is measured as 284mL where the total pressure of the gas is 764torr. What volume would nitrogen occupy if it was dry and the pressure was 760torr? (The vapour pressure of water at 22°C is 19.8 torr)

Solution

By Dalton's law of partial pressure: $P_T = P_{N_2} + P_{H_2O} = 764 \text{ torr}$

But $P_{H_2O} = 19.8 \text{ torr}$

Then $P_{N_2} = P_T - P_{H_2O} = (764 - 19.8) \text{ torr} = 744.2 \text{ torr}$

If temperature and number of moles (mass) of N_2 remain constant

$$P_1 V_1 = P_2 V_2 \quad (\text{Boyle's law})$$

Substituting $744.2 \times 284 = 760 \times V_2$

$$\text{From which } V_2 = \frac{744.2 \times 284}{760} \text{ mL} = 278 \text{ mL}$$

Hence the volume would be 278mL

Example 11

A mixture of helium and oxygen is used in diving tanks instead of nitrogen which at elevated pressure a large quantity is dissolved in blood producing an agonizing condition called the 'bend'. For a particular dive 40litres of oxygen at 25°C and 1atm was pumped along with 12litres of helium at 25°C and 1atmosphere into a tank with volume of 5litre. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C.

Solution

For oxygen gas: $V = 40\text{L}, T = 25^\circ\text{C} = 298\text{K}, P = 1\text{atm}$

From $PV = nRT$

$$n = \frac{PV}{RT} = \frac{1 \times 40}{0.082 \times 298} \text{ moles} = 1.64 \text{ moles}$$

$$\text{The partial pressure of oxygen in 5L container} = \frac{nRT}{V} = \frac{1.64 \times 0.082 \times 298}{5} \text{ atm} = 8 \text{ atm}$$

Thus the partial pressure of oxygen gas, P_{O_2} is 8atm

For helium gas

$V = 12\text{L}, T = 25^\circ\text{C} = 298\text{K}, P = 1\text{atm}$, From $n = \frac{PV}{RT}$

$$\text{Then } n_{\text{He}} = \frac{1 \times 12}{0.082 \times 298} \text{ moles} = 0.491 \text{ moles}$$

$$\text{So } P_{\text{He}} = \frac{n_{\text{He}} RT}{V} = \frac{0.491 \times 0.082 \times 298}{5} \text{ atm} = 2.4 \text{ atm}$$

Hence partial pressure of Helium is 2.4atm

By Dalton's law of partial pressure; total pressure, P_T , in the tank is given by:

$$P_T = P_{O_2} + P_{\text{He}} = (8 + 2.4) \text{ atm} = 10.4 \text{ atm}$$

Hence total pressure in the tank is 10.4 atm

Alternative solution

Since temperature is kept constant, Boyle's law is applicable

$$\text{That is } P_1 V_1 = P_2 V_2 \text{ or } P_2 = \frac{P_1 V_1}{V_2}$$

For oxygen gas: $P_1 = 1\text{atm}$; $V_1 = 40\text{L}$, $V_2 = 5\text{L}$

$$\text{Then } P_2 = \frac{1 \times 40}{5} \text{ atm} = 8\text{atm}$$

Hence the partial pressure of oxygen gas is 8atm

For Helium gas: $P_1 = 1\text{atm}$, $V_1 = 12\text{L}$, $V_2 = 5\text{L}$

$$\text{Then } P_2 = \frac{1 \times 12}{5} \text{ atm} = 2.4\text{atm}$$

Hence the partial of oxygen gas is 2.4atm

By Dalton's law of partial pressure: $P_T = P_{O_2} + P_{He} = (8+2.4) \text{ atm} = 10.4\text{atm}$

Hence the total pressure in the tank is 10.4atm

GRAHAM'S LAW OF DIFFUSION OR EFFUSION

To understand the Graham's law of diffusion, we must first understand the two terms accompanied with the law: diffusion and effusion. If Graham's law of diffusion (or effusion) is the main course meal, then diffusion and effusion are delicious appetizers for our meal! Another great appetizer in the menu is the rate of diffusion and of course the rate of effusion.

Let us start with diffusion! Though diffusion and effusion are interchangeably used many times, they have actually different meaning. In gas perspective, the process through which the gas particles move from one gas to another gas is what we call diffusion. It causes significant disorder in the entire system. Diffusion is not a phenomenon which we only observe in gases; we can also observe diffusion (although at slower rates) in liquids as well. The leading cause of this phenomenon is the concentration level differences. When the particles of a material are in an area of low concentration, they tend to move to the content with a high area of concentration. A straightforward example of this process is when we use perfume in one part of the room, and then we can smell it in the entire room. Diffusion is involved in this whole scenario.

On another hand, the change in volume of diffusing gas particles over time is called the rate of diffusion. That is all about, the diffusion and its rate; let us put effusion and its rate on our dining table!

When the gaseous particles move from a tiny opening into the vacuum of space or open container, then the process is called effusion. This space can be a vacuum, any other gas or atmosphere. In this case, the molecules of material try to escape from a closed container through the aperture. The best example of you can observe effusion is in the car tyre with slow puncture whereby air in the tyre is slowly escaping from the tyre into the atmosphere until the tyre become flat. We can term this as effusion of air (gas) into the atmosphere.

On another hand, the change in volume of effusing gas particles over time is known as the rate of effusion. That is all about our appetizer! But before the main dish, let us assemble the terms together and concisely defining them.

Diffusion of a gas is the spread up of gas particles throughout the space from the side of higher gas concentration to that of lower concentration.

Effusion of a gas is the escaping of the gas from the container through a tiny hole.

Rate of diffusion (or effusion) of a gas is the volume of the gas diffused (or effused) per unit time.

$$\text{So the rate of diffusion} = \frac{\text{Volume of the gas diffused (or effused)}}{\text{Time taken}}$$

Graham's law of diffusion

The Graham's law describes the relationship between rate of diffusion (or effusion) of gases and their densities at given temperature and pressure.

The law state that, "The rate of diffusion (or effusion) of gases at given temperature and pressure vary inversely proportional to the square root of their densities."

$$\text{Thus } R \propto \frac{1}{\sqrt{\rho}}$$

Where **R** is the rate of diffusion (or effusion).

ρ is the density of the gas.

$$\text{For two gases, say A and B; } R_A \propto \frac{1}{\sqrt{\rho_A}} \text{ or } R_A = \frac{k}{\sqrt{\rho_A}}$$

$$R_B \propto \frac{1}{\sqrt{\rho_B}} \text{ or } R_B = \frac{k}{\sqrt{\rho_B}}$$

$$\text{Then } \frac{R_A}{R_B} = \frac{k}{\sqrt{\rho_A}} \div \frac{k}{\sqrt{\rho_B}}$$

$$\text{From which } \frac{R_A}{R_B} = \sqrt{\frac{\rho_B}{\rho_A}}$$

Since density of the gas varies directly proportional to its molar mass then $\frac{R_A}{R_B} = \sqrt{\frac{M_B}{M_A}}$

Since the rate of diffusion = $\frac{\text{Volume of the gas diffused}}{\text{Time taken}}$

$$\text{Then } \frac{R_A}{R_B} = \frac{V_A/t_A}{V_B/t_B} = \sqrt{\frac{M_B}{M_A}}$$

If $t_A = t_B = t$ (constant time)

$$\text{Then } \frac{V_A}{V_B} = \sqrt{\frac{M_B}{M_A}}$$

If $V_A = V_B = V$

$$\text{Then } \frac{t_B}{t_A} = \sqrt{\frac{M_B}{M_A}}$$

Since volume of a gas varies directly proportional to its number of moles (according to Avogadro's law) That is $V \propto n$ or $V = kn$

$$\text{Then } \frac{V_A}{V_B} = \frac{kn_A}{kn_B} = \sqrt{\frac{M_B}{M_A}}$$

$$\text{Hence, } \frac{n_A}{n_B} = \sqrt{\frac{M_B}{M_A}}$$

Be careful!

The relationship between density of gases and their molar masses can be derived from either Avogadro's law or ideal gas equation when both temperature and pressure are kept constant.

- That is $\frac{\rho_A}{\rho_B} = \frac{M_A}{M_B}$ at constant temperature and pressure.
- So if temperature and pressure are not kept constant, the relationship does not hold and hence the formula $\frac{R_A}{R_B} = \sqrt{\frac{M_A}{M_B}}$ becomes **invalid**.

Below is the derivation of the appropriate formula for dealing with the case when temperature and pressure are not kept constant

- Consider the basic conclusion of the Graham's law which is $\frac{R_A}{R_B} = \sqrt{\frac{\rho_B}{\rho_A}}$

But from ideal gas equation it can be shown that; $\rho = \frac{PM_r}{RT}$

Thus $\rho_A = \frac{P_A M_A}{RT_A}$ and $\rho_B = \frac{P_B M_B}{RT_B}$

Thence $\frac{\rho_B}{\rho_A} = \frac{P_B M_B}{RT_B} \times \frac{RT_A}{P_A M_A} = \frac{P_B M_B T_A}{P_A M_A T_B}$

Therefore the equation: $\frac{R_A}{R_B} = \sqrt{\frac{\rho_B}{\rho_A}}$ becomes; $\frac{R_A}{R_B} = \sqrt{\frac{P_B M_B T_A}{P_A M_A T_B}}$

The above formula is applicable if both P and T for two gases (A and B) are different.

- If the pressure (P) is kept constant, ($P_A = P_B = P$) while temperatures are different, the formula becomes $\frac{R_A}{R_B} = \sqrt{\frac{P M_B T_A}{P M_A T_B}} = \sqrt{\frac{M_B T_A}{M_A T_B}}$

If temperature (T) is kept constant ($T_A = T_B = T$) while pressures are different, the formula becomes

$$\frac{R_A}{R_B} = \sqrt{\frac{P_B M_B T}{P_A M_A T}} = \sqrt{\frac{P_B M_B}{P_A M_A}}$$

- If both temperature and pressure are kept constant ($P_A = P_B = P$ and $T_A = T_B = T$), the formula becomes $\frac{R_A}{R_B} = \sqrt{\frac{P M_B T}{P M_A T}} = \sqrt{\frac{M_B}{M_A}}$

Applications Graham's law

Graham's law has various uses in daily life. The main application of Graham's law is in the separation process. Different gases with different density can be separated by using this law. Also the formula of Graham's law, can be used to compare the rates of diffusion two gases and then to calculate molar mass of an unknown gas and thereafter identifying the unknown gas from the calculated molar mass. Furthermore, it can even be used to separate the isotopes of a given gas. The typical example of this process is the separation of heavy and light uranium from isotopes of uranium. In summary, Graham's law has the following applications:

1. Separation of gases with different densities.
2. Determination of densities and molar masses of gases
3. Identification of unknown gas by calculating molar mass of unknown gas.
4. Separation of isotopes of some elements (e.g. uranium isotopes).

Example 12

A gas diffuses through a porous plug at the rate of $1.43 \text{ cm}^3/\text{s}$. Carbon dioxide diffuses through the plug at the rate of $0.43 \text{ cm}^3/\text{s}$. Calculate the molar mass of the gas.

Solution

By Graham's law of diffusion:

$$\frac{R_{\text{CO}_2}}{R_g} = \sqrt{\frac{M_g}{M_{\text{CO}_2}}} \text{ or } M_g = M_{\text{CO}_2} \left(\frac{R_{\text{CO}_2}}{R_g} \right)^2 = 44 \left(\frac{0.43}{1.43} \right)^2 = 3.98 \text{ g/mol}$$

Hence molar mass of the gas is approximately 4g/mol.

Example 13

10.25cm³ of ethane effuses through a small aperture in 40s. What is the time taken by 25 cm³ of carbon dioxide?

Solution

From Graham's law of diffusion: $\frac{R_e}{R_{\text{CO}_2}} = \sqrt{\frac{M_{\text{CO}_2}}{M_e}}$

But the rate of diffusion = $\frac{\text{Volume diffused}}{\text{Time taken}}$

$$\text{Then } \frac{R_e}{R_{\text{CO}_2}} = \frac{V_e/t_e}{V_{\text{CO}_2}/t_{\text{CO}_2}} = \frac{V_e t_{\text{CO}_2}}{V_{\text{CO}_2} t_e} = \sqrt{\frac{M_{\text{CO}_2}}{M_e}}$$

Where:

$M_{\text{CO}_2} = 44 \text{ g mol}^{-1}$, M_e = molar mass of ethane (C_2H_6) = 30 g mol^{-1} , $V_{\text{CO}_2} = 25 \text{ cm}^3$,

V_e = volume of ethane diffused = 10.25 cm^3 , t_e = time taken by ethane to diffuse = 40s

$$\frac{10.25 t_{\text{CO}_2}}{25 \times 40} = \sqrt{\frac{44}{30}}$$

From which $t_{\text{CO}_2} = 118 \text{ s} = 1 \text{ min } 58 \text{ sec}$

Hence the time taken by CO_2 is 1min58 sec.

Example 14

A certain volume of hydrogen gas takes 2min10sec to diffuse through a porous plug and an oxide of nitrogen taken 10min23sec. What is:

- the molar mass of oxide
- the formula of oxide of nitrogen.

Solution

By Graham's law of diffusion; $\frac{t_o}{t_{\text{H}_2}} = \sqrt{\frac{M_o}{M_{\text{H}_2}}}$ or $M_o = M_{\text{H}_2} \left(\frac{t_o}{t_{\text{H}_2}} \right)^2$

Where $t_o = 10 \text{ min } 23 \text{ sec} = 623 \text{ sec}$, $t_{\text{H}_2} = 2 \text{ min } 10 \text{ sec} = 130 \text{ sec}$, $M_{\text{H}_2} = 2 \text{ g/mol}$

$$\text{Thus } M_o = 2 \times \left(\frac{623}{130} \right)^2 = 46 \text{ g/mol}$$

- Hence the molar mass of the oxide is 46g/mol.
- Oxides of nitrogen are N_2O , NO , N_2O_3 , NO_2 and N_2O_4

The formula of the oxide with molar mass of 46g/mol (from a mentioned oxide) is NO_2 .

Hence the formula of oxide is NO_2 .

MISCELLANEOUS WORKED EXAMPLES ON GAS LAWS**Example 15**

For each of the following, show how the final volume (V_f) is related to initial volume (V_i) for fixed mass of a gas:

- (i) The pressure is decreased from 3atm to 1atm while the temperature remain constant
- (ii) The temperature is risen from 200K to 300K while pressure is increased from 2atm to 3atm
- (iii) The temperature is lowered from 400K to 100K while the pressure remain constant

Solution

- (i) Since temperature is kept constant, Boyle's law is applicable.

By Boyle's law: $P_i V_i = P_f V_f$

But $P_i = 3 \text{ atm}$; $P_f = 1 \text{ atm}$

Then $3V_i = 1 \times V_f$

Hence $V_f = 3V_i$

- (ii) Since both pressure and temperature have been changed, general gas equation is applicable.

Using $\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$ (General gas equation)

Where, $P_i = 2 \text{ atm}$, $P_f = 3 \text{ atm}$, $T_i = 200\text{K}$, $T_f = 300\text{K}$

Then $\frac{2V_i}{200} = \frac{3V_f}{300}$

Hence $V_f = V_i$

- (iii) Since pressure is kept constant, Charles's law is applicable.

By Charles's law: $\frac{V_i}{T_i} = \frac{V_f}{T_f}$

Where $T_1 = 400\text{K}$ and $T_2 = 100\text{K}$

Then $\frac{V_i}{400} = \frac{V_f}{100}$

Hence $V_f = \frac{V_i}{4}$

Example 16

By using Avogadro's law, deduce a relationship between the molar mass and the vapour density of a substance.

Solution

By definition:

$$\begin{aligned} \text{Vapour density (relative density of a gas)} &= \frac{\text{Density of the gas}}{\text{Density of hydrogen gas}} \\ &= \frac{\text{Mass of given volume of the gas}}{\text{Mass of an equal volume of hydrogen gas}} \end{aligned}$$

But from Avogadro's law: equal volumes of gases contain the same number of moles of gas molecules at given temperature and pressure.

That means that: Volume of one mole of the gas = volume of one mole of hydrogen gas

If follows that:

$$\text{Vapour density} = \frac{\text{Mass of one mole of the gas}}{\text{Mass of one mole of hydrogen gas}}$$

But mass of one mole = Molar mass

$$\text{Then, vapour density} = \frac{\text{Molar mass of the gas}}{\text{Molar mass of hydrogen gas}} = \frac{\text{Molar mass of the gas}}{2\text{g/mol}}$$

$$\text{Hence vapour density} = \frac{\text{Molar mass of the gas}}{2\text{g/mol}}$$

$$\text{Or Molar mass of the gas} = \text{Vapour density} \times 2\text{g/mol}$$

Example 17

A 2g sample of water is vapourised completely into 10L container at 200°C. Calculate the pressure of vapour in this container at 200°C

Solution

From ideal gas equation: $PV = nRT$

$$\text{Then } P = \frac{nRT}{V} = \frac{mRT}{M_r V}$$

Substituting given values

$$P = \frac{2 \times 0.082 \times 473}{18 \times 10} \text{ atm} = 0.43 \text{ atm}$$

Hence the pressure of vapour in the container is 0.43atm

Example 18

At room temperature pyridine is colourless liquid containing 75.9%C. 6.37%H and nitrogen. At 110°C and 630mmHg the density of the gas is 2.12g/L. Determine the molecular formula of pyridine.

Solution

$$\%C + \%H + \%N = 100\%$$

$$\text{Substituting given value: } 75.9 + 6.37 + \%N = 100$$

$$\text{From which } \%N = 17.73\%$$

Then calculating empirical formula of the given compound as follows;

Composition by element	C	H	N
Percentage of each by mass	75.9	6.37	17.73
Mass of each in 100g of the compound	75.9g	6.37g	17.73g
Number of moles of each. Using: $n = \frac{m}{M_r}$	$\frac{75.9\text{g}}{12\text{g/mol}}$ = 6.325mol	$\frac{6.37\text{g}}{1\text{g/mol}}$ = 6.37mol	$\frac{17.73\text{g}}{14\text{g/mol}}$ = 1.266mol
Dividing by the smallest number of moles in each so as to get simpler ratio	$\frac{6.325\text{mol}}{1.266\text{mol}}$ = 5	$\frac{6.37\text{mol}}{1.266\text{mol}}$ = 5	$\frac{1.266\text{mol}}{1.266\text{mol}}$ = 1

Hence the empirical formula of the compound is C_5H_5N

Calculating molar mass of the compound

$$\text{From ideal gas equation: } PV = nRT \text{ but } n = \frac{m}{M_r}$$

$$\text{Then } PV = \frac{m}{M_r} RT \text{ or } M_r = \frac{mRT}{PV} \text{ but } \frac{m}{V} = \rho$$

$$\text{Thus } M_r = \frac{\rho RT}{P}$$

$$\text{Where } \rho = \frac{2.12\text{g}}{\text{L}}, R = 0.082, T = 110^\circ\text{C} = 383\text{K}, P = 630\text{mmHg} = \frac{630}{760} \text{ atm}$$

$$\text{Then } M_r = \frac{2.12 \times 0.082 \times 383 \times 760}{630} \text{ g/mol} = 80 \text{ g/mol}$$

Let molecular formula of the compound be $(\text{C}_5\text{H}_5\text{N})_n$

$$\text{Then } 60n + 5n + 14n = 80 \text{ or } 79n = 80 \text{ or } n = 1$$

Hence the molecular formula of the compound is $\text{C}_5\text{H}_5\text{N}$

Example 19

From the ideal gas equation, deduce the following:

- (i) Boyle's law
- (ii) Charles's law
- (iii) Pressure law
- (iv) Avogadro's law
- (v) Dalton's law of partial pressure

Solution

(i) From ideal gas equation: $PV = nRT$

For fixed mass of a gas, n is constant

So if T (temperature) is constant, nRT must be also constant.

$$\text{Thus } PV = \text{constant or } V = \frac{\text{constant}}{P}$$

And hence $V \propto \frac{1}{P}$ which is equivalent to Boyle's law and states that: The volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature.

(ii) From ideal gas equation: $PV = nRT$

For fixed mass of a gas, number of moles, n is constant

So if P (pressure) is constant, $\frac{nR}{P}$ must be also constant

$$\text{Thus from } PV = nRT \text{ or } V = \left(\frac{nR}{P}\right)T \text{ but } \frac{nR}{P} \text{ constant}$$

Then $V = \text{constant} \times T$ or $V \propto T$ which is equivalent to Charles's law and it states that: The volume of fixed mass of a gas varies directly proportional to its absolute temperature at constant pressure

(iii) From ideal gas equation: $PV = nRT$

For given mass of a gas, n is constant

So if volume, V is constant, $\left(\frac{nR}{V}\right)$ must be also constant

$$\text{And from } PV = nRT$$

$$P = \left(\frac{nR}{V}\right)T \text{ but } \frac{nR}{V} = \text{constant}$$

$$\text{So } P = \text{constant} \times T$$

or $P \propto T$ which is equivalent to pressure's law and the law states that: The pressure of given mass of a gas varies directly proportional to its absolute temperature provided that the volume of the gas is constant.

(iv) From ideal gas equation: $PV = nRT$

If P and T are constant, $\frac{RT}{P}$ must be constant also.

And from $PV = nRT$ or $V = \left(\frac{RT}{P}\right)n$ but $\frac{RT}{P} = \text{constant}$

Then $V = \text{constant} \times n$ or $V \propto n$ which is equivalent to Avogadro's law and it states that: The volume of a gas varies directly proportional to its number of moles at constant temperature and pressure

(v) Consider three gases, say **A**, **B** and **C** are mixed in a container of volume, V at temperature, T

Total number of moles of all gases which will exert pressure in the container = $n_A + n_B + n_C$

Thus $P_T V = (n_A + n_B + n_C)RT$

Where P_T is the total pressure exerted by the gaseous mixture in the container

Rewriting equation $P_T V = (n_A + n_B + n_C)RT$; $P_T V = n_A RT + n_B RT + n_C RT$

From which $P_T = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \frac{n_C RT}{V}$

But $\frac{n_A RT}{V} = P_A$, $\frac{n_B RT}{V} = P_B$, $\frac{n_C RT}{V} = P_C$

Where P_A , P_B and P_C are partial pressures of A, B and C respectively

Hence $P_T = P_A + P_B + P_C$ which is the Dalton's law of partial pressure

Example 20

Show that the density of gases varies directly proportional to their molar masses.

Solution

Using density of gas, $\rho = \frac{\text{Mass of the gas, } m}{\text{Volume } V \text{ of the gas, } V} = \frac{\text{Mass of one mole of the gas}}{\text{Volume of one mole of the gas}}$

But mass of one mole of the gas = molar mass of the gas, M_r

Volume of one mole of the gas = Gas molar volume, GMV or $\rho = \frac{M_r}{GMV}$

But at given temperature, GMV is constant for all gases (From Avogadro's law).

Then $\rho = \frac{M_r}{C}$ where C is constant; so $\frac{1}{C}$ gives another constant, say k

Therefore $\rho = kM_r$ and hence $\rho \propto M_r$

Example 21

Oxygen can be converted to ozone according to the reaction equation: $3O_2(g) \rightarrow 2O_3(g)$

In an experiment conducted in a physical chemistry laboratory to study this conversion, a form six student used 12L of oxygen gas and all of this oxygen was converted to Ozone at s.t.p. Calculate the volume of Ozone produced.

Solution

From the given equation: $3O_2(g) \rightarrow 2O_3(g)$

Mole ratio of O_2 to O_3 is 3:2

But from Avogadro's law, mole ratio = volume ratio (For gases)

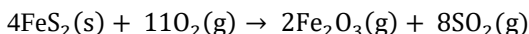
Thus 3L of O_2 produces 2L of O_3

Hence 12L of O_2 will produce $\frac{2}{3} \times 12L = 8L$

Therefore, the volume of ozone produced was 8 Litre of ozone

Example 22

Sulphur dioxide (SO₂) used in manufacturing of sulphuric acid is obtained from sulphide ores according to the following equation:



Find the mass of oxygen in grams reacting when 75 Litres of SO₂ is produced at 100°C and pressure of 1.04atm.

Solution

From the given equation: $4\text{FeS}_2(\text{s}) + 11\text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s}) + 8\text{SO}_2(\text{g})$

8L of SO₂ are produced by 11L of O₂ (For gases: mole ratio = volume ratio)

Thus 75L of SO₂ will be produced by $\frac{11}{8} \times 75\text{L}$ of O₂ = 103.125L of O₂

Thus 75L of SO₂ is produced by 103.125L of O₂

From ideal gas equation: $PV = \frac{m}{M_r}RT$ or $m = \frac{PVM_r}{RT}$

Where $P = 1.04\text{atm}$, $V = 103.125\text{L}$, $M_r = 32\text{g/mol}$, $R = 0.082$

$T = 100^\circ\text{C} = (100 + 273)\text{K} = 373\text{K}$

$$m = \frac{1.04 \times 103.125 \times 32}{0.082 \times 373} \text{ g} = 112.2\text{g}$$

Hence mass of oxygen is 112.2g

Example 23

A 2dm³ flask containing 4g of oxygen at 27°C;

- (a) What is the pressure in the flask?
- (b) When 3g of nitrogen gas is introduced in the flask (still containing oxygen gas)
 - (i) What is the total pressure exerted by the gaseous mixture in the flask?
 - (ii) What is the total number of molecules?
 - (iii) The mixture is exploded so that nitrogen gas and oxygen gas react according to the equation.
 $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$, what is the new pressure in the flask?

Solution

(a) From ideal gas equation: $PV = nRT$

But $n = \frac{m}{M_r}$ then $PV = \frac{m}{M_r}RT$ or $P = \frac{mRT}{VM_r}$

Where: $m = 4\text{g}$, $R = 0.082$, $T = 27^\circ\text{C} = (27 + 273)\text{K} = 300\text{K}$, $M_r = 32\text{g/mol}$

$$V = 2\text{dm}^3$$

$$\text{Then } P = \frac{4 \times 0.082 \times 300}{2 \times 32} \text{ atm} = 1.5375 \text{ atm}$$

Hence the pressure exerted by oxygen gas in the flask is 1.5375atm

(b) (i) When 3g of nitrogen gas is introduced in the flask:

By Dalton's law of partial pressure; total pressure exerted by gaseous mixture in the flask is given by;

$$P_T = P_{\text{O}_2} + P_{\text{N}_2}$$

But from ideal gas equation: $PV = nRT$

$$\text{From which } P = \frac{nRT}{V}$$

$$\text{Then } P_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{V} \text{ and } P_{\text{N}_2} = \frac{n_{\text{N}_2}RT}{V}$$

$$\text{Thus } P_T = \frac{n_{O_2}RT}{V} + \frac{n_{N_2}RT}{V}$$

$$P_T = (n_{O_2} + n_{N_2}) \frac{RT}{V}$$

$$P_T = \left(\frac{m_{O_2}}{M_{O_2}} + \frac{m_{N_2}}{M_{N_2}} \right) \frac{RT}{V}$$

$$P_T = \left(\frac{4}{32} + \frac{3}{28} \right) \times \frac{0.082 \times 300}{2} \text{ atm} = 2.855 \text{ atm}$$

Hence total pressure exerted by gaseous mixture in flask is 2.855 atm

$$(ii) \ n_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{4}{32} \text{ moles} = 0.125 \text{ moles.}$$

$$n_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{3}{28} \text{ moles} = 0.107 \text{ moles}$$

Using $N = nN_A$

Where N is the number of molecules of a gas

n is the number of moles of the gas

N_A is the Avogadro's number (constant) = 6.02×10^{23}

$$\begin{aligned} \text{Hence total number of molecules} &= 0.125 \times 6.02 \times 10^{23} + 0.107 \times 6.02 \times 10^{23} \\ &= 1.39664 \times 10^{23} \text{ molecules} \end{aligned}$$

Hence there are 1.39664×10^{23} molecules in the flask

(iii) If the mixture is allowed to explode: (Explosions occur for very fast chemical reactions which always occur between gases).

Equation for the reaction: $N_2(g) + O_2(g) \rightarrow NO(g)$

Since mole ratio of N_2 to O_2 is 1:1, oxygen gas present in excess.

Thus $(0.125 - 0.107)$ moles = 0.018 moles of oxygen gas remains unreacted at the end of chemical reaction

From above equation; mole ratio of N_2 (**limited reactant**) to NO is 1:2

Thus number of moles of NO produced is 2×0.107 moles = 0.214 moles

So at the end of the chemical reaction (after explosion) there are:

- 0.018 moles of unreacted oxygen gas
- 0.214 moles of produced NO(g)

Then by Dalton's law of partial pressure:

$$\begin{aligned} P_T &= P_{O_2} + P_{NO} = \frac{n_{O_2}RT}{V} + \frac{n_{NO}RT}{V} = (n_{O_2} + n_{NO}) \frac{RT}{V} \\ &= (0.214 + 0.018) \times \frac{0.082 \times 300}{2} = 2.8536 \text{ atm} \end{aligned}$$

Hence the new pressure in the flask is 2.8536 atm

Example 24

A vessel contains 8g of oxygen at 25°C and pressure of 5 atm. Assume the gas behaves ideally

- What is the volume of the vessel?
- What is the final pressure when one mole of hydrogen molecules is added at 25°C without changing volume?
- If the mixture in (b) above is now allowed to explode and allowed to cool to 25°C, what will be the final pressure in the vessel (In your calculations; neglect vapour pressure of water)

Solution

(a) From $PV = nRT$, $V = \frac{nRT}{P}$

But $n = \frac{m}{M_r}$

Thus $V = \frac{mRT}{PM_r} = \frac{8 \times 0.082 \times 298}{5 \times 32} \text{ dm}^3 = 1.2218 \text{ dm}^3$

Hence the volume of the vessel is 1.2218 dm^3

(b) By Dalton's law of partial pressure:

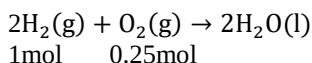
Total pressure, $P_T = P_{O_2} + P_{H_2} = \frac{n_{O_2}RT}{V} + \frac{n_{H_2}RT}{V} = (n_{O_2} + n_{H_2}) \frac{RT}{V}$

But $n_{O_2} = \frac{8}{32} \text{ moles} = 0.25 \text{ moles}$

$P_T = (1 + 0.25) \times \frac{0.082 \times 298 \text{ atm}}{1.2218} = 25 \text{ atm}$

Thus the final pressure is 25 atm.

(c) Equation for the reaction (allowing the mixture to explode means the reaction between hydrogen and oxygen is allowed to take place)



From above equation; mole ratio of oxygen to hydrogen is 1:2, thus 0.25 moles of oxygen require $(2 \times 0.25) \text{ moles} = 0.5 \text{ moles}$ of hydrogen.

Thus $(1 - 0.5) \text{ moles} = 0.5 \text{ moles}$ of hydrogen remains unreacted at the end of the reaction.

So the gas which remains after explosion (reaction) is only 0.5 moles of hydrogen gas and this amount of the gas will account for final pressure in the vessel.

That is; $P = \frac{n_{H_2}RT}{V} = \frac{0.5 \times 0.082 \times 298}{1.2218} \text{ atm} = 10 \text{ atm}$

The final pressure in the vessel is 10 atm

Example 25

A closed bulb contains 0.01 moles of helium and sample of solid ammonium chloride. The pressure of helium is measured at 27°C and is found to be 114 mmHg. The bulb is heated to 327°C where all ammonium chloride decomposed according to the equation:



The final pressure in the bulb after complete decomposition was found to be 908 mmHg. Assume the ideal behaviour, calculate;

- The partial pressure of $\text{HCl}(\text{g})$ at 327°C
- The amount of ammonium chloride originally present in the bulb

Solution

(i) Gases which present at 327°C are (after decomposition of solid NH_4Cl):

- Helium gas
- Ammonia (NH_3) gas and
- Hydrogen chloride (HCl) gas

By Dalton's law of partial pressure, total pressure exerted by gaseous mixture at 327°C is given by;

$P_T = P_{\text{He}} + P_{\text{NH}_3} + P_{\text{HCl}}$

But from the given equation, mole ratio of NH_3 to HCl is 1:1

$$\text{Thus } n_{\text{HCl}} = n_{\text{NH}_3} = n$$

$$\text{And hence } P_{\text{HCl}} = P_{\text{NH}_3} = P$$

$$\text{So } P_{\text{T}} = P_{\text{He}} + 2P$$

But P_{He} at 327°C may be found by pressure law as follows;

$$P_1 = 114\text{mmHg} \quad T_1 = 27^\circ\text{C} = 300\text{K}$$

$$\text{And } T_2 = 327^\circ\text{C} = 600\text{K}$$

$$\text{By pressure law (keeping volume constant): } \frac{P_2}{T_2} = \frac{P_1}{T_1}$$

$$\text{or } P_2 = \left(\frac{P_1}{T_1}\right) T_2 = \frac{600 \times 114}{300} \text{mmHg} = 228\text{mmHg}$$

Thus P_{He} at 327°C is 228mmHg

$$\text{But } P_{\text{T}} = P_{\text{He}} + 2P = 908\text{mmHg}$$

$$\text{Then } 908 = 228 + 2P$$

$$\text{Or } P = 340\text{mmHg}$$

Hence the partial pressure of HCl at 327°C is 340mmHg

$$\text{(ii) But } P_{\text{HCl}} = \frac{n_{\text{HCl}}RT}{V}$$

$$\text{From which: } n_{\text{HCl}} = \frac{P_{\text{HCl}}V}{RT} = \frac{340 \times V}{760 \times 0.082 \times 600}$$

$$\text{Using } PV = nRT; \quad V = \frac{nRT}{P}$$

But for helium:

When $T = 300\text{K}$ (27°C), $n = 0.01$ moles and $P = 114\text{mmHg}$

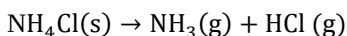
$$V = \frac{0.01 \times 0.082 \times 300 \times 760}{114} \text{dm}^{-3}$$

Then substituting the value of V in

$$n_{\text{HCl}} = \frac{340V}{760 \times 0.082 \times 600}$$

$$n_{\text{HCl}} = \frac{340 \times 0.01 \times 0.082 \times 300 \times 760}{760 \times 0.082 \times 600 \times 114} \text{ moles} = 0.0149 \text{ moles}$$

But from the given equation



Moles ratio of NH_4Cl to HCl is 1:1

Thus number of moles of NH_4Cl originally present in the flask was also 0.0149 moles

$$\text{Using } m = nM_r$$

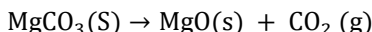
Where molar mass of NH_4Cl is 53.5g

$$\text{Then } m = 0.0149 \times 53.5 = 0.797\text{g}$$

Hence amount of NH_4Cl was approximately 0.8g

Example 26

MgCO₃ is heated in a closed vessel of 1dm³; the container is at start filled with air at 1atm and 20°C. At 800°C, the compound is completely decomposed according to the equation:



The total pressure after reaction at this temperature (800°C) is found to be 5atm. Calculate:

- The partial pressure of CO₂.
- The amount of MgCO₃ originally present in the vessel
(In your calculation neglect the volume of the solid and the change of volume of the container)

Solution

(i) From Pressure law: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ or $P_2 = P_1 \left(\frac{T_2}{T_1} \right)$

Then for air:

$$P_1 = 1\text{atm } T_1 = 20^\circ\text{C} = 293\text{K and } T_2 = 800^\circ\text{C} = 1073\text{K}$$

$$\text{It follows that: } P_2 = \frac{1\text{atm} \times 1073\text{K}}{293\text{K}} = 3.66\text{atm}$$

Thus the partial pressure of air at 800°C is 3.66atm

By Dalton's law of partial pressure:

$$P_T = P_{\text{CO}_2} + P_{\text{air}} \text{ or } P_{\text{CO}_2} = P_T - P_{\text{air}} = 5\text{atm} - 3.66\text{atm} = 1.34\text{atm}$$

Hence the partial pressure of CO₂ is 1.34 atm.

(ii) Using $n_{\text{CO}_2} = \frac{P_{\text{CO}_2}V}{RT} = \frac{1.34 \times 1}{0.082 \times 1073} \text{ moles} = 0.0152 \text{ moles}$

From the given equation:

Mole ratio of CO₂ to MgCO₃ is 1:1

$$\text{Thus number of moles of CO}_2 = \text{number of moles of MgCO}_3 = 0.0152\text{mol}$$

$$\text{Using } m = nM_r$$

$$\text{Mass of MgCO}_3 = 0.0152 \times 84\text{g} = 1.2768\text{g}$$

Hence amount of MgCO₃ was approximately 1.3g

Example 27

A sample of butane (C₄H₁₀) of unknown mass is introduced into a vessel of volume, V at 28°C and 560mmHg. To this vessel is introduced 8.6787g of Neon gas until the final pressure in the vessel is 1420 mmHg at the same temperature. Calculate the volume of the vessel and the mass of butane introduced (Atomic mass of Ne is 20).

Solution

For Butane:

$$P_b V = n_b RT \dots \dots \dots (i)$$

When Neon is introduced in the vessel:

$$P_T = P_b + P_{\text{Ne}} \quad (\text{By Dalton's law of partial pressure})$$

$$= \frac{n_b RT}{V} + \frac{n_{\text{Ne}} RT}{V} \text{ or } PV = (n_b + n_{\text{Ne}})RT \dots \dots \dots (ii)$$

It follows that $\frac{(i)}{(ii)}$ gives; $\frac{P_T}{P_b} = \frac{n_b + n_{Ne}}{n_b}$

$$\text{But } n_{Ne} = \frac{8.6787}{20} \text{ moles} = 0.434 \text{ moles}$$

And it is given that: $P_T = 1420 \text{ mmHg}$, $P_b = 560 \text{ mmHg}$

$$\text{Then } \frac{1420}{560} = \frac{n_b + 0.434}{n_b}$$

From which $n_b = 0.2826 \text{ moles}$

$$\text{But from (i); } V = \frac{n_b RT}{P_b} = \frac{0.2826 \times 0.082 \times 301 \times 760}{560} \text{ dm}^3 = 9.466 \text{ dm}^3$$

Hence the volume of the vessel is an approximately 9.5 dm³.

$$\text{Using } n = \frac{m}{M_r} \text{ or } m = nM_r$$

Thus mass of butane, $m_b = n_b M_b$

Where $n_b = 0.2826 \text{ moles}$, $M_b = 58 \text{ gmol}^{-1}$

$$\text{Then } M_b = 0.2826 \times 58 \text{ g} = 16.3908 \text{ g}$$

Hence mass of butane was approximately 16.4g

Alternative solution

By Dalton's law of partial pressure; $P_T = P_{Ne} + P_b$ or $P_{Ne} = P_T - P_b$

Where $P_T = 1420 \text{ mmHg}$; $P_b = 560 \text{ mmHg}$

$$\text{Thus } P_{Ne} = (1420 - 560) \text{ mmHg} = 860 \text{ mmHg}$$

$$\text{But } P_{Ne} = \frac{n_{Ne} RT}{V} \text{ where } n_{Ne} = \frac{m_{Ne}}{M_{Ne}}$$

$$\text{So } P_{Ne} = \frac{m_{Ne} RT}{VM_{Ne}} \text{ or } V = \frac{m_{Ne} RT}{M_{Ne} P_{Ne}} = \frac{8.6787 \times 0.082 \times 301 \times 760}{20 \times 860} \text{ dm}^3 = 9.5 \text{ dm}^3$$

Hence the volume of the vessel is 9.5 dm³.

$$\text{Then } n_b = \frac{P_b V}{RT} = \frac{560 \times 9.5}{760 \times 0.082 \times 301} \text{ moles} = 0.2836 \text{ moles}$$

$$\text{Then } m_b = n_b M_b = 0.2836 \times 58 \text{ g} = 16.4488 \text{ g}$$

Hence mass of butane was approximately 16.4g

Example 28

A 600cm³ flask contains a mixture of water vapour and nitrogen gas at 127°C and 950mmHg. The flask is cooled to 27°C, the new pressure is found to be 380mmHg. What are masses of water and nitrogen in the flask?

Solution

Given that:

Pressure at 127°C = 950mmHg

Pressure at 27°C = 380mmHg

Volume of flask = 600cm³ = 0.6L

When the flask is cooled to 27°C, water vapour condenses to liquid so pressure in the flask is exerted by nitrogen gas only. Thus $P_{N_2} = 380 \text{ mmHg}$ at 27°C or 300K

Thus at 27°C:

$$n_{N_2} = \frac{P_{N_2} V}{RT} = \frac{380 \times 0.6}{760 \times 0.082 \times 300} \text{ moles} = 0.0122 \text{ moles}$$

At 127°C; pressure is exerted by both nitrogen gas and water vapour.

$$\text{Using } P_T = \frac{(n_{H_2O} + n_{N_2})RT}{V},$$

$$\text{Then } \frac{950}{760} = \frac{(n_{H_2O} + 0.0122) \times 0.082 \times 400}{0.6}$$

From which $n_{H_2O} = 0.011 \text{ moles}$

Using $m = nM_r$, where M_r of H_2O and N_2 are 18 and 28 gmol^{-1} respectively.

Then: Mass of water = $0.011 \times 18 \text{ g} = 0.198 \text{ g}$

Mass of nitrogen gas = $0.0122 \times 28 \text{ g} = 0.3416 \text{ g}$

Example 29

Nickel forms a carbonyl $Ni(CO)_n$. Deduce the value of n from the fact that: Carbon monoxide diffuses 2.46 times faster than the carbonyl compound.

(Atomic mass of Ni is 59)

Solution

By Graham's law of diffusion:

$$\frac{R_{CO}}{R_{Ni(CO)_n}} = \sqrt{\frac{M_{Ni(CO)_n}}{M_{CO}}} \quad \text{or } M_{Ni(CO)_n} = M_{CO} \left(\frac{R_{CO}}{R_{Ni(CO)_n}} \right)^2 \dots \dots \dots (i)$$

But $\frac{R_{CO}}{R_{Ni(CO)_n}} = 2.46$ (CO diffuses 2.46 times faster than carbonyl compound)

And $M_{CO} = 28 \text{ g/mol}$.

So by substituting above values in (i) gives; $M_{Ni(CO)_n} = 2.46^2 \times 28 \text{ gmol}^{-1} = 169 \text{ gmol}^{-1}$

Then: $59 + 28n = 169$

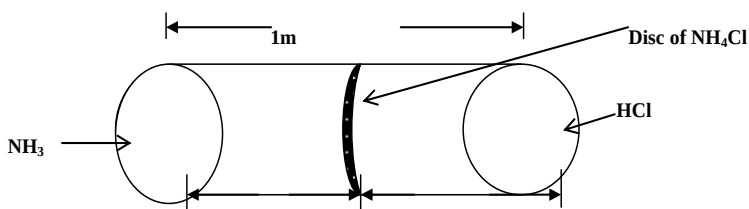
$$28n = 110 \quad \text{or } n = 4.$$

Hence the value of n is 4.

Example 30

Plugs of cotton wool are soaked in concentrated ammonia solution and the other soaked in concentrated hydrochloric acid solution are inserted into opposite ends of horizontal glass tube. A disc of solid ammonium chloride forms in the tube. If the tube is 1m long, how far from the ammonia plug is the solid deposit?

Solution



From Graham's law of diffusion: $\frac{R_{\text{NH}_3}}{R_{\text{HCl}}} = \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}}$

But the rate of diffusion is direct proportional to the distance travelled by the compound in the diffusion:

Thus $\frac{R_{\text{NH}_3}}{R_{\text{HCl}}} = \frac{l_{\text{NH}_3}}{l_{\text{HCl}}} = \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}}$; Then $\frac{x}{1-x} = \sqrt{\frac{36.5}{17}}$

Solving above equation gives $x = 0.59\text{m}$

Hence the solid deposit is 0.59m or 59cm from the ammonia plug

Example 31

A mixture of carbon dioxide and carbon monoxide diffuse through a porous diaphragm in one half the time taken for the same volume of bromine vapour to diffuse through the same diaphragm. What is the composition by volume of the mixture?

Solution

From the Graham's law of diffusion: $\frac{t_{\text{mixture}}}{t_{\text{Br}_2}} = \sqrt{\frac{M_{\text{mixture}}}{M_{\text{Br}_2}}}$ but $t_{\text{mixture}} = \frac{1}{2}t_{\text{Br}_2}$

Then $\frac{\frac{1}{2}t_{\text{Br}_2}}{t_{\text{Br}_2}} = \sqrt{\frac{M_{\text{mixture}}}{M_{\text{Br}_2}}} = \sqrt{\frac{M_{\text{mixture}}}{160}}$

From which $M_{\text{mixture}} = \left(\frac{1}{2}\right)^2 \times 160\text{g mol}^{-1} = 40\text{g mol}^{-1}$

Thus the average molar mass of the mixture is 40g/mol

Let the percentage by volume of CO be x then the percentage of CO_2 will be $100 - x$

Where molar masses of CO and CO_2 are 28g/mol and 44g/mol respectively

So $\left(\frac{28x}{100}\right) + \left(\frac{100 - x}{100}\right) \times 44 = 40$

$28x + 4400 - 44x = 4000$

$16x = 400$ or $x = 25$ and $100 - x = 100 - 25 = 75$

Hence:

The percentage of CO is 25%

The percentage of CO_2 is 75%

Example 32

In 4 minutes, 16.2cm^3 of water vapour effuse through a small hole in the same time 8.1cm^3 of the mixture of NO_2 and N_2O_4 effuse through the same hole. Calculate the percentage by volume of NO_2 in the mixture.

Solution:

By Graham's law of diffusion:

$\frac{V_{\text{water vapour}}}{V_{\text{mixture}}} = \sqrt{\frac{M_{\text{mixture}}}{M_{\text{water}}}}$ or $M_{\text{mixture}} = M_{\text{water}} \left(\frac{V_{\text{water vapour}}}{V_{\text{mixture}}}\right)^2$

Then $M_{\text{mixture}} = 18 \left(\frac{16.2}{8.1}\right)^2 = 72\text{g/mol}$

Let the percentage by volume of NO_2 be x

Then the percentage by volume of N_2O_4 will be $100 - x$.

Where molar mass of NO_2 is 46g/mol

Molar mass of N_2O_4 is 92 g/mol

$$\text{Then } \left(\frac{46x}{100}\right) + 92\left(\frac{100-x}{100}\right) = 72$$

$$46x + 9200 - 92x = 7200$$

$$46x = 2000$$

$$x = 43.5 \text{ and } 100 - x = 100 - 43.5 = 56.5$$

Hence: The percentage of NO_2 is 43.5 %

The percentage of N_2O_4 is 56.5%

Example 33

At 27°C hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of hydrogen leaked through the same hole for 20 minutes. After the effusion of gases, the mixture exerts a pressure of 6 atmospheres. The hydrogen content of the mixture is 0.7 moles. If the volume of the container is 3 litres, what is the molecular weight of unknown gas?

Solution

By Dalton's law of partial pressure:

$$P_T = P_{\text{H}_2} + P_U$$

$$\text{But } P_T = 6\text{atm and } P_{\text{H}_2} = \frac{n_{\text{H}_2} RT}{V} = \frac{0.7 \times 0.082 \times 300}{3} \text{atm} = 5.74\text{atm}$$

$$\text{So } P_U = P_T - P_{\text{H}_2} = 6\text{atm} - 5.74\text{atm} = 0.26\text{atm}$$

$$\text{Using } n = \frac{PV}{RT};$$

$$\text{So number of moles of unknown gas diffused} = \frac{0.26 \times 3}{0.082 \times 300} = 0.0317\text{moles}$$

According to Avogadro's law: number of moles of gases diffused must be directly proportional to their volume diffused;

$$\text{Thus } \frac{V_{\text{H}_2}}{V_U} = \frac{n_{\text{H}_2}}{n_U} = \sqrt{\frac{M_U}{M_{\text{H}_2}}}$$

$$\text{From which; } M_U = M_{\text{H}_2} \left(\frac{V_{\text{H}_2}}{V_U}\right)^2 = 2 \left(\frac{0.7}{0.0317}\right)^2 \text{ g mol}^{-1} = 975\text{g mol}^{-1}$$

Hence the molecular weight of unknown gas is 975g mol^{-1}

Example 34

Gas **A** of a certain volume diffuses for 580 seconds at 15°C and 1.02atm. Find the time required for the same volume of the gas **J** to diffuse at 25°C and 1.1atm. Given that;

Molar mass of **A** = 120g/mol

Molar mass of **J** = 32g/mol

Solution

From Graham's law of diffusion: $\frac{R_A}{R_J} = \frac{V_A/t_A}{V_J/t_J} = \frac{V_A t_J}{V_J t_A} = \sqrt{\frac{\rho_J}{\rho_A}}$

But $V_A = V_J$ (the same volume of two gases was diffused)

It follows that: $\frac{t_J}{t_A} = \sqrt{\frac{\rho_J}{\rho_A}}$

But $\rho = \frac{PM_r}{RT}$ (from ideal gas equation)

Thus $\frac{\rho_J}{\rho_A} = \frac{P_J M_J}{RT_J} \times \frac{RT_A}{P_A M_A} = \frac{P_J M_J T_A}{P_A M_A T_J}$

Then $\frac{t_J}{t_A} = \sqrt{\frac{P_J M_J T_A}{P_A M_A T_J}}$

Substituting $\frac{t_J}{580s} = \sqrt{\frac{1.1 \times 32 \times 288}{1.02 \times 120 \times 298}}$; from which $t_J = 306s$

Hence the time required by gas J is 306 seconds

DIGGING DEEPER EXERCISE 1

EXERCISE 1A: BINDER QUESTIONS

Question 1

Explain whether you agree or you disagree with the following statement: *According to Boyle's law, equal mass of hydrogen and oxygen kept in different containers of the same volume at the same temperature exerts the same pressure.*

Question 2

According to Charles's law, increasing the temperature of the gas from 10°C to 20°C doubles its volume. Is this statement correct or incorrect? Explain.

Question 3

In the discussion of Gay-Lussac's law with her classmate, **Kipute** argued that, *"The increase of temperature from 27°C to 327°C doubles the pressure of a given amount of a gas provided that the volume is kept constant."* Her classmate challenged **Kipute** that her statement is wrong because Gay-Lussac's law needs the temperature to double for doubling the pressure of the gas and the increase in temperature (327°C) mentioned by **Kipute** is not twice the initial one (27°C). Do you support or oppose **Kipute's** classmate challenge? Explain.

Question 4

Can you use the ideal gas law for liquids? Give reason.

Question 5

- (i) Derive an ideal gas equation.
- (ii) Why the ideal gas equation is also known as equation of state?

Question 6

One way to state Boyle's law is; *"All other things being equal, the pressure of a gas is inversely proportional to its volume."*

- (i) What is the meaning of the term "inversely proportional?"
- (ii) What are the "other things" that must be equal?

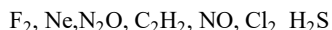
Question 7

An alternate way to state Avogadro's law is; *"All other things being equal, the number of molecules in a gas is directly proportional to the volume of the gas."*

- (i) What is the meaning of the term "directly proportional?"
- (ii) What are the "other things" that must be equal?

Question 8

Which of the following gases diffuse more slowly than oxygen?



Question 9

Pressure exerted by 4g of oxygen in a container at certain temperature is twice the pressure exerted by 2g of hydrogen gas in the same container at the same temperature. With correct reasoning state whether this statement is true or false.

Question 10

- (a) How the following are related to the amount of pressure exerted by a gas in a container?
 - (i) Collision frequency
 - (ii) Collision intensity
- (b) How can these factors (mentioned in (a) above) be changed?

Question 11

Gay-Lussac's pressure law is contained in the merger of Boyle's law and Charles's law. Justify.

Question 12

In a flask containing 2atm of oxygen gas and 3atm of helium gas, 2mol of neon gas are added;

- (i) Is there any change of amount of total pressure in the flask after the addition of neon? Explain.
- (ii) What is the effect on partial pressures of oxygen and helium after the addition of neon? Explain.

EXERCISE 1B: REAL QUESTIONS**Question 13**

Why hot-air balloon floats in air?

Question 14

Propane tanks should not be kept at extreme temperatures. Explain.

Question 15

Air pressure in a car tyre increases during driving. Explain

Question 16

Kipute is a big funny of potato chips. One evening she went to the supermarket and bought number of bags of potato chips. She ate some of them and she found that the taste amazingly delicious. However, she was unable to finish all chips in the bags. Worrying that unconsumed potato chips would lose their wonderful flavour, she decided to store the bags of potato chips into a freezer. In the morning of the next day she taken the stored chips and started eating; surprisingly she felt disappointment-the chips are no longer delicious on the contrary to her yesterday's experience! **In terms of gas laws, offer possible explanation for this.**

Question 17

Sometimes leaving a bicycle in the sun on a hot day will cause a blowout. Explain.

Question 18

The tyres in cars are inflated to a slightly lower pressure in the summer than in the winter. Explain.

Question 19

A balloon filled with helium weighs much less than an identical balloon filled with oxygen.

- (i) Which gas law provides better explanation of this observation?
- (ii) Explain the observation by reference of the law mentioned in (i) above

Question 20

Bakery products like bread are fluffy. Explain why.

Question 21

Aerated water bottles are kept under water during summer. Explain.

Question 22

A flat tyre takes up less space than an inflated tyre. Explain.

Question 23

Account for the role of Amontons's law in the working of pressure cooker.

Question 24

Why a football inflated inside and then taken outdoors on a winter day shrinks slightly?

Question 25

Throwing an aerosol can into a fire may cause it to explode. Explain.

Question 26

Kipute is the form five student and beloved friend of yours. She learned in chemistry that according to Boyle's law, pressure and volume of the gas are inversely proportional. However, she got confusion after thinking the inflation a tyre and saw like it goes against what she learned in the chemistry. She came to you and explained her doubts; *"If you pump air into a tyre, you're increasing the pressure, and the tyre expand. Which means when the pressure is increased, the volume increases too. Isn't this a violation of Boyle's law?"* She asked. Please, assist your friend to eliminate this 'contradiction' and help her understand the inflation of the tyre in terms of gas laws.

EXERCISE 1C: HOT QUESTIONS**Question 27**

Consider the flask in the following diagram

- (a) What are the final partial pressures of Helium and argon after the stopcock between the two flasks is opened?
 (b) What is the total pressure?

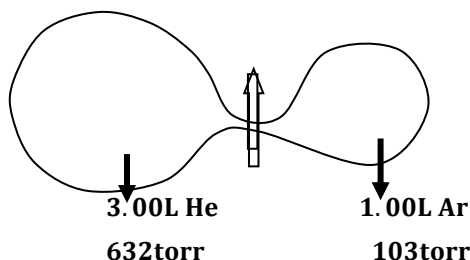
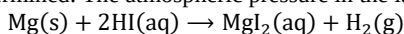


Figure 1.3 Diagram for question 1

Question 28

Magnesium metal is reacted with excess HI to produce hydrogen gas. The gas is collected over water. 45.82 mL of the wet hydrogen gas is collected at 30°C. The water level in the eudiometer is equalized with in another vessel before the volume of H₂ gas is determined. The atmospheric pressure in the laboratory is 738.72 mmHg.



- (a) What is the vapour pressure of H₂ gas in the eudiometer?
 (b) What mass of magnesium metal was consumed in the reaction? (Vapour pressure of water at 30°C is 31.824 mmHg).

Question 29

If equal amounts of the helium and argon are placed in a porous container and allowed to escape, which gas will escape faster and how much faster?

Question 30

What is the molecular weight of a gas which diffuses $\frac{1}{50}$ as fast as hydrogen?

Question 31

2.278×10^{-4} mol of an unidentified gaseous substance effused through a tiny hole in 95.7 s. Under identical conditions, 1.738×10^{-4} mol of argon takes 81.6 s to effuse. What is the molar mass of the unidentified substance? (Molar mass of argon = 39.948 g/mol)

Question 32

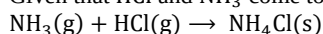
If a molecule of CH₄ diffuse a distance of 0.530 m from a point source, calculate the distance that a molecule of N₂ would diffuse under the same conditions for the same period of time.

Question 33

What is the rate of effusion for a gas that has molar mass twice that of a gas that effuses at rate of 3.62 mol/min?

Question 34

Given that HCl and NH₃ come together to form a solid NH₄Cl according to the following reaction,



If a 2 litre container of HCl and 5 litre container of NH₃ (both at stp) were connected and then allowed to react, what would the final pressure be after reaction?

Question 35

Suppose that 2 atm H₂ and 3 atm O₂ are put into a 10 litre container. If a spark is added and oxygen and hydrogen react to form gaseous water, calculate total pressure inside the container after reaction. Assume that the temperature and volume of the container remain constant.

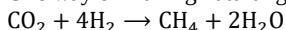
Question 36

A 10 litre container at stp is filled with both O_2 and N_2 . 25% of all the atoms in the container are oxygen. Using this information, answer the following questions:

- What is the partial pressure of O_2 ?
- How many moles of N_2 are there in the container?
- What will the partial pressure of oxygen be if 2.5 mole of argon are introduced in the container?

Question 37

One way of making natural gas is by the so called water-gas reaction,



- An experiment took 20 litres of CO_2 reacted with 75 litres of H_2 at STP. How many grams of CH_4 would be produced?
- Calculate the final pressure assuming all products and reactants are ideal gases
- What is the mole fraction of the water in the final mixture?
- Explain briefly why would the final pressure in the reaction vessel mixture after reaction be much less than the prediction made in (b) above?

Question 38

A 2 litre tank containing oxygen at 0.5atm pressure is connected by means of a valve to a 3 litre tank containing nitrogen at 2atm at the same temperature.

- If the valve is opened, what will the new pressure be if the temperature remains constant?
- What is the partial pressure of the oxygen?
- What is the mole fraction of nitrogen?

Question 39

A 10L container has 0.3mole fraction argon. When the temperature of the container is increased by $50^\circ C$, the pressure increases by factor of 1.4. If the total number of mole of gas in the container is 1.3 moles, what was the original pressure of the argon in the container?

Question 40

If we open the taps given in the figure below, find the total final pressure exerted by gases.

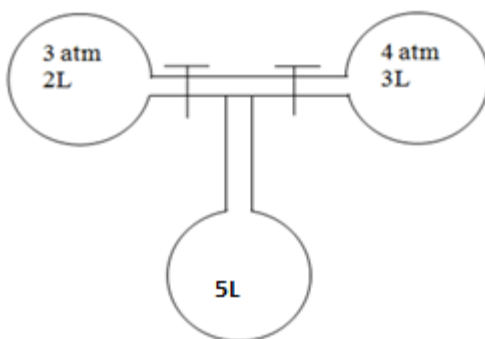


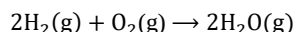
Figure 1.4 Diagram for question 14

Question 41

A rigid 8.2L flask contains a mixture of 2.5moles of H_2 , 0.5mol of O_2 , and sufficient argon so that the partial pressure of argon in the flask is 2 atm. The temperature is $127^\circ C$.

- Calculate the total pressure in the flask.
- Calculate the mole fraction of H_2 in the flask
- Calculate the density (in $g L^{-1}$) of the mixture in the flask

The mixture in the flask is ignited by a spark and the reaction represented below occurs until one of the reactants is entirely consumed.



(d) Give the mole fraction of all species present in the flask at the end of the reaction.

Question 42

KClO_3 is decomposed by the following reaction: $2\text{KClO}_3(\text{s}) \rightarrow 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g})$

The O_2 produced was collected by the displacement of water at 22°C at a total pressure of 760torr. The volume of gas collected was 1.2L and the vapour pressure of water at 22°C is 21torr. Calculate:

- (i) The partial pressure of O_2 in the gas collected and
- (ii) The mass of KClO_3 in the sample that was decomposed

Question 43

Oxygen gas is collected over water at 22°C . If the gas was collected in a 250mL container at 740mmHg atmospheric pressure, how many grams of oxygen were collected?

Vapour pressure of water at $22^\circ\text{C} = 19.8\text{mmHg}$

Question 44

Hydrogen gas is collected over water at 22°C . If the gas was collected at 800mmHg atmospheric pressure, what pressure of H_2 gas was collected?

Given that: vapour pressure of water at 15°C is 12.8mmHg

Question 45

It takes x seconds for 100cm^3 of gas A to diffuse at certain pressure and temperature of 20°C . How long will take 200cm^3 of gas B to diffuse at 30°C under the same pressure?

Given that:

Molar mass of A = 32g/mol

Molar mass of B = 71g/mol

Question 46

If 3atm of carbon monoxide (CO) is mixed with 2atm of oxygen in a container at 30°C , the total pressure in the container will be 5atm. Is this argument correct? If it is correct, give clear reason to support your answer, and if it is not correct, calculate the correct value.

Question 47

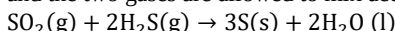
A mixture of excess carbon monoxide and oxygen gas was allowed to diffuse through a porous diaphragm (after their reaction) in one half the time taken for the same volume of bromine vapour to diffuse through the same diaphragm. What is the composition by volume of the mixture?

Question 48

A certain dry gas is composed of 21% by volume of oxygen, 1% of argon and 78% of nitrogen. Find its density in grams per dm^3 at 20°C and 98.65kNm^{-2} pressure.

Question 49

Two gas burettes, one containing 10cm^3 of sulphur dioxide (SO_2) and the other containing 30cm^3 of hydrogen sulphide (H_2S) both at 1 atmosphere and at 0°C are initially separated by a stop cork. The stop cork is then opened and the two gases are allowed to mix according to the reaction:



Calculate the final pressure (in atmospheres) after the reaction has ended and the apparatus has regained its temperature of 0°C . (Assume liquid water does not exert pressure).

Question 50

Two glass bulbs of equal volumes joined by a narrow tube of negligible volume are containing gas at s.t.p. When one of the bulbs is lowered into a container containing melting ice and other kept in hot water, the new pressure in the bulb is 877.6mmHg. Determine the temperature of the water.

Chapter 2

KINETIC MOLECULAR THEORY OF GASES

The gas laws that we have studied in the previous chapter, are empirical (they have been derived from experimental observations). Although these laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships. The **kinetic molecular theory** (KMT) is a simple model that effectively explains the gas laws.

Kinetic molecular theory of gases explains the behaviour of gases with respect to motion of its molecules (particles). It holds for ideal gases only and hence is also known as **assumptions for ideal gas law**.

ASSUMPTIONS OF KINETIC MOLECULAR THEORY OF GASES

Assumption 1: A gas consists of very small particles (molecules) in a random motion of which there is a collision between gas particles themselves and the collision between gas particles and the walls of the container, thus exerting a pressure.

Assumption 2: Force of gravity (gravitational force) has no effect on the motion of gas particles.

Assumption 3: Intermolecular forces of attraction are negligible in the motion of gas particles.

Assumption 4: Kinetic energy of gas particles varies directly proportional to the absolute temperature

Assumption 5: The collision between gas particles and walls of the container is completely elastic (There is no loss in kinetic energy in the collisions).

Assumption 6: Volume of individual gas particles is negligible compared to the volume of the whole gas or the volume of the container.

The reader should understand that:

Since assumptions of KMT are based on microscopic particles found in gases, the kinetic molecular theory is sometimes known as the **microscopic model of gases**.

DERIVATION OF KINETIC EQUATION FROM KMT

Consider N molecules of gases in the cube (container) are moving in three dimensions (directions) such that $N/3$ molecules are moving in each direction as shown below:

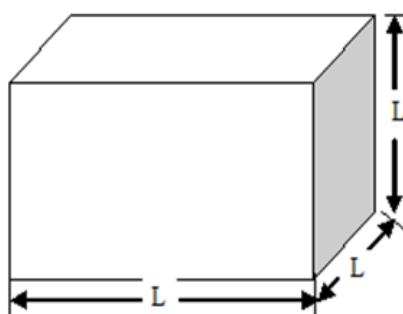


Figure 2.1 Gas container

Consider $N/3$ molecules which are moving in X- direction

For a particle of mass, m moving in X- direction with root mean square speed, c ;

Momentum of a particle before collision with the wall of the container = mc ,

After collision, the velocity of a particle will change from c to $-c$ as the collision is completely elastic.

Thus momentum of a particle after collision = $-mc$;

So change in momentum of the particle = $mc - (-mc) = 2mc$

Force of exerted by the particle on the wall of the container, $F = \frac{\Delta mc}{t} = \frac{2mc}{t}$

Thus total force exerted on the wall of the container by $N/3$ molecules = $\frac{2Nmc}{3t}$

A particle will move a distance of $2L$ before making another collision.

Thus $c = \frac{2L}{t}$ or $t = \frac{2L}{c}$

Substituting $t = \frac{2L}{c}$ in $F = \frac{2Nmc}{3t}$; $F = \frac{Nmc^2}{3L}$

Using Pressure, $P = \frac{\text{Force}}{\text{Area}}$; but $\text{Area} = L^2$ and $\text{Force} = \frac{Nmc^2}{3L^2}$; then $P = \frac{Nmc^2}{3L^3}$;

But $L^3 = \text{Volume of the container, } V$. So $P = \frac{Nmc^2}{3V}$

Hence **$PV = \frac{Nmc^2}{3}$**

The final result is known as kinetic equation of gases.

Kinetic energy of gases from kinetic equation

From the kinetic equation: $PV = \frac{Nmc^2}{3}$

But the kinetic energy of N molecules = $\frac{1}{2}Nmc^2$

Where m is the mass of one molecule and Nm is the total mass of N molecules.

So from $K.E = \frac{1}{2}Nmc^2$, $Nmc^2 = 2K.E$

Then substituting $Nmc^2 = 2K.E$ to the above kinetic equation gives: $PV = \frac{2}{3} K.E$

Thus **$K.E = \frac{3}{2} PV$**

But from ideal gas equation: $PV = nRT$

So **$K.E = \frac{3}{2} nRT$** for n moles of gas

If $n = 1$ (for one mole of the gas): **$K.E = \frac{3}{2} RT$**

Since **R** is constant, **$\frac{3}{2}R$** is also constant and hence the result of kinetic energy confirm one of the assumption of kinetic theory of gases which state that: The kinetic energy of gas molecules varies directly proportional to the absolute temperature.

Root mean square speed of a gas, c , from kinetic equation

From the kinetic equation of gases: $PV = \frac{1}{3} Nmc^2$

If $N = N_A = 6.02 \times 10^{23}$ molecules, $n = 1$ (n is the number of moles of the gas)

And $Nm = N_A m = M_r$ (M_r is the molar mass of the gas)

Then $PV = \frac{M_r c^2}{3}$ but for $n = 1$, $PV = RT$

Then $RT = \frac{M_r c^2}{3}$ or $c^2 = \frac{3RT}{M_r}$

$$\text{Hence } c = \sqrt{\frac{3RT}{M_r}}$$

Where c is the root mean square (r.m.s) speed or velocity of gas molecules

Be careful!

In the formula, $c = \sqrt{\frac{3RT}{M_r}}$; R must be $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ (**not** $0.082 \text{ atm L mol}^{-1} \text{ K}^{-1}$) and M_r must be in kg/mol (**not** g/mol) so as to give the value of c in m/s .

The kinetic energy (K.E) can also be deduced from the above equation for the root mean square speed as follows: From $c = \sqrt{\frac{3RT}{M_r}}$

But kinetic energy (K.E) of the gas $= \frac{1}{2} mc^2$ where m is the given mass of the gas

$$\text{But } c = \sqrt{\frac{3RT}{M_r}}$$

$$\text{Then K.E} = \frac{1}{2} m \left(\sqrt{\frac{3RT}{M_r}} \right)^2 = \frac{3mRT}{2M_r}$$

But $\frac{m}{M_r} = n$; So **K.E** $= \frac{3}{2} nRT$ for n moles of the gas

When $n = 1$, the equation become **K.E** $= \frac{3}{2} RT$ for 1 mole of the gas

Derivation of Boyle's law and Charles's law from kinetic equation of gases

From the kinetic equation of gases: $PV = \frac{N}{3} mc^2$; but **K.E** $= \frac{1}{2} Nmc^2$ or $Nmc^2 = 2 \text{ K.E}$

$$\text{Then } PV = \frac{2}{3} \text{ K.E}$$

From one of the assumption of kinetic theory of gases; **K.E** $\propto T$

Thus **K.E** $= kT$ where k is the constant for proportionality

$$\text{Therefore; } PV = \frac{2}{3} kT \dots \dots \dots (i)$$

If T is constant:

$$\frac{2}{3} kT = \text{Constant and therefore (i) become: } PV = \text{Constant or } V = \frac{\text{Constant}}{P}$$

$$\text{Hence } V \propto \frac{1}{P}$$

The result is Boyle's law which states that: The volume of the fixed mass of the gas varies inversely proportional to its pressure at constant temperature.

If P is constant:

$$\frac{2k}{3P} = \text{Constant and therefore the equation (i) above become: } V = \text{Constant} \times T$$

$$\text{Hence } V \propto T$$

The result is Charles's law which states that: The volume of the fixed mass of the gas varies directly proportional to its absolute temperature at constant pressure.

Similarly pressure-temperature law can be deduced by keeping volume, V constant in the equation: $PV = \frac{2}{3}kT$ (On your own try to confirm this).

Derivation of general gas equation from kinetic equation of gases

From the kinetic equation of gases; $PV = \frac{Nmc^2}{3}$

But K. E = $\frac{1}{2}Nmc^2$ or $Nmc^2 = 2K. E$

Then $PV = \frac{2}{3}K. E$

From one of the assumption of kinetic theory of gases; $K. E \propto T$

Thus $K. E = kT$ where k is the constant for proportionality

Therefore; $PV = \frac{2}{3}kT$

But $\frac{2}{3}k = \text{Constant}$; so $PV = \text{Constant} \times T$ or $\frac{PV}{T} = \text{Constant}$

Hence $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3} = \dots \dots \dots = \frac{P_nV_n}{T_n}$ which is general gas equation

Derivation of Avogadro's law from kinetic equation of gases

From the kinetic equation of gases; $PV = \frac{Nmc^2}{3}$

For two gases, say 1 and 2

$$P_1V_1 = \frac{N_1m_1c_1^2}{3} \dots \dots \dots \text{(i)}$$

$$P_2V_2 = \frac{N_2m_2c_2^2}{3} \dots \dots \dots \text{(ii)}$$

But kinetic energy of one molecule of a gas, $K. E = \frac{1}{2}mc^2$; then $2K. E = mc^2$

$$\text{Equation(i) is then become } P_1V_1 = \frac{N_1K. E_1}{3} \dots \dots \dots \text{(iii)}$$

$$\text{Equation(ii) is then become } P_2V_2 = \frac{N_2K. E_2}{3} \dots \dots \dots \text{(iv)}$$

But $K. E \propto T$ or $K. E = kT$ (From one of the assumption of kinetic theory of gases)

$$\text{Equation (iii) is then become } P_1V_1 = \frac{2}{3}N_1kT_1 \dots \dots \dots \text{(v)}$$

$$\text{Equation (iv) is then become } P_2V_2 = \frac{2}{3}N_2kT_2 \dots \dots \dots \text{(vi)}$$

For constant pressure and temperature; $P_1 = P_2 = P$ and $T_1 = T_2 = T$

The last two equations are then become:

$$PV_1 = \frac{2}{3}N_1kT \dots \dots \dots \text{(vii)}$$

$$PV_2 = \frac{2}{3}N_2kT \dots \dots \dots \text{(viii)}$$

$$\frac{(viii)}{(vii)} \text{ gives: } \frac{V_2}{V_1} = \frac{N_2}{N_1}$$

(This is the form of **Avogadro's law** which states that: The volume of the gas varies directly proportional to its number of molecules or moles at constant temperature and pressure)

If $V_1 = V_2$ (Equal volume of two gases)

$$\text{Then } \frac{V_2}{V_1} = 1, \text{ so } \frac{V_2}{V_1} = \frac{N_2}{N_1} = 1$$

Hence $N_1 = N_2$ which is more famous forms of Avogadro's law which states that: Equal volume of different gases at constant conditions of temperature and pressure contain the same number of molecules (or moles).

Derivation of Graham's law of diffusion / effusion from kinetic equation of gases

$$\text{From kinetic equation of gases: } PV = \frac{N}{3} mc^2$$

But Nm is the total mass for N molecules of the gas, m_g ;

$$\text{It follows that: } PV = \frac{m_g c^2}{3}$$

$$\text{From which } P = \frac{m_g c^2}{3V}$$

But $\frac{m_g}{V}$ density of the gas, ρ_g

$$\text{Thus } P = \frac{\rho_g c^2}{3} \text{ or } c^2 = \frac{3P}{\rho_g}$$

$$\text{Whence } c = \sqrt{\frac{3P}{\rho_g}}$$

If pressure P , is constant, $\sqrt{3P} = \text{constant}$

$$\text{Then it becomes; } c = \frac{\text{constant}}{\sqrt{\rho_g}} \text{ or } c \propto \frac{1}{\sqrt{\rho_g}}$$

Since the speed of the gas is directly proportional to the rate of diffusion (or effusion) of the gas, it can be concluded that:

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{\rho_g}} \text{ which is the Graham's law of diffusion}$$

The final result is equivalent to **Graham's law of diffusion or effusion** which state that: The rates of diffusion or effusion of gases at given (constant) temperature and pressure varies inversely proportional to the square root of their densities.

Derivation of ideal gas equation from kinetic equation of gases

$$\text{From the kinetic equation of gases; } PV = \frac{Nmc^2}{3}$$

$$\text{But } K.E = \frac{1}{2} mc^2 \text{ (for one molecule of the gas)}$$

$$\text{Or } mc^2 = 2K.E; \text{ Then } PV = \frac{2}{3} N \times K.E$$

But from one of the assumptions of kinetic theory of gases: $K.E \propto T$

$$\text{Then } K.E = kT \text{ where } k \text{ is constant for proportionality and } PV = \frac{2}{3} NkT$$

$$\text{But } \frac{N}{N_A} = n \text{ or } N = nN_A \text{ where } n \text{ is the number of moles of the gas}$$

$$\text{Substituting } N = nN_A \text{ to } PV = \frac{2}{3} NkT \text{ gives } PV = \frac{2}{3} nN_A kT$$

Since N_A is constant, $\frac{2}{3} N_A k$ gives another constant, R

Hence $PV = nRT$ this is ideal gas equation.

Example 1

Deduce the Dalton's law of partial pressure from kinetic equation of gases:

Solution

From kinetic equation of gases: $PV = \frac{Nmc^2}{3}$ or $P = \frac{Nmc^2}{3V}$

For mixture of three gases say, **A**, **B** and **C** with their respective number of molecules (which exert total pressure, P_T in the container) N_A , N_B and N_C

$$\text{Thus } P_T = \frac{(N_A + N_B + N_C)mc^2}{3V} = \frac{N_A mc^2}{3V} + \frac{N_B mc^2}{3V} + \frac{N_C mc^2}{3V}$$

$$\text{But: } \frac{N_A mc^2}{3V} = P_A, \frac{N_B mc^2}{3V} = P_B, \frac{N_C mc^2}{3V} = P_C$$

Where P_A , P_B and P_C are partial pressures of **A**, **B** and **C** respectively

Hence $P_T = P_A + P_B + P_C$ which is Dalton's law of partial pressure and the law states that: "The total pressure exerted in the container of the mixture of two or more gases is equal to the summation of their partial pressures provided that the gases do not react"

Example 2

How long will it take a nitrogen dioxide molecule to travel 25 metres at STP?

Solution

Velocity (c) of the gas is given by the following equation:

$$c = \sqrt{\frac{3RT}{M_r}} \text{ where } R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, T = 273 \text{ K}, M_r = 46 \text{ g/mol} = 4.6 \times 10^{-2} \text{ kg/mol}$$

$$\text{Substituting } c = \sqrt{\frac{3 \times 8.314 \times 273}{4.6 \times 10^{-2}}} \text{ m/s} = 384.74 \text{ m/s}$$

$$\text{Time} = \frac{\text{Distance travelled}}{\text{Velocity}} = \frac{25}{384.74} \text{ s} = 0.06498 \text{ s}$$

It will take 0.06498 seconds

Example 3

Given that: $PV = \frac{1}{3} Nmc^2$, calculate the energy of 1 mole of an ideal gas at 27°C .

Solution

$$\text{Given that: } PV = \frac{Nmc^2}{3}$$

$$\text{But the kinetic energy of } N \text{ molecules} = \frac{1}{2} Nmc^2$$

Where m is the mass of one molecule and Nm is the total mass of N molecules.

$$\text{So from K.E} = \frac{1}{2} Nmc^2, Nmc^2 = 2 \text{ K.E}$$

$$\text{Then substituting } Nmc^2 = 2 \text{ K.E to the above kinetic equation gives: } PV = \frac{2}{3} \text{ K.E}$$

$$\text{Thus } \text{K.E} = \frac{3}{2} PV$$

$$\text{But from ideal gas equation: } PV = nRT$$

$$\text{So K.E} = \frac{3}{2} nRT \text{ for } n \text{ moles of gas}$$

$$\text{If } n = 1 \text{ (for one mole of the gas): K.E} = \frac{3}{2} RT$$

$$R = 8.314, T = 25^\circ\text{C} = 298 \text{ K}$$

$$\text{K.E} = \frac{3}{2} \times 8.314 \times 298 \text{ J} = 3716.358 \text{ J}$$

Hence kinetic energy for one mole of the gas is 3716.358 J or 3.716358 kJ

DIGGING DEEPER EXERCISE 2

EXERCISE 2A: BINDER QUESTIONS

Question 1

What is the kinetic theory's main foundation?

Question 2

What are the three main components of the kinetic molecular theory of gases?

Question 3

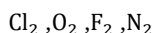
How does the concept of pressure follow from the kinetic molecular theory?

Question 4

What is the kinetic gas equation?

Question 5

Arrange the following gases in order of increasing their average molecular speed at 25°C.

**Question 6**

At certain temperature, hydrogen molecules move at an average velocity of $1.84 \times 10^3 \text{ m/s}$. Estimate the molar mass of a gas whose molecules have an average velocity of 311 m/s . (molar mass of hydrogen gas = 2.02 g/mol).

EXERCISE 2B: REAL QUESTIONS

Question 7

Observations about real gases can be explained at the molecular level according to the kinetic molecular theory of gases and ideas about intermolecular forces. Explain how each of the following observations can be interpreted according to those concepts.

- When a gas-filled balloon is cooled, it shrinks in volume; this occurs no matter what gas is originally placed in the balloon.
- When the balloon described in (i) is cooled further, the volume does not become zero; the gas becomes a liquid or solid.

Question 8

When NH_3 gas is introduced at one end of a long tube and HCl gas is introduced simultaneously at the other end, a ring of white ammonium chloride is observed to form in the tube after a few minutes. This ring is closer to the HCl end of the tube than the NH_3 end. Explain.

Question 9

A flag waves in wind. Explain.

Question 10

If helium gas is cooled, will the distribution of velocities look more like that of H_2 or of H_2O ? Explain your answer.

Question 11

It is harder to smell perfume in the cold room. Explain.

EXERCISE 2C: HOT QUESTIONS**Question 12**

At what temperature will the velocity of oxygen equal the velocity of hydrogen at 25°C?

Question 13

At what temperature does nitrogen have exactly twice velocity of chlorine gas? $N_2 = 28\text{g/mol}$ and $Cl_2 = 70.9\text{ g/mol}$ (Assume chlorine is at 25°C)

Question 14

Give qualitative explanation on how Boyle's law, Charles's law and Avogadro's law agree with kinetic molecular theory of gases.

Question 15

Using the postulates of the kinetic molecular theory, explain why a gas uniformly fills a container of any shape.

Question 16

Can the speed of a given molecule in a gas double at constant temperature? Explain your answer.

Question 17

Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:

- (i) The pressure of the gas is increased by reducing the volume at constant temperature.
- (ii) The pressure of the gas is increased by increasing the temperature at constant volume.
- (iii) The average velocity of the molecules is increased by a factor of 2.

Chapter 3

DEVIATION OF REAL GAS FROM IDEAL GAS LAW

Both gas laws and kinetic molecular theory we have studied so far are only compatible with ideal behaviour of gases. Those laws and theory are just 'shadow' of real truth of behaviour of gases we are experiencing in our real life. The simple truth that all gases can be liquefied, is quite opposite to what these laws and theory told us! It is no doubt evidence that there are intermolecular forces existing between gas molecules, the real truth which is completely against the 'truth shadow' we had seen in the previous chapters. Not only the presence of intermolecular forces breaks what we can call splendid gas laws and our beloved KMT theory, but there are also other real observations which altogether are going to establish new facts about how gas behave in the real world of imperfection!

In the ideal world where perfection exists, there are **ideal gases** (also known as **perfect gases**) which may be defined as *gases which obey Charles's law, Boyle's law as well as ideal gas equation and their behaviour are well explained by kinetic molecular theory of gases.*

However, in the real world where perfection does not exist, the concept of ideal gas is just hypothetical because all gases are **real (non-ideal)**, that is, there is no gas which is totally ideal due to the following reasons:

- There are intermolecular forces of attraction existing between gas molecules.
- Individual gas molecules occupy space (have volume).
- Collision between gas molecules and container's wall is **not** perfectly elastic.

Among the four variables (P, V, n and T) of gaseous state, pressure and volume are only victims of such imperfection. Consequently, we have two types of deviations of real gas from ideal behaviour which are **pressure deviation** and **volume deviation**.

PRESSURE DEVIATION OF REAL GASES

At high temperature, gas molecules are moving so fast that the high kinetic energy they possess tends to break any possible intermolecular attraction immediately.

- Thus the effect of the intermolecular forces of attraction in properties of gases at high temperature is negligible.

When the temperature decreases, the gas molecules move more slowly, and therefore they have small kinetic energy. This kinetic energy is not enough to break all of the intermolecular attraction between them.

- Thus at lower temperature, the intermolecular forces of attraction between gas molecules cannot be neglected and consequently the gas does not behave like ideal gas.

How do these intermolecular attractions affect properties of real gases?

When the intermolecular attractions between gas molecules are significant, the measured pressure of a real gas becomes less than the pressure predicted by the ideal gas equation.

That is $P_{\text{real gas}} < P_{\text{ideal gas}}$

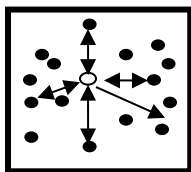
Where;

$P_{\text{real gas}}$ is the measured pressure

$P_{\text{ideal gas}}$ is the pressure calculated from the ideal gas equation with measured T and V by using $\frac{nRT}{V}$

Digging deeper!

To have clear understanding of why the pressure of real gas is less than the predicted pressure for ideal gas, consider a single gas molecule moving in the container with millions of gas molecules.



Where ○ represents the gas molecule in our consideration

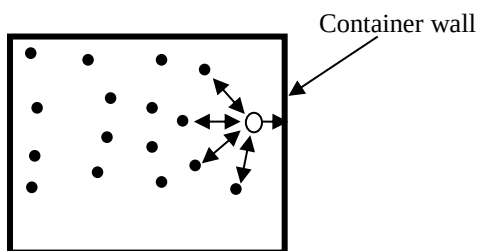
● represents other gas molecules in the container

↔ represents intermolecular attraction between the gas molecule in our consideration and other gas molecules

→ represents the direction of the gas molecule in our consideration (the head of the arrow directs where the gas is going in the container).

When the gas molecule in our consideration is in the middle of the container, there is no net effect of the intermolecular attraction. It will be attracted to some extent to all the other molecules around it, but on average, those attractions will cancel out to each other as for any attraction acting upon the molecule on one direction there is corresponding attraction acting upon the molecule on opposite direction.

- So despite all the intermolecular attraction it is experiencing, our molecule will just continue to move in the same direction at the same speed. But that is different if our molecule is just about to hit the wall of the container.



From the above figure, it is clearly seen that:

- When our gas molecule is just about to hit the container wall, there is no any gas molecule in front of it and hence there is net intermolecular attraction acting backward on the molecule (the molecule is pulled backward).
- The pull (intermolecular attraction acting backward of the gas molecule) lowers the speed of the gas molecule and therefore:

The intensity of collision between the gas molecule and the wall of the container becomes weak. Consequently, the changes in momentum become small and hence the force exerted by the molecule on the wall becomes small too.

The frequency of the collisions between the gas molecule and the container wall is lowered.

The above two 'dots' explain why intermolecular forces of attraction is said to decrease the pressure of the gas.

Extra fact you should understand!

The decrease in speed as result of the intermolecular forces of attraction makes the collision between gas molecules and wall of the container inelastic. This is because some of kinetic energy are transformed into potential (intermolecular) energy.

- This fact is different to the one of assumptions of kinetic theory of gas which states that; the collision between gas molecules and walls of the container is perfect elastic which means that no kinetic energy is lost during the collision.

Factors affecting extent of deviation of real gas pressure from ideal gas pressure

There are three main factors which determine the strength of intermolecular forces and therefore degree of deviation of real pressure from ideal pressure of the gas; these are;

1. Nature of the gas
2. Temperature of the gas
3. Concentration of the gas.

1. Nature of gas

Different gases with equal concentrations at the same conditions of temperature and pressure still have different degree of deviation of their pressure from the ideal one.

- This is because each gas has unique structure and therefore different strength of their intermolecular forces. As an example, consider the following few cases:

Ammonia gas shows greater deviation of its measured pressure (from the ideal pressure) than nitrogen gas because the ammonia (NH_3) has intermolecular hydrogen bonds which are stronger intermolecular forces than London dispersion forces existing between molecules of nitrogen (N_2).

Chlorine gas (Cl_2) shows greater deviation of its measured pressure than oxygen gas (O_2) because Cl_2 having larger molecular weight has stronger London dispersion forces (Van der Waals dispersion forces) than O_2 .

Hydrogen and helium gas show smallest deviation of their measured pressure from ideal pressure. This because with only two electrons, the two gases have weakest London dispersion forces of all other gases.

- However, the two gases can be liquefied at very low temperature and pressure, justifying presence of intermolecular forces between their molecules. Among the two gases, helium being mono-atomic has weaker intermolecular forces than hydrogen gas which is diatomic (hydrogen exist as H_2) and therefore making electrons in H_2 to have more space to move around and hence stronger dispersion forces in H_2 than in He.

2. Temperature of the gas

The same gas with the same concentration show different degree of deviation at different temperature.

- As explained earlier, the lower the temperature is, the stronger intermolecular attraction there are between molecules, and the more the real gas pressure deviates from the ideal pressure.
- Gases show maximum deviation in their measured pressure (from ideal pressure) when their temperatures are very close to their boiling points (just before their liquefaction).

3. Concentration of the gas

The same gas at the same temperature, show different degree of deviation of its measured pressure (from the ideal pressure) if its concentration is changed.

- The higher the concentration of the gas is, the shorter the average distance between the gas molecules; and if the gas molecules are closer together, more of them will be close enough to experience significant intermolecular attraction. This greater attraction in the direction away from the wall decreases the pressure against the wall compared to that it would be if there were fewer attractions (in the low gas concentration) between the molecules.
- Therefore, although the pressure of a real gas increases as the concentration increases, it does not increase as much as it would if there were no attractions between the molecules.
- With a greater concentration of gas, there are more molecules pulling a molecule back to the centre of the container at the instant before it hits the wall.

Very important point to understand!

The concentration $\left(\frac{n}{V}\right)$ of a gas can be increased in two ways; either by:

- 1) Decreasing the volume of given amount of the gas or
- 2) Adding more gas to a given volume.

Thus:

The given amount of gas shows greater deviation of its measured pressure if its volume is lowered.

- The volume of the gas may be decreased by either using the container of lower volume or compressing the gas through application of higher external pressure.

With a given volume of a gas, the gas will show greater deviation to its measured pressure compared to the ideal pressure if mass (or number of moles) of gas is larger.

Warning!

I have personally met with students who say that;

*"Because pressure is the **force** per area, the increase in pressure will increase the intermolecular **forces** of attraction between gas molecules."* It sounds good but it is actually technically incorrect explanation! How force from external pressure is transformed to the intermolecular forces? What is the relation (if any) between the two?

The correct explanation (as explained earlier) is that;

Increase in external pressure; compress the gas and therefore decreasing its volume. Decrease in volume of the gas means its concentration is increased, decreasing the average distance between gas molecules and hence an intermolecular force of attraction is increased.

VOLUME DEVIATION OF REAL GASES

When a gas behaves like an ideal gas, we can calculate its volume by measuring its T, P and n and then substituting them to the ideal gas equation; $V = \frac{nRT}{P}$.

- Kinetic theory of gases assumes that, the volume taken up by the gas molecules is negligible compared to the volume of the container. So if this assumption is correct, it means that; the volume calculated by the above formula $\left(V = \frac{nRT}{P}\right)$ is the volume of the container.

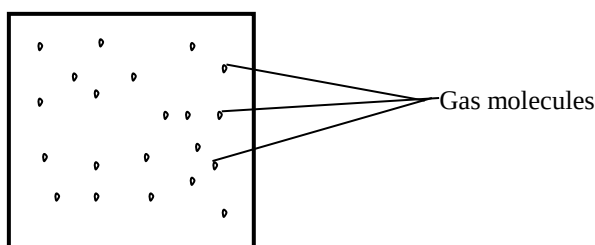
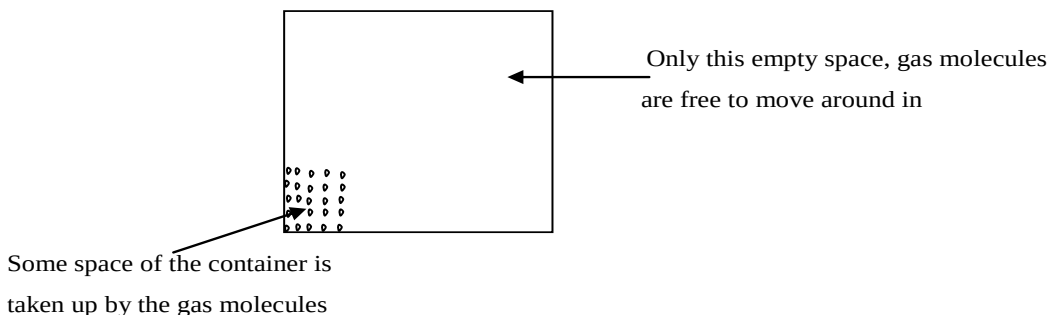


Figure 3.1 Volume in ideal gas

Whole space is available for being occupied by gas molecules

- However, for real gases, that assumption is not true. The volume of real gas (measured volume of the container) is greater than the volume that would be calculated from the ideal gas equation. The reason is that, although gas molecules are very small, **they do constitute part of its volume.**
- Thus the space in the container available for gas molecules to move around in is less than the measured volume of the container.

**Figure 3.2** Volume in real gas

(In the above figure; gas molecules are just intentionally kept together, just to enable you to imagine the total volume of gas molecules. But in fact, they are randomly moving in different part of the container, not settled in that ways shown in the figure).

In other words:

$$V_{\text{real gas}} \text{ or } V_{\text{container}} = V_{\text{gas molecules}} + V_{\text{empty space}}$$

Where $V_{\text{empty space}} = V_{\text{ideal gas}} = \frac{nRT}{p}$

Thus we can conclude that:

Because the gas molecules of real gas do occupy a finite volume, the real or measured volume of a gas is larger than the ideal volume calculated from ideal gas equation.

That is $V_{\text{real gas}} > V_{\text{ideal gas}}$

Factors affecting extent of deviation of real gas volume from ideal gas volume

There are three factors for this which are:

1. Amount of the gas (number of gas molecules in the container)
2. Amount of external pressure
3. Size of gas molecules

1. Amount of the gas

As the mass of the gas is increased in the container, the number of gas molecules increases and therefore the percentage of the volume (of the container) occupied by the gas molecules also increases. When volume of gas molecules is increased, the volume of empty space automatically decreases; thus the increase in amount of gas increases the deviation of real gas volume from ideal gas volume by doing the following:

- It increases volume of gas molecules
- It decreases the volume of empty space (where the gas molecules can move around in)

This leads to greater difference between the measured volume of real gas and the volume ideal gas and hence greater deviation of real gas volume from the ideal volume (calculated from ideal gas equation).

2. Amount of external pressure

Compressing the gas through application of very high external pressure, decreases the volume of empty space and hence the percentage of the volume occupied by gas molecules increases.

Thus greater external pressure means greater deviation of real gas volume from ideal gas volume (if the compression is so high that the gas molecules are touching each other, the volume available for them to move around is zero and the deviation become maximum).

The above two factors may be combined to single factor of 'concentration of gas' but I have intentionally separated them due to difference on approach of their explanation and due to the way the factor of number of molecules (amount of the gas) appears on Van der Waals equation as we will see later.

In one sentence:

Application of high external pressure increases the deviation of real gas volume from ideal gas volume by decreasing the volume of empty space where the gas molecules can move around in.

3. Size of the gas molecule (nature of the gas)

A gas with larger molecular size, its molecules occupy greater space and therefore the gas shows greater deviation in its measured volume compared to its corresponding ideal volume because:

- Larger sized molecules occupy larger space and therefore larger volume of gas molecules.
- Large sized molecules occupy larger space and therefore smaller empty space is left in the container for gas molecules to move around in.

The molecular size is determined by two factors which are:

Atomic size. Greater atomic size (radius) in the molecule greater molecular size. For example Cl having larger atomic size than F, $\text{Cl}_2(\text{g})$ has larger molecular size than F_2 .

Number of atoms per one molecule. For example H_2 having greater number of atoms (two atoms) per molecule than He (it is mono-atomic with only one atom per molecule) has larger molecular size

Roughly gas with molecules of large size, have large molecular weight.

However, if the difference in the molecular weight is small, sometimes you may find the gas with lower molecular weight has larger molecular size either due to greater number of atoms per molecule or larger size of atoms which comprise the gas or both. For example CH_4 has larger molecular size than H_2O although molecular weight of CH_4 (16g/mol) slight lower than that of H_2O (18g/mol) because atomic size of C is larger than that of O and also because CH_4 has four hydrogen atoms while H_2O has only two of them. So we are expecting methane gas (CH_4) to show greater volume deviation from ideal volume than water vapour.

Do you remember this fact?

A gas with large molecular size also has stronger dispersion intermolecular forces and therefore greater deviation of measured pressure compared to ideal gas pressure. So we may conclude that:

The gas with large molecules deviate more from ideal behaviour because:

- Has stronger London dispersion intermolecular forces and therefore greater deviation of its measured pressure from its corresponding ideal pressure.
- Occupy larger space and therefore greater deviation of its measured volume from its corresponding ideal volume.

VAN DER WAALS EQUATION FOR REAL GASES

The Van der Waals equation for real gases is modified equation from ideal gas equation which expresses the variation of pressure and volume of real gas with respect to variation of temperature and amount of the gas. It is the **equation of state** for real gases.

The Van der Waals equation can be written as follows:

$$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT \text{ for } n \text{ moles of the real gas}$$

But for one mole of the gas, that is $n = 1$, the equation become: $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

Where: $\frac{a}{V^2}$ is the factor for pressure correction of real gases to ideal behaviour. It is known as **internal pressure**.

a is a **coefficient of attraction**, that is, attraction per unit volume. Its unit is $\text{L}^2\text{atm mol}^{-2}$

b is the factor for volume correction of real gas to ideal behaviour. It is **effective volume** or **vibratory volume** of one mole of gas molecules. Its unit is Lmol^{-1} .

Strictly speaking b does not reflect the actual volume of the gas molecule and has been theoretically shown to be roughly equal to 4 times the volume of the gas molecule and to thus b is also called **vibratory volume** or **effective volume** of the gas molecule.

P is the pressure of real gas

V is the volume of real gas

T is the absolute temperature in Kelvin

$P + a\left(\frac{n}{V}\right)^2$ is the pressure of a gas if the gas would be ideal i.e. $P_{\text{ideal gas}} = P_{\text{real gas}} + a\left(\frac{n}{V}\right)^2$

$V - nb$ is the volume of a gas if the gas would be ideal; i.e. $V_{\text{ideal gas}} = V_{\text{real gas}} - nb$

Also from the Van der Waals equation: $\left(P + a\left(\frac{n}{V}\right)^2\right) = \frac{nRT}{V-nb}$

But $P + a\left(\frac{n}{V}\right)^2$ is the pressure of a gas if the gas would be ideal

Hence $P_{\text{ideal}} = \frac{nRT}{V-nb}$

Digging the Van der Waals equation!

Below are miscellaneous facts associated with terms which appear in the Van der Waals equation;

$$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$$

- Greater strength of intermolecular forces in the gas, greater value of **a**.
- $a\left(\frac{n}{V}\right)^2$ represents deviation of real pressure from ideal pressure,

That is the pressure deviation, $\Delta P = a\left(\frac{n}{V}\right)^2$

- Greater value of **a** (intermolecular forces) means greater the deviation as explained earlier.
- Greater value of $\frac{n}{V}$ (concentration) means greater deviation as explained earlier. (Also a greater value of **n** means greater deviation while greater **V** means smaller the deviation).
- **b** is the effective volume of **one mole** of gas molecules.
- **b** depends on the molecular size of the gas; larger molecular size means greater the value of **b**.
- **nb** is the total effective volume occupied by **n** moles of gas molecules.

Thus the volume deviation, $\Delta V = nb$

From which:

- Greater value of **b** (molecular size) means greater deviation as explained earlier.
- Greater value of **n** (number of moles of gas molecules) means greater deviation as explained earlier.

Below are Van der Waals constants for some gases (you should be able to explain the trend drawn on the constant values for **a** and **b** separately as explained in different parts of this chapter).

Table 3.1 Van der Waals constants for some gases

Gas	Molar mass (g/mol)	a (L ² atm mol ⁻²)	b (Lmol ⁻¹)
Hydrogen (H ₂)	2	0.244	0.0266
Helium (He)	4	0.034	0.0237
Methane (CH ₄)	16	2.25	0.0428
Water (H ₂ O)	18	5.46	0.0305
Nitrogen (N ₂)	28	1.39	0.0391
Carbon dioxide (CO ₂)	44	3.59	0.0427
Carbon tetrachloride (CCl ₄)	154	20.4	0.1383

POSITIVE AND NEGATIVE DEVIATION OF REAL GAS FROM IDEAL BEHAVIOUR

The reader should recall that, for ideal gas; $PV = nRT$ where P and V are measured pressure and measured volume respectively.

But for real (non-ideal) gas, $PV \neq nRT$; it may be either $PV > nRT$ or $PV < nRT$

- The measure of deviation of real gas from ideal behaviour is known as **compression factor (Z)** or simply **compressibility**.

By definition:

Compression factor is the ratio of the real (actual) volume to the volume predicted by the ideal gas equation.

$$\text{That is } Z = \frac{\text{Real volume}}{\text{Ideal volume}}$$

If V represents real volume, the formula becomes: $Z = \frac{V}{\text{Ideal volume}}$

But ideal volume can be calculated from ideal gas equation with measured (actual) P , T and n

$$\text{That is } V = \frac{nRT}{P} \quad (\text{From } PV = nRT)$$

Where V is the ideal volume.

$$\text{Then the formula } Z = \frac{V}{\text{ideal volume}} \text{ becomes } Z = \frac{V}{\frac{nRT}{P}} = \frac{PV}{nRT}$$

$$\text{Thus the compression factor, } Z = \frac{PV}{nRT}$$

Where P is the measured (real) pressure

V is the measured (real) volume

n is the measured number of moles

T is the measured temperature

But for ideal gas; $PV = nRT$

Hence $Z = 1$ for ideal gas

Effect of the pressure deviation in the value of compression factor

Pressure of real gas is less than the ideal pressure (Recall; $P_{\text{ideal}} = P_{\text{real}} + a\left(\frac{n}{V}\right)^2$)

- Then because $P_{\text{real}} < P_{\text{ideal}}$; $P_{\text{real}} V < nRT$ (Neglecting effect of the volume deviation)
- It follows that, from $Z = \frac{PV}{nRT}$; it is clearly understood that if: $PV < nRT$ (numerator value is less than denominator value), Z (quotient) will automatically be less than 1.
- That is $Z < 1$ due to deviation of real pressure from the ideal pressure.
- Because the compression factor is less than 1, in that situation the gas is said to deviate negatively from ideal behaviour (remember $Z = 1$ for real gas) and hence such kind of deviation is known as **negative deviation** of real gas.

In one sentence we can conclude that:

Deviation of pressure of real gas from the ideal pressure leads to negative deviation of real gas from ideal behaviour.

Effect of the volume deviation in the value of compression factor

Volume of real gas is larger than the ideal volume (Recall; $V_{\text{ideal}} = V_{\text{real}} - nb$)

- Thus because $V_{\text{real}} > V_{\text{ideal}}$; $PV_{\text{real}} > nRT$ (Neglecting effect of the pressure deviation)

- It follows that, from $Z = \frac{PV}{nRT}$; it is clearly understood if $PV > nRT$, Z will be greater than 1.
- That is $Z > 1$ due to deviation of real volume from ideal volume
- Because the compression factor is greater than 1, in such situation the gas is said to deviate positively from the ideal behaviour and hence such kind of deviation is known as **positive deviation** of real gas.

In one sentence.....!

Deviation of volume of real gas from the ideal volume leads to the positive deviation of real gas from ideal behaviour.

Have you seen the contradiction?

The pressure deviation tries to make $Z < 1$ whereas at the same time the volume deviation compete (with pressure deviation) to make $Z > 1$! What a result is actually observed? Is the pressure deviation more dominant such that $Z < 1$? Or, is the volume deviation more dominant such that $Z > 1$? Or, are the two factors counterbalance each other such that $Z = 1$?

- Experimentally it has been proved that pressure deviation is dominant at low pressure while volume deviation is dominant at high pressure
- Thus we can conclude that; at low pressure real gases tend to show negative deviation while at high pressure they tend to show positive deviation.

Why do real gases show negative deviation at low pressure?

At low pressure, volume of the gas (V) is very large such that the volume of individual molecules can be neglected compared to the volume of whole gas. Thus the deviation of real gas will only be significantly explained by the pressure deviation leading to the negative deviation.

Digging deeper!

From $V_{\text{ideal}} = V_{\text{real}} - nb$

When V_{real} is very large (at low pressure), b become negligible and therefore;

$$V_{\text{real}} - nb \approx V_{\text{real}} = V_{\text{ideal}}$$

Then the Van der Waals equation,

$$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT \text{ becomes;}$$

$$\left(P + a\left(\frac{n}{V}\right)^2\right)V = nRT$$

And hence $PV < nRT$ or $\frac{PV}{nRT} (Z) < 1$ (Negative deviation)

Why do real gases show positive deviation at high pressure?

At high pressure, the volume of the gas is small, and therefore the volume of individual gas molecules cannot be neglected while because the pressure is very large the effect of intermolecular forces can be neglected. Thus the deviation of real gas will only be significantly explained by the volume deviation leading to the positive deviation.

Digging deeper!

$$\text{From } P_{\text{ideal}} = P_{\text{real}} + a\left(\frac{n}{V}\right)^2$$

When P_{real} is very large, $a\left(\frac{n}{V}\right)^2$ can be neglected and therefore;

$$P_{\text{real}} + a\left(\frac{n}{V}\right)^2 = P_{\text{real}} = P_{\text{ideal}}$$

Then the Van der Waals equation;

$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$ becomes;

$$P(V - nb) = nRT$$

And hence $PV > nRT$ or $\frac{PV}{nRT} (Z) < 1$ (positive deviation)

Graphical representation of deviation of real gas from ideal behaviour

Positive and negative deviation of real gas from ideal behaviour can well be illustrated graphically and the resulting graph is known **Amagat's curve** which is the plot of compression factor (Z) against pressure of gases.

- For different gases say H_2 , N_2 and CO_2 (at constant temperature), the Amagat's curve will look as follows:

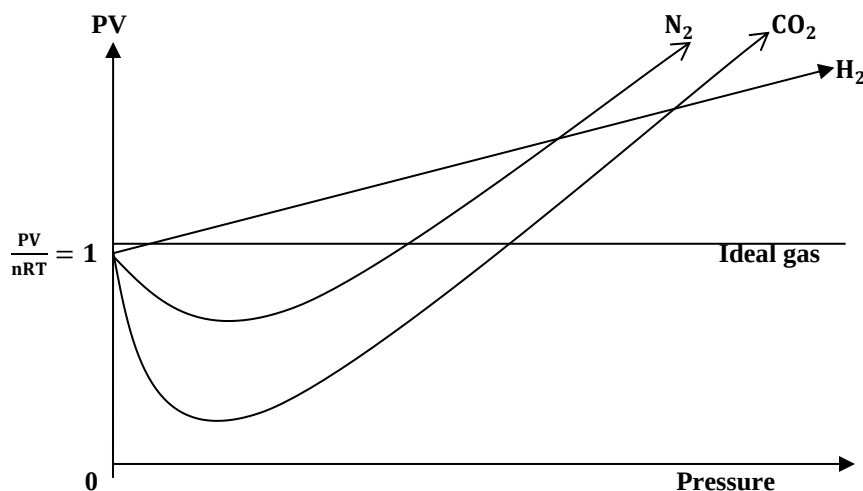


Figure 3.3 Amagat's curve for H_2 , N_2 and CO_2 gas

Things to note from the graph:

- At low pressure, gases show negative deviation (the curve pass below straight line with $Z = 1$ for ideal gas).
- At high pressure, gases show positive deviation.
- At that temperature (where data are taken), hydrogen does not show negative deviation at all. This because, H_2 have very small molecular weight and therefore very weak Van der Waals dispersion intermolecular forces.
- CO_2 shows greatest negative deviation of all gases because it has greatest molecular weight of the three gases and hence strongest Van der Waals dispersion intermolecular forces.

For the same gas at different temperatures, the Amagat's curve will look as follows:

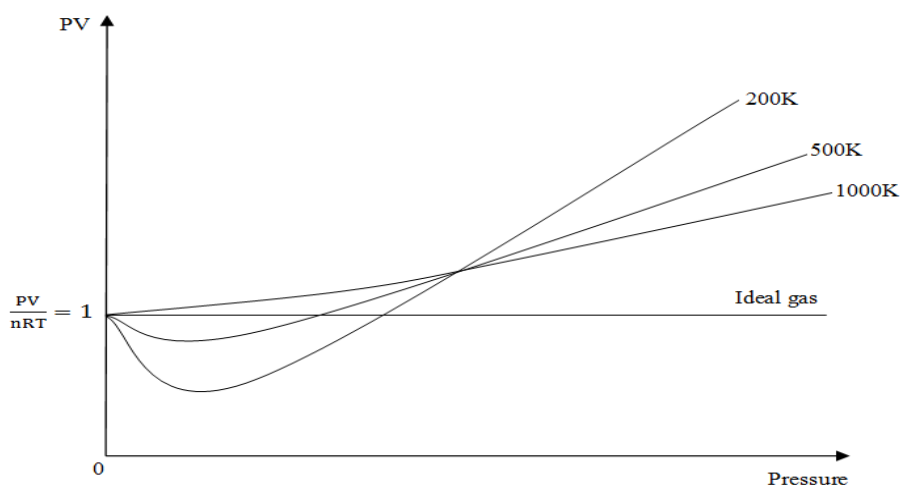


Figure 3.4 Amagat's curve for the same gas at different temperatures

Things to note from the graph:

- At low pressure the gas shows negative deviation while at high pressure it shows positive deviation.
- Greatest deviation is observed at lowest temperature (200K) of the three (on your own, you should be able to explain this).
- When temperature is very large (1000K), the gas does not show negative deviation at all. (You should be able to explain this too)

COMPARISON BETWEEN REAL GAS AND IDEAL GAS

Ideal and real gases resemble in the following ways:

- They both made of small particles that have mass
- The both constitute of mostly empty space
- They both have low density.
- They both constitute of particles which are in constant random straight line motion.

Differences between ideal and real gases are summarised in the table below.

Table 3.2 Differences between ideal gas and real gas

	IDEAL GASES		REAL GASES
01	Obey all gas laws under all conditions of temperature and pressure	01	Obey gas laws only at low pressure and high temperature
02	The volume occupied by the gas molecules is negligible as compared to the total volume occupied by the gas	02	The volume occupied by the gas molecules is not negligible compared to the total volume of the gas
03	The force of attraction between gas molecules are negligible	03	The force of attraction between the gas molecules are not negligible
04	Obey ideal gas equation, $PV = nRT$	03	Obey Van der Waals equation $\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$
05	Collisions between gas molecules and walls of the container is elastic	05	Collisions between the gas molecules and walls of the container is not elastic

However, the reader should understand that:

Gases become approximately ideal at the following conditions:

- High temperature
- Low pressure

At high temperature and low pressure gas molecules are more randomly moving very far apart with higher speed so that the intermolecular forces of attraction can be neglected and the gas contain the whole space of available of the container which make able to neglect the volume of the gas molecule compared to the volume of the whole gas.

Example 1

According to one of postulates of kinetic theory of gases, "*Gas exerts pressure in the container due to collision between gas molecules and the container's wall.*" Based on this postulate, explain clearly the effect of the each of the following factors on the pressure exerted by the gas:

- Decreasing the volume of the container at the same temperature.
- Increasing the temperature of the container.
- Adding amount of the gas in the container at the same temperature

Solution

- Decreasing the volume of the container will decrease the distance between walls of the container and therefore gas molecules will hit the container's walls more frequent leading to higher pressure.
- Increasing temperature, increases the speed of gas molecules and therefore making collisions between gas molecules and container's walls more energetic and more frequent and hence higher pressure.
- Adding amount of the gas in the container increases the concentration of the gas leading to more frequent collision between gas molecules and container's walls and hence higher pressure.

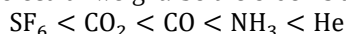
Example 2

Arrange the following gases in order of increasing their magnitude of volume correction in Van-der-Waals equation.



Solution

The magnitude of volume correction increases as molecular size (volume) of gas increases. Gases with larger molecular size have large molecular weight. So the order is as follows:



Example 3

- Under what set of experimental condition is the Van der Waals equation more applicable than the ideal gas equations?
- Use the Van der Waals equation: Calculate the pressure of 10moles of NH_3 gas in 10L vessel at 0°C 'a' = $4.2\text{L}^2\text{atm/mol}^2$, 'b' = 0.037 L/mol .

Solution

- Low temperature and high pressure.
- From Van-der-Waals equation: $\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$

Substituting given value: $\left(P + 4.2\left(\frac{10}{10}\right)^2\right)(10 - (10 \times 0.037)) = 10 \times 0.082 \times 273$

From which $P = 19.0461\text{atm}$

Hence the pressure of ammonia gas is 19.0461atm

Example 4

The Van-der-Waals equation for 'n' moles of real gas can be written as follows:

$$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$$

- (i) Which single word can be used to represent the $\frac{n}{V}$?
- (ii) How does the larger value of the ratio $\frac{n}{V}$ affect the pressure of the real gas?
- (iii) Explain how would you make the value of the ratio, $\frac{n}{V}$ bigger?

Solution

- (i) Concentration
- (ii) Larger value of the ratio means greater pressure deviation and hence the real pressure will be much smaller compared to ideal pressure.
- (iii) The ratio can be increased by decreasing the volume of fixed amount of the gas by either using the container of smaller volume or compressing the gas through the application of higher external pressure. Another way of increasing the ratio is by adding amount of the gas to the fixed volume.

DIGGING DEEPER EXERCISE 3

EXERCISE 3A: BINDER QUESTIONS

Question 1

From the standpoint of the kinetic molecular theory, explain briefly the properties of gas molecules that cause deviations from ideal behaviour.

Question 2

What are the shortcomings of kinetic theory for gases?

Question 3

At 25°C and 1 atmosphere pressure, which of the following gases shows greatest deviation from ideal behaviour? give two reasons for your choice.

**Question 4**

Real gases approach ideality at low pressure, high temperature or both. Explain these observations.

Question 5

The concept of ideal gas is just ideal. Justify.

Question 6

The Van-der-Waals equation for 'n' moles of real gas can be written as follows:

$$\left(P + a \left(\frac{n}{V} \right)^2 \right) (V - nb) = nRT$$

- (i) The real gas becomes more ideal with smaller value or larger value of the ratio $\frac{n}{V}$? Explain.
- (ii) For given gas, is it possible to alter the value of constants 'a' and 'b'? Explain.

Question 7

Comment on the following statement: The molecular attraction between gas molecules is high at low temperature.

Question 8

"Collision between gas particles and walls of a container is completely elastic." What is wrong with this statement?

Question 9

In Van der Waals equation for real gases, the value of constant, 'a' is larger for NH₃ gas than for N₂ gas but that of 'b' is larger for N₂ gas. Explain.

Question 10

Predict which of the substances;

NH₃, N₂, CH₂Cl₂, Cl₂, CCl₄ has:

- (i) The smallest Van der Waals 'a' constant
- (ii) The largest 'b' constant

Question 11

20 moles of He is in 10L cylinder at 120atm pressure. Calculate the temperature by using:

- (a) Van der Waals equation
- (b) Ideal gas equation

$a = 0.0341 \text{ L}^2 \text{ atm mol}^{-2}$, $b = 0.0237 \text{ L mol}^{-1}$

EXERCISE 3B: REAL QUESTIONS**Question 12**

It easier to liquefy ammonia gas than fluorine gas. Explain.

Question 13

Explain how deviation of real gas from ideal behaviour is beneficial in both gas transportation and its storage.

Question 14

Greater amount of investment is required in building a plant for liquefaction of helium than that of carbon dioxide. Explain.

Question 15

Explain how knowing compressibility factor of a gas is crucial in daily life.

Question 16

You have been employed in **BYAKATONDA ENERGY COMPANY**, as petroleum engineer. As one of its core activities, the company prepares liquefied natural gas (LNG). You have been visited by form six students from **MTWARA TECHNICAL SCHOOL**, who need to understand the liquefaction process as one of objectives in their study tour. Give a summary of your presentation by outlining two important steps in the process.

EXERCISE 3C: HOT QUESTIONS**Question 17**

When the molecular weight of a volatile liquid is calculated from the mass, volume, temperature, and pressure of a sample of the liquid when vapourised, the assumption is usually made that the gases behave ideally. In fact, at a temperature not far above the boiling point of the liquid, the liquid gas is not ideal. Explain how this would affect the results of the molecular weight determination.

Question 18

The Van der Waals equation of state for one mole of real gas is as follows:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

For any given gas, the values of the constants, 'a' and 'b' can be determined experimentally.

- Indicate which physical properties of molecule determine the magnitudes of the constants 'a' and 'b'
- Which of the two molecules, H_2 or H_2S , has the higher value for 'a' and which has the higher value for 'b'? Explain
- One of the Van der Waals constants can be correlated with the boiling point of a substance. Specify which constant and how it is related to the boiling point

Question 19

Carbon dioxide gas (1mole) at 373K occupies 536mL of 50 atmosphere pressure. What is the calculated value of the pressure using?

- Ideal gas equation
- Van der Waals equation

Calculate the % deviation of each value from that observed.

Given that; Van der Waals constants for carbon dioxide:

$$a = 3.61L^2 \text{ atm mol}^{-2} \quad b = 0.0428 \text{ Lmol}^{-1}$$

Question 20

2mol of oxygen gas in 5L container at 25°C shows greater deviation from ideal behaviour than 1mol of the oxygen gas in the container of the same volume at the same temperature. Explain whether you agree or you disagree with this statement.

Question 21

Explain the following: Doubling number of moles of a real gas in a container at given temperature does not double its pressure.

Question 22

Pressure deviation of real gas from ideal pressure is maximum at its boiling temperature. Explain.

Question 23

Clearly differentiate ideality of gas at its boiling temperature and its critical temperature.

Question 24

Helium behave more as a gas than chlorine. Explain.

Question 25

Identify the postulate of the kinetic molecular theory most closely identified with the Van – der – Waals constant 'a' and explain the relationship. Repeat the procedure for the constant 'b'.

Question 26

The Van-der-Waals equation for 'n' moles of real gas can be written as follows:

$$\left(P + a \left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$$

- (i) Which constant (a or b) is related to the gas's ability to undergo liquefaction? Give a reason to support your answer.
- (ii) Does the ability of the gas to be liquefied favoured with large value or small value of the constant mentioned in (i) above? Explain.

Question 27

Then Van der Waals equation for real gases is: $\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$; where all symbols carry their usual meaning.

- (i) Explain briefly the significance of the term $\frac{n^2a}{V^2}$ and nb in the equation.
- (ii) The compressibility factor for one mole of a real gas at 273K and 100 atm pressure is found to be 0.5. Assuming that the volume of gas molecules is negligible, calculate Van der Waals constant. Show your work clearly including manipulation of units.

Chapter 4

MOLAR MASS MEASUREMENT FOR VOLATILE SUBSTANCES

Volatile substances are substances which are capable of undergoing evaporation at normal temperatures and pressures. They tend to form vapour easily. One of the practical applications of gas laws is their usefulness in determining molecular mass and thus molar mass of these volatile substances.

Molecular mass is the total mass of all atoms present in one molecule of the substance while molar mass is the total mass of Avogadro's number (one mole) of molecules of the substance. One of interesting fact about molecular mass and molar mass is that, if molecular mass is given as **relative** molecular mass, then its numerical value will be equal to that of molar mass; so theoretical aspect of determining molecular mass (which is commonly given as relative molecular mass) and molar mass can be applied interchangeably.

After proper treatment of experimental results, the molar mass of a volatile liquid or solid can be calculated from measured vapour density or mass of a sample of the volatile substance by using one of the following relations:

$$M_r = 2 \times \text{Vapour density} \text{ or } M_r = \frac{mRT}{PV}$$

There are various methods which may be employed in molar mass determination by using above formulae. In this book we are going to discuss two of them which are:

- Victor Meyer's method
- Duma's method

VICTOR MEYER'S METHOD

Determination of molar mass of volatile substance by using this method is done by using by an apparatus which is known as **Victor Meyer's apparatus**.

What Victor Meyer's apparatus consisting?

The victor Meyer's apparatus consists of four parts:

1. A syringe

This is used to inject a known volume (and hence known mass if its density is known by using $m = \rho v$) of a volatile substance.

2. A vapourisation chamber

This is used to vapourise a sample of the volatile substance.

The vapourisation chamber is surrounded by a steam (hot vapours of water) jacket which is responsible for doing the vapourisation of the sample. So to be able to be vapourised the sample must have boiling point below 100°C; otherwise the steam would not be able to cause the vapourisation.

3. A gas burette

The gas burette contains water as the indicating liquid and has associated with it a side tube of the same diameter which is open to the atmosphere. It is used for measuring the volume of air displaced by the vapour of the sample formed in the vapourisation chamber.

The air displaced from the vapourisation chamber by the vapourised sample is cooled at room temperature and its volume is carefully measured by the gas burette.

Where, **volume of air displaced = volume of the vapourised sample**

(Therefore substitution of air by the actual vapour provides a means of determining the volume of the known mass of the vapour would occupy at room temperature if it could be cooled without condensation. Remember that air is still a gas at room temperature while our volatile substances condense to liquid at room temperature).

4. A steam generator

This is connected to the heating (steam) jacket surrounding the vapourisation chamber. It ensures constant supply of the steam for doing vapourisation in the vapourisation chamber.

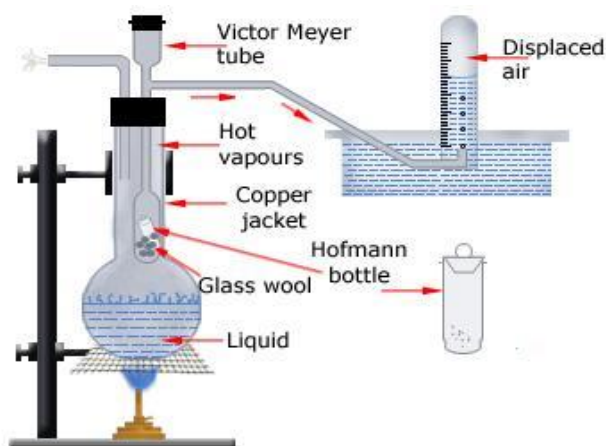


Figure 4.1 Victor Meyer's apparatus

DUMA'S METHOD

With this method, molar mass is calculated by measuring the mass of a known volume of a vapourised substance (liquid). The measurements are done in round flask which is known as **Duma's bulb**.

- A sample of a volatile substance is added to a pre-weighed flask (Duma's bulb).
- The flask is submerged in a boiling water bath to vapourise the substance.
- Upon heating, the vapour that is created initially pushes the air out of the flask and then the vapour begins exiting the flask until the pressure inside the flask is equal to the atmospheric pressure.
- The mass of the vapour remaining in the flask is obtained by reweighing the flask

That is; mass of the vapourised sample in the flask (Duma's bulb)

$$= \text{mass of Duma's bulb with the vapour} - \text{mass of empty Duma's bulb}$$

- Once mass of the vapourised sample has been determined, molar mass of the substance may be calculated after doing additional measurement of the pressure, temperature and the volume of the vapourised sample in the flask.

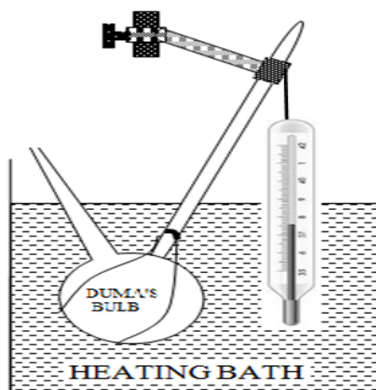


Figure 4.2 Duma's bulb

Example 1

In a Victor Meyer determination; 0.292g of a substance displaced 61cm³ of air at 22°C and 755mmHg. Calculate molar mass of the substance.

Given that: Vapour pressure of water at 22°C = 22mmHg

Solution

Volume of air displaced = volume of the sample = 61cm³ = 0.061dm³

Mass of the sample = 0.292g

Pressure exerted by the vapour of the sample = Total pressure – Vapour pressure of water
= (755 – 22)mmHg = 733mmHg

From general gas equation;

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}; V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

Volume of the gas at stp(T = 273, P = 760mmHg) may be found if;

P₁ = 733mmHg, P₂ = 760mmHg, V₁ = 0.061dm³

T₁ = 295K And T₂ = 273K

Substituting V₂ = $\frac{733 \times 0.061 \times 273}{760 \times 295}$ dm³ = 0.0544dm³

But at stp, 1mol of the gas, occupies 22.4dm³ and therefore mass of the gas in 22.4dm³ (at STP) is the molar mass of the gas

Also it is given that 0.292g of the gas occupies 0.061dm³ (which is equivalent to 0.0544dm³ at STP).

Using; $n = \frac{V}{22.4 \text{ dm}^3/\text{mol}} = \frac{m}{M_r}$

Substituting $\frac{0.0544 \text{ dm}^3}{22.4 \text{ dm}^3/\text{mol}} = \frac{0.292 \text{ g}}{M_r}$

From which; $\frac{22.4}{0.0544} \times 0.292 \text{ g/mol}$ or 120.2g/mol

Hence molar mass of the substance is 120.2g/mol

The reader should understand that: Modern Victor Meyer's method experiment (of course in the modern Duma's method as well) uses the ideal gas law which is easier as shown below.

Using ideal gas equation, PV = nRT from which it can be shown that; $M_r = \frac{mRT}{PV}$.

With:

m = 0.292g, T = 295K, P = 733mmHg, V = 0.061dm³;

$M_r = \frac{0.292 \times 0.082 \times 295}{\frac{733}{760} \times 0.061}$ or 120.1g/mol

Example 2

Calculate the relative molecular mass of volatile liquid X from the following data:

Mass of Dumas bulb full of air at 10°C and 770 mmHg = 25.700g

Mass of bulb sealed full of vapour of X at 100°C and 770mmHg = 25.759g

Mass of bulb full of water = 265.1 g

Given: 1 dm³ of air of s.t.p has mass of 1.293 g

Solution

Mass of water which fill the bulb = $(265.1 - 25.7)\text{g} = 239.4\text{g}$

Volume of bulb = volume of water = $\frac{m}{\rho} = \frac{239.4\text{g}}{1\text{g/cm}^3} = 239.4\text{cm}^3$

But at s.t.p 1dm^3 of air contain 1.293g

$$P_1 = 760\text{mmHg}, V_1 = 1\text{dm}^3, T_1 = 273\text{K}$$

$$P_2 = 770\text{mmHg}, T_2 = 283\text{K}, V_2 = ?$$

$$V_2 = \left(\frac{283}{273}\right) \left(\frac{760}{770}\right) \times 1\text{dm}^3 = 1.0232\text{dm}^3$$

Thus mass of air filled in the bulb = $\frac{0.2394 \times 1.293}{1.0232} = 0.303\text{g}$

So mass of the bulb is $(25.7 - 0.303)\text{g} = 25.397\text{g}$

Mass of vapour of X = $(25.759 - 25.397)\text{g} = 0.362\text{g}$

$$M_r = \frac{mRT}{PV} = \frac{0.362 \times 0.082 \times 373 \times 760}{770 \times 0.2394} = 45.6\text{g/mol}$$

Hence the relative molecular mass of X is 45.6g/mol

ABNORMAL RESULT IN MOLAR MASS MEASUREMENT OF GASES

Sometimes measurement of molar mass of gases gives unexpected results by giving measured molar mass of either greater or smaller than the expected one. This may be either due to **dissociation** or **association**.

Dissociation of gases

This is splitting of a large molecule into two or smaller molecules. Thus dissociation leads to increase in number of gas particles such that the observed number of gas particles (molecules) becomes greater than the expected number of gas particles.

But increase in number of gas molecules (particles) leads to increase in volume of the gas. So from the ideal gas equation which can be written as $PV = \frac{m}{M_r}RT$; it is clearly understood that the volume (V) of the gas varies inversely proportional to its molar mass (M_r). So **the increase in volume of the gas as the result of dissociation leads to decrease in molar mass of the gas.**

Hence the dissociation makes the measured (or observed) molar mass of the gas to be smaller than the expected one as its normal molecular formula suggests.

A fraction of gas molecules which has been dissociated is known as a **degree of dissociation, α**

$$\text{Thus } \alpha = \frac{\text{Number of gas molecules dissociated}}{\text{Original number of gas molecules before dissociation}}$$

A good example of dissociation is the dissociation of nitrogen tetraoxide (N_2O_4) into nitrogen dioxide (NO_2) and oxygen gas according to the following equation: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

Association of gases

This is the combining of more than one small molecule to form one larger molecule. So association leads to decrease in number of gas molecules so that the observed number of gas molecules becomes smaller than the expected one.

The decrease in number of gas molecules leads to decrease in volume of the gas, so from the ideal gas equation; $PV = \frac{m}{M_r}RT$ where volume of the gas varies inversely proportional to its molar mass, **the molar mass of the gas must increase as result of association.** Hence association makes the measured molar mass to be greater than the expected one as its normal molecular formula suggests.

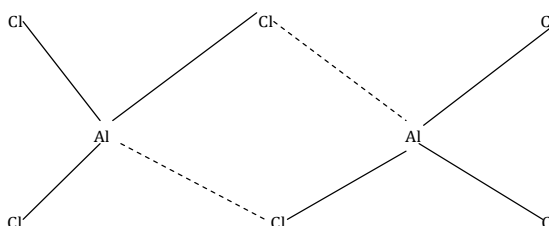
A fraction of gas molecules which has been associated is known as the **degree of association, α**

$$\text{Thus } \alpha = \frac{\text{Number of gas molecules associated}}{\text{Original number of gas molecules before association}}$$

A good example of association is the association in aluminum chloride:

In vapour phase two molecules of aluminum chloride associates (**dimerises**) to form a single larger molecule which is known as **dimer**. The process of **dimerisation** in aluminum chloride makes its observed (measured) molar mass to be twice the expected one.

This can be illustrated as follows:



Dimer of aluminum chloride which correspond to the molecular formula of Al_2Cl_6

Calculations of degree of dissociation and association

Degree of dissociation

Consider one molecule of a gas A_xB_y which dissociate to form **a** molecules of A_c and **b** molecules of B_d where $\mathbf{a} + \mathbf{b} = \mathbf{N}$ which is the total number of molecules formed after dissociation.

That is: $\text{A}_x\text{B}_y(\text{g})$	$\rightleftharpoons$	$\mathbf{a}\text{A}_c(\text{g})$	+	$\mathbf{b}\text{B}_d(\text{g})$	
1		0		0	Initial number of molecules before dissociation
$1 - \alpha$		$\mathbf{a}\alpha$		$\mathbf{b}\alpha$	Number of molecules after dissociation

Where α is numerically equal to degree of dissociation = fraction of the molecules dissociated.

From the above equation:

Expected number of molecules (without dissociation) = 1

Observed number of molecules (after dissociation) = $1 - \alpha + \mathbf{a}\alpha + \mathbf{b}\alpha = 1 + \alpha(\mathbf{a} + \mathbf{b} - 1)$

But $\mathbf{a} + \mathbf{b} = \mathbf{N}$

So observed number of molecules = $1 + \alpha(\mathbf{N} - 1)$

The ratio of observed number of particles to expected number of particles is known as **Vant Hoff's factor, i**

$$\text{Thus } i = \frac{\text{Observed number of particles}}{\text{Expected number of particles}} = \frac{1 + \alpha(\mathbf{N} - 1)}{1} \text{ or } i = 1 + \alpha(\mathbf{N} - 1)$$

$$\text{Hence } \alpha = \frac{i - 1}{\mathbf{N} - 1}$$

Where α is the degree of dissociation

i is the Van't Hoff's factor

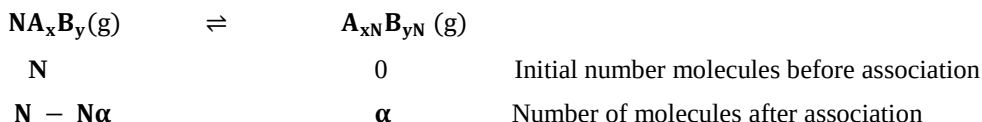
N is the number of molecules formed after dissociation

It should be noted that:

For dissociation; $i > 1$; because observed number of particles must be greater than the expected one.

Degree of association

Consider N molecules of A_xB_y associate to form one molecule of $A_{xN}B_{yN}$ according to the following equation:



Where α is the degree of association

Expected number of molecules (without association) = N

Observed number of molecules (after association) = $N - N\alpha + \alpha$

$$= N + \alpha(1 - N)$$

$$\text{Then } i = \frac{\text{Observed number of particles(molecules)}}{\text{Expected number of particles(molecules)}} = \frac{N + \alpha(1 - N)}{N} \text{ or } \alpha = \frac{iN + N}{1 - N}$$

$$\text{Dividing by } N \text{ throughout the expression } \frac{iN + N}{1 - N} \text{ gives } \alpha = \frac{i - 1}{\frac{1}{N} - 1}$$

$$\text{Hence degree of association is given by; } \alpha = \frac{i - 1}{\frac{1}{N} - 1}$$

It should be noted that:

- For association, $i < 1$; because observed number of particles must be less than the expected one.
- If $i = 1$ then there is neither dissociation nor association.
- Degree of dissociation (or association) may be given as a fraction or percentage.

The reader should understand that:

$$\text{From } i = \frac{\text{Observed number of particles}}{\text{Expected number of particles}};$$

- Since number of gas particles varies directly proportional to its volume, then:

$$i = \frac{\text{Observed(measured)volume of the gas}}{\text{Expected volume of the gas}}$$

- As number of gas particles varies directly proportional to the pressure exerted by the gas, then:

$$i = \frac{\text{Observed(measured) pressure of the gas}}{\text{Expected pressure of the gas}}$$

- Since number of gas particles varies directly proportional to the volume of the gas which in turn varies inversely proportional to the molar mass of the gas, then:

$$i = \frac{\text{Expected molar mass}}{\text{Measured(observed) molar mass}}$$

Example 3

Nitrogen dioxide exists in an equilibrium mixture: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

The relative molar mass of nitrogen dioxide at 25°C is 80. What is the percentage of molecules in the mixture is N_2O_4 ?

Solution

Expected molar mass of N_2O_4 is $92\text{g/mol } ((2 \times 14) + (4 \times 16)) = 92\text{g/mol}$

Measured molar mass of N_2O_4 is 80g/mol

$$\text{Using } i = \frac{\text{Expected molar mass}}{\text{Measured molar mass}} = \frac{92\text{g mol}^{-1}}{80\text{g mol}^{-1}} = 1.15$$

From the equation: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$1 - \alpha \quad 2\alpha \quad \text{After association } N = 2$$

$$\text{Using } \alpha = \frac{i - 1}{N - 1} = \frac{1.15 - 1}{2 - 1} = 0.15 \text{ or } 15\%$$

But total number of molecules of N_2O_4 after dissociation:

$$= 1 - \alpha + 2\alpha = (1 + \alpha) \text{ Molecules}$$

$$\%N_2O_4 \text{ in the mixture} = \frac{n_{N_2O_4}}{n_T} \times 100\% = \frac{1-\alpha}{1+\alpha} \times 100\% = \left(\frac{1-0.15}{1+0.15}\right) \times 100\% = 73.9\%$$

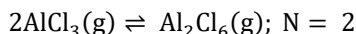
Hence the percentage of N_2 in the mixture is 73.9%

Example 4

A 10.32g of $AlCl_3$ are allowed to vapourise in 1dm^3 vessel at 80°C a pressure of $1.7 \times 10^5 \text{ Nm}^{-2}$ develops. What is the degree of association of $AlCl_3$ into Al_2Cl_6 .

Solution

An equation to show association of $AlCl_3$ into Al_2Cl_6



$$\text{From } PV = \frac{m}{M_r} RT \text{ or } M_r = \frac{mRT}{PV}$$

Where: $m = 10.32\text{g}$, $R = 8.314$, $T = 80^\circ\text{C} = 353\text{K}$, $P = 1.7 \times 10^5 \text{ Nm}^{-2}$

$$V = 1\text{dm}^3 = 103 \text{ m}^3$$

$$M_r = \frac{10.32 \times 8.314 \times 353}{1.7 \times 10^5 \times 10^{-3}} \text{ g mol}^{-1} = 178\text{g mol}^{-1}$$

$$i = \frac{\text{Expected molar mass}}{\text{Measured(observed) molar mass}}$$

But expected molar mass of $AlCl_3 = (27 + (3 \times 35.5)) = 133.5\text{g mol}$

$$i = \frac{133.5}{178} = 0.75$$

$$\text{Degree of associaton, } \alpha \text{ is given by; } \alpha = \frac{i - 1}{\frac{1}{N} - 1} = \frac{0.75 - 1}{\frac{1}{2} - 1} = 0.5\% \text{ or } 50\%$$

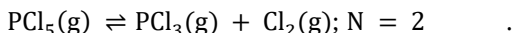
Hence degree of association of $AlCl_3$ into Al_2Cl_6 is 50%

Example 5

20.85g of phosphorous (V) chloride are allowed to vapourise in 5 dm^3 vessel at 175°C . A pressure of $1.04 \times 10^5 \text{ Pa}$ develops. Calculate the degree of dissociation of PCl_5 into PCl_3 and Cl_2

Solution

An equation to show the dissociation of PCl_5 ;



$$\text{From } M_r = \frac{mRT}{PV}$$

Where $m = 20.85\text{g}$, $R = 8.314$, $T = 175^\circ\text{C} = 448\text{K}$, $P = 1.04 \times 10^5\text{ Pa}$

$$V = 5\text{dm}^3 = 5 \times 10^{-3}\text{ m}^3$$

$$M_r = \frac{20.85 \times 8.314 \times 448}{1.04 \times 10^5 \times 5 \times 10^{-3}} \text{gmol}^{-1} = 149 \text{gmol}^{-1}$$

But expected molar mass of PCl_5 is 208.5gmol^{-1}

$$i = \frac{\text{Expected molar mass}}{\text{Measured molar mass}} = \frac{208.5}{149} = 1.4$$

$$\text{Using } \alpha = \frac{i - 1}{N - 1} = \frac{1.4 - 1}{2 - 1} = 0.4 \text{ or } 40\%$$

Hence degree of dissociation of phosphorous (V) chloride is 0.4 or 40%

Example 6

(a) Calculate the relative molecular mass of Iron (III) chloride.

(b) Calculate another value from the following data.

When 1g of Iron (III) chloride was volatilised at 300°C , its vapour displaced 76cm^3 of air measured at 27°C and 101 KPa (758mmHg) pressure.

Comment on your two values of parts (a) and (b) (r. a. m. $\text{Cl} = 35.5$, $\text{Fe} = 55$)

Solution

(a) Molecular mass of $\text{FeCl}_3 = 55 + (3 \times 35.5) = 161.5\text{g/mol}$

Hence molecular mass of Iron (III) chloride is 161.5g/mol .

(b) Volume of air displaced at 27°C is 76cm^3

That is $V_1 = 76\text{cm}^3$, $T_1 = 27^\circ\text{C}$ or 300K

So the volume of air at 300°C (573K) may be found by applying Charles's law as follows:

$$\text{From Charles's law: } \frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ or } V_2 = \left(\frac{T_2}{T_1}\right) V_1 = \frac{573}{300} \times 76\text{cm}^3 = 145.16\text{cm}^3$$

But volume of air displaced = volume of Iron (III) chloride vapour

Thus the volume of FeCl_3 vapour is 145.16cm^3

$$\text{Using } M_r = \frac{mRT}{PV} = \frac{1 \times 0.082 \times 573 \times 760}{758 \times 145.16 \times 10^{-3}} = 324.5\text{g/mol}$$

Hence molar mass of FeCl_3 is 324.5g/mol

Comment:

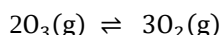
The obtained molar mass in (b) is approximately twice the value obtained in (a) because in the vapour phase two molecules of Iron (III) chloride associates (dimerises) to form a dimer which corresponds to the molecular formula of Fe_2Cl_6

Example 7

The relative vapour density of a sample of ozone at a certain temperature was 18.3. What is the degree of dissociation of ozone into oxygen under these conditions? (Ozone is O_3 , trioxygen)

Solution

O_3 dissociates according to the following equation:



Rewriting the equation to show number of molecule of O_2 produced by one molecule of ozone by dividing with 2 throughout the above equation gives: $O_3(g) \rightleftharpoons \frac{3}{2}O_2(g)$

$$\text{So } N = \frac{3}{2} = 1.5$$

Using $\alpha = \frac{i-1}{N-1}$ Where α is the degree of dissociation and i is the Van't Hoff's factor.

$$\text{But } i = \frac{\text{Expected relative vapour density}}{\text{Observed relative vapour density}}$$

$$\text{Where Expected relative vapour density} = \frac{\text{Expected molar mass (of } O_3)}{2g/mol} = \frac{48g/mol}{2g/mol} = 24$$

$$\text{Then } i = \frac{24}{18.3} = 1.31$$

$$\text{It follows that } \alpha = \frac{1.31-1}{1.5-1} = 0.62$$

Hence the degree of dissociation is 0.62 or 62%.

DIGGING DEEPER EXERCISE 4

EXERCISE 4A: BINDER QUESTIONS

Question 1

- What is the role of combined gas law and Avogadro's law on determination of molecular mass of volatile substance by Victor Meyer's method?
- Instead of combined gas law and Avogadro's law (in (a) above), what alternative can be applied?
- Between the two alternatives ((a) and (b)), which one you would prefer most? Give reason(s) to support your choice.

Question 2

The experimentally determined molar mass of a substance is not always the same as that suggested by its molecular formula. Explain.

Question 3

List down at least two advantages and three disadvantages of employing Victor Meyer's method in the determination of molecular mass of volatile substances.

Question 4

What are two main assumptions in determining molecular mass of a volatile substance by the Duma's method?

Question 5

In the determination of molecular mass by Victor Meyer's method, 0.60 g of volatile substance expelled 123 mL of air measured over water at 20 °C and 757.4 mmHg. Find the molecular mass of the substance if the vapour tension of water at 20°C is 17.4 mmHg.

Question 6

In the Duma's bulb technique for determining the molar mass; you vapourise the sample of a liquid that boils below 100°C in a boiling-water bath and determine the mass of vapour required to fill the bulb. From the following data, calculate the molar mass of the unknown vapour: mass of unknown vapour, 1.012 g; volume of bulb, 354 cm³ pressure, 742 torr; temperature, 99°C.

EXERCISE 4B: REAL QUESTIONS

Question 7

Victor's Meyer method cannot be used in the determination of molar mass of table salt. Explain.

Question 8

Why molecular mass of methanol cannot be determined by Victor Meyer's method although it is volatile with boiling point of only 64.7°C?

Question 9

Determination of molecular mass of substances is crucial in the real life. How the molecular masses obtained from Duma's bulb or Victor Meyer's apparatus are useful?

Question 10

Mr. Akilikubwa is a laboratory technician at your school. He was experimentally demonstrating to you the determination of molar mass of volatile liquid by Duma's method. During the demonstration, he didn't weigh the amount of liquid initially put into the flask. Was this correct? Explain.

Question 11

Your beloved friend, **Kipute**, was given a homework assignment of calculating molecular mass of a substance from data that were collected in the Victor Meyer's experiment. However, she got the wrong answer of 116.56 g/mol because she didn't include vapour pressure of water in her calculations. She came to your home, seeking for the help so that she can understand both correct solution of the problem and correct molar mass of the substance. Unfortunately, she forgot to carry her counter book for homework assignment, but she is still able to recall all data except that of total pressure. She told you that other data were: 0.292 g of a substance displaced 61 cm³ of air at 22°C and the vapour pressure of water at 22°C was given as 22 mmHg. Without seeking her to go and carry her forgotten counter book, provide the much needed help to your great friend, **Kipute**!

EXERCISE 4C: HOT QUESTIONS**Question 12**

What is wrong with this statement: *Dissociation of gas increases number of gas particles and therefore increasing its volume in accordance to Avogadro's law. According to Boyle's law the increase in volume as a result of dissociation leads to the decrease in pressure of the gas and hence it can be concluded that the dissociation of the gas decreases amount of the pressure exerted by the gas.*

Question 13

0.143g of a volatile liquid, when vapourised in a Victor Meyer apparatus displaced 30.4cm^3 of air at 17°C and 99350Nm^{-2} (745mm Hg) pressure. Calculate

- (a) The relative vapour density
- (b) The relative molecular mass of the liquid
- (c) The vapour pressure of water at 17°C is 2000Nm^{-2} (15mmHg)

Question 14

In Dumas method for the estimation of nitrogen, 0.25 g of an organic compound gave 40 mL of nitrogen collected at 27°C temperature and 725 mmHg pressure. If the vapour pressure of water at 27°C is 25 mmHg, what is the percentage of nitrogen in the compound?

Question 15

When a glass bulb with a stop cock is evacuated, weighed, and then filled with oxygen, the weight increases by 0.25g. When the same bulb is evacuated and filled with another unknown gas under the same conditions of temperature and pressure, the mass increases by 0.5525g. If the molecular mass of oxygen is 32;

- (a) Calculate the molecular mass of the unknown gas.
- (b) Calculate the volume of the glass bulb assuming that it does not change appreciably with the change in pressure and temperature.

Question 16

A 6.19g sample of PCl_5 is placed in an evacuated 2L flask and is completely vapourised at 252°C .

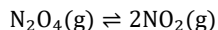
- (a) Calculate the pressure in the flask if no chemical reaction were to occur.
- (b) Actually at 252°C , the PCl_5 is partially dissociated according to the following equation:



The observed pressure is found to be 1.00atm. In view of this observation, calculate the partial pressure of PCl_5 and PCl_3 in the flask at 252°C .

Question 17

The vapour density of N_2O_4 at certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature.



EXAMINATION QUESTIONS FOR PART ONE

Question 1

- (a) Give brief explanation to argue against or to argue for the following statement: *Liquid state of a substance cannot exist above its critical temperature.*
- (b) 140cm^3 of water vapour measured at 150°C and 100700 Nm^{-2} (755mmHg) pressures have a mass of 0.071g. Show that these figures are in accordance with the formula H_2O for steam.

Question 2

- (a) In your own words, explain what will happen to the pressure when 4g of nitrogen gas stored in 1L container kept in a certain room is now stored in the new container of the 2.5L in the same room.
- (b) Beryllium chloride was known to contain 11.3% of beryllium but the oxidation number of the metal was uncertain. The chloride was found to have a relative vapour density of 40. Determine the oxidation number of beryllium in the compound and hence its relative atomic mass.

Question 3

- (a) What is the pressure-volume law governing gas behaviour?
- (b) In a diffusion experiment, the time required for water to cover the space between two marks on a tube as oxygen diffused out of it was 240 seconds. In identical conditions, the time required for another gas, X, was three and three – quarters minutes. Calculate the relative molecular mass of X

Question 4

- (a) Based on Charles's law, justify the following statement, "*Negative Kelvin is nonsense.*"
- (b) A certain volume of hydrogen diffuses from an apparatus in one minute. Calculate the time required for the diffusion of the same volume of ozonide oxygen, containing 10% of ozone by volume, from the apparatus under identical conditions. (ozone is O_3 , trioxxygen)

Question 5

- (a) Compare diffusion and effusion of gases.
- (b) The relative vapour density of nitrogen dioxide at 1050°C is 24; calculate the degree of dissociation (by mass) of the gas in these conditions.

Question 6

- (a) The critical temperature of nitrogen is 126K and that of helium is 5.3K. With reason, predict which of the gases will liquefy first?
- (b) If phosphorous pentachloride is 20% dissociated at a certain temperature, calculate the relative vapour density of the equilibrium mixture of the pentachloride, trichloride and chlorine at this temperature.

Question 7

- (a) Give your understanding on meaning of the following terms with reference to gases:
- Critical temperature
 - Critical volume
 - Critical pressure
- (b) The relative vapour density of iodine at 1 atmosphere pressure and 125°C is 87. Calculate the percentage dissociation of iodine, I_2 into its corresponding atoms in these conditions.

Question 8

- (a) The Van der Waals equation of state for one mole of real gas is as follows:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

For any given gas, the values of the constants, 'a' and 'b' can be determined experimentally.

- Indicate which physical properties of molecule determine the magnitudes of the constants 'a' and 'b'
- Which of the two molecules, H_2 or H_2S , has the higher value for 'a' and which has the higher value for 'b'? Explain
- One of the Van der Waals constants can be correlated with the boiling point of a substance. Specify which one.

- (b) 1g of hydrogen iodide was heated to a certain temperature and the products suddenly cooled. The iodine which had been liberated required 15cm^3 of 0.1M sodium thiosulphate for complete reaction. Calculate the percentage by mass of hydrogen iodide which remained undissociated at that temperature.

Question 9

- (a) Predict which of the substances;
 NH_3 , N_2 , CH_2Cl_2 , Cl_2 , CCl_4 has:
(i) The smallest Van der Waals 'a' constant
(ii) The largest 'b' constant
- (b) 2.5g of calcium carbonate are placed in a globe of capacity 850cm^3 . The globe is evacuated and heated to a temperature of 800°C at which the temperature the carbon dioxide evolved exerts a pressure of 26660Nm^{-2} (200mmHg). Calculate the percentage of the calcium carbonate which is decomposed.

Question 10

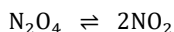
- (a) From kinetic equation of gases, derive a mathematical equation of kinetic energy of one mole of a gas and hence show that the kinetic energy varies directly proportional to absolute temperature.
- (b) 1cm^3 of water measured at 4°C is heated until has attained a temperature of 2500°C ; if steam of this temperature is 3.98% of mass dissociated into molecules of hydrogen and oxygen, Calculate the volume the gasses should occupy. Assume that the gas laws apply at the temperature given. Pressure is 760mmHg throughout.

Question 11

- (a)
(i) State gas law which govern breathing in human.
(ii) At what conditions the law stated in (i) above obeys strictly?
- (b) What volume of 0.165M sodium thiosulphate would be required to react with iodine from 3g of hydrogen iodine? If the latter were heated to a temperature where it is 16% dissociated; what mass of hydrogen would remain uncombined?

Question 12

- (a) Explain the concept of absolute zero of temperature.
- (b) At 27°C dinitrogen tetraoxide is 20% dissociated into nitrogen dioxide. 1dm^3 of this mixture was heated to (i) 100°C and (ii) 600°C . At 100°C the dinitrogen tetraoxide is 90% dissociated and at 600°C it is completely dissociated into nitrogen oxide and oxygen. Calculate the volume the gasses would occupy under condition (a) and (b). All measurements are made at 760mmHg .

**Question 13**

- (a) Explain the effect of dissociation and association in the experimental determination of molar mass of volatile substances.
- (b) At a certain temperature and under identical conditions, the volumes of oxygen and dinitrogen tetraoxide diffusing from an apparatus in a given time were in the ratio of 3 to 2. Calculate the degree of dissociation of dinitrogen tetraoxide of this temperature.

Question 14

- (a) Show that Boyle's law and Charles's law are contained in the kinetic equation of gases.
- (b) 24cm^3 of a mixture of methane and ethane were exploded with 90cm^3 of oxygen. After cooling to room temperature, the volume of gas was noted. It was found to decrease by 32cm^3 when treated with KOH solution (pressure is constant throughout). Calculate the composition of the mixture.

Question 15

- (a) Show that if kinetic equation of gases is valid, Graham's law of diffusion must be valid too.
- (b) 32cm^3 of a mixture of carbon monoxide, methane and hydrogen were mixed with 50cm^3 of oxygen and exploded. After cooling to room temperature, the volume was noted. It was reduced by 22cm^3 when exposed to KOH solution, leaving 16cm^3 of excess oxygen. Calculate the composition of the mixture.

Question 16

- (a) Which one of the following statements is correct, and which one is incorrect? For incorrect statement(s) give reason(s) to support your choice.

Statement 1: Critical volume is the molar volume of a fluid at its critical temperature and critical pressure.

Statement 2: One mole of an ideal gas at room temperature and pressure occupies a volume of 22.4L.

- (b) 65 cm³ of a mixture of hydrogen, carbon monoxide and nitrogen are mixed with 50 cm³ of oxygen at room temperature. The mixture is exploded and allowed to cool. The residual volume is 55 cm³. After absorption with KOH solution the final volume is 25 cm³, calculate the percentage by volume of each gas in the original mixture (Temperature and pressure constant room values).

Question 17

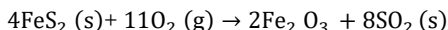
- (a) From kinetic equation of gases, derive the equation for root mean square speed (c) of a gas with molar mass, M_r, at absolute temperature, T, and hence deduce the mathematical equation which will enable you to calculate kinetic energy of 'n' moles of the gas.
- (b) 100 cm³ of a sulphurous acid solution required 11.2 cm³ of 0.05M iodine solution for complete reaction. Calculate the volume of dissolved sulphur dioxide at 15°C and 742 mmHg per dm³ of the acid.

Question 18

- (a) Duma's method is useless in the experimental determination of molar mass of glucose.
- (b) The carbon dioxide in the air of a room was estimated by drawing 200 dm³ of air at 14°C and 753 mmHg through potassium hydroxide bulbs of known mass. The increase in mass of bulbs was 0.157g. Calculate the percentage by volume of carbon dioxide in the air.

Question 19

SO₂ used in the air manufacture of sulphuric acid, is obtained from sulphide ores (iron pyrites):



The SO₂ is then treated with suitable reagent to produce sulphurous acid and finally sulphuric such that one mole of SO₂ produces one mole of sulphuric acid

- (a) How many kg of iron pyrites, FeS₂, would be required to produce 100kg of sulphuric acid containing 98 % H₂SO₄?
- (b) How many m³ of air containing 21% of oxygen by volume and measured at 15°C and 750 mmHg, would be required for complete combustion of pyrites in (a) above?

Question 20

- (a) Under what conditions do real gases fail to obey Charles's and Boyle's law?
- (b) 141.4 cm³ of an inert gas diffused through a porous plug in the same time as it took 50 cm³ of oxygen to diffuse through the same plug under identical conditions. Calculate the relative atomic mass of inert gas.

Question 21

- (a) Write down two assumptions of kinetic theory of gases that are not considered to be negligible under real gas behaviour.
- (b) A quantity of 2.4g of a compound fills 934 cm³ as a vapour at 298K and 740 mmHg. It contains 37.21% carbon 7.8% hydrogen and 55% chlorine. What is its molecular formula?

Question 22

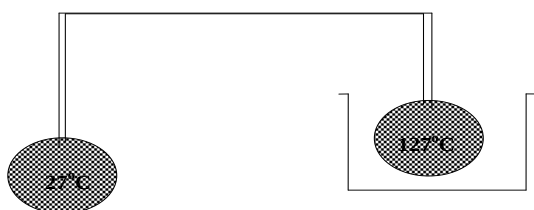
- (a) At what conditions does real gas obey the ideal gas equation?
- (b) Using Van der Waals equation, calculate the constant 'a' when two moles of a gas contained in a 4 litre flask exerts a pressure of 11 atmosphere at temperature of 300K. the values of b is 0.05 Lmol⁻¹

Question 23

- (a) Under what conditions (s), does Dalton's law of partial pressure apply?
- (b) For 10 minutes each, at 27°C , from two identical holes nitrogen and an unknown gas are leaked into a common vessel of 3L capacity. The resulting pressure is 4.18atm and the mixture contains 0.4 mole of nitrogen. What is the molar mass of unknown gas?

Question 24

- (a) What each of the following gas laws does?
- Boyle's law
 - Charles's law
 - Gay-Lussac's law
 - Avogadro's law
- (b) Two flasks of equal volumes are connected by a narrow tube of negligible volume. Initially both flasks are at 27°C and each contains 0.35 moles of hydrogen gas at 0.5 atm. One of the flasks is then immersed in an oil bath at 127°C as shown below:



Calculate:

- The number of moles of hydrogen gas in each flask.
- The final pressure of the system.

Question 25

- (a) "A gas consists of very small molecules in a random motion of which there is a collision between gas molecules and walls of the container"
- What is the characteristics feature of that collision? (Assume the gas is ideal)
 - The collision will result into important property of the gas: mention it.
 - Explain clearly how, the presence of intermolecular forces in real gas, will affect facts mentioned in (i) and (ii) above
- (b) Pyridine contains 75.92% C, 6.37% H and the rest being N. At 110°C and 630mmHg the density of gaseous pyridine was 2.12gdm^{-3} . Determine the empirical formula and molecular formula of pyridine.

Question 26

- (a) What does each of the following say about? In each case give their corresponding mathematical equation.
- Gay-Lussac's law
 - Combined gas law
- (b) A gaseous compound X has 46.1%C and 53.9% H; in 20 seconds, 50cm^3 of X diffused through a porous plug and the same volume of O_2 diffused in 15.7 seconds. Determine the molecular mass of X. What volume of CO_2 would diffuse in 20 seconds under the same conditions as before?

Question 27

- (a) A reaction mixture for combustion of SO_2 was prepared by opening a stop cock connecting two separate chambers, one having volume of 2.125L, filled at 0.75 atm with SO_2 and other having a 1.5L volume filled at a pressure of 0.5 atm with O_2 , both gases at 80°C

What were the:

- Mole fraction of SO_2 in the mixture
- The total pressure
- The partial pressure of SO_2

- (b) If the mixture was passed over a catalyst that promote the formulation of SO_3 and then was returned to the original connected vessels. What were the:
- The mole fraction of SO_3 in the final mixture.
 - The final total pressure.

Question 28

- (a) State four postulates under kinetic theory of gases.
- (b) At the start of an experiment one end of the U tube of 6mm glass is immersed in a concentrated ammonia solution and other end is immersed in concentrated acid solution. At the point in the tube where the vapours of NH_3 and HCl meet a white cloud of NH_4Cl forms. At what fraction of distance along the tube from the ammonia the white clouds first forms?

Question 29

- (a) What does each of the following law say?
- Boyle's law
 - Avogadro's law
 - Graham's law
- (b) At the top of mountain the thermometer reads 0°C and barometer reads 710mmHg. At the bottom of the mountain the temperature is 30°C and the pressure is 760 mmHg. Compare density of the air at the top with that at the bottom.

Question 30

- (a) What does ideal gas law say?
- (b) A 15L vessel containing 5.65g of nitrogen (N_2) is connected by means of valve to a 6L vessel containing 5g oxygen (O_2). After the valve is opened and the gases were allowed to mix, what would be partial pressure of each gas and the total pressure at 27°C ?

Question 31

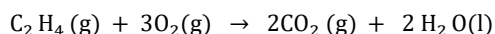
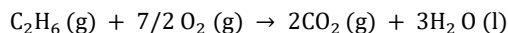
- (a)
- State the law which governs the total pressure in the container of mixture of two or more gases.
 - From kinetic equation of gases, derive the law stated in (i) above.
- (b) The pressure in a vessel that contained pure oxygen dropped from 2000 torr to 1500torr in 55 minutes as the oxygen leaks through a small hole into a vacuum. When the vessel was filled with another gas, the pressure dropped from 2000 torr to 1500 torr in 85 minutes. What is the molecular weight of the second gas?

Question 32

- (a) From the fundamental gas equation, derive an ideal gas equation.
- (b) Calculate the kinetic energy of 1mol of an ideal gas at 27°C .

Question 33

A mixture of gases ethane, ethene and helium is contained in a container of unknown volume at 300K and 680 mmHg. The mixture is burned with excess oxygen and all the carbon is converted into carbon dioxide and hydrogen into water. The carbon dioxide is collected in a container of volume 0.25dm^3 and found to exert a pressure of 561.3mmHg at 300K. The Helium is also collected in a separate container of volume 0.25 dm^3 and exerts a pressure of 187.1 mmHg at 300K.



- How many moles of Helium are in the original vessel?
- How many moles of carbon dioxide are produced?
- What is the partial pressure of Helium in the original vessel?
- What is the volume of original vessel?

Question 34

- (a) What is the physical meaning of the 'a' and 'b' constants in the Van der Waals equation?
- (b) Calculate the pressure of real gases of 0.02mol occupied in 1.6L bulb at 20°C

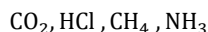
Given that: $a = 1.34 \text{ atm L}^2 \text{ mol}^{-2}$ and $b = 0.32 \text{ L mol}^{-1}$

Question 35

- (a) At 110°C and 454mmHg, 0.11g of ethanoic acid vapour occupies 63.7cm³. At 156°C and 458mmHg, 0.081g of ethanoic acid vapour occupies 66.4cm³. Calculate the molar mass of ethanoic acid in the vapour phase at each temperature.
- (b) Give the interpretation of the results in 35(a) above.

Question 36

- (a) Which of the following gases would be nearly impossible to collect over water? Why?



- (b) A 3.2m³ vessel contains a mixture of 86.2g of oxygen and 1.5 g of hydrogen at 88°C. Calculate the total pressure in the vessel.

Question 37

- (a) What is Dalton's law of partial pressure doing?
- (b) Gas A of a certain volume diffuses for 580.8s while the same volume of gas J diffuses for 300s under identical experimental conditions. Calculate the relative molecular mass of J if the relative molecular mass of gas A is 120.

Question 38

- (a) Compressibility factor, **Z**, is used to test ideality and non-ideality of real gases:
- Derive an expression for **Z**
 - At what value of Z a real gas shows ideal behaviour, positive and negative deviation from ideality?
- (b) A certain compound Y has an approximate RMM of 207. At 80°C and in a 3 litres vessel, the vapour of this compound exerts a pressure of about 0.12atmosphere. What is the mass in grams of the vapour of this compound?

Question 39

- (a)
- State the meaning of an ideal gas.
 - Derive an ideal gas equation.
- (b) 267cm³ of a certain gas at 18°C and 100400 Pa pressure has a mass of 0.162g; calculate:
- Normal density of the gas at s.t.p
 - Relative density of the gas at s.t.p

Question 40

- (a) State at least one application of each of the following:
- Graham's law of diffusion
 - Dalton's law of partial pressures
 - Avogadro's hypothesis
- (b) 200cm³ of oxygen gas takes 250 seconds to diffuse through a porous diaphragm. Under identical conditions, 200cm³ of an unknown gas T takes 177 seconds to diffuse. Calculate the relative molecular mass for unknown gas.

Question 41

- (a) List down error free postulates of kinetic theory of gases.
- (b) 1 mole of hydrogen gas was reacted with 1 mole of iodine vapour. Calculate the number of moles of hydrogen iodide formed at t seconds. After t seconds; 0.8moles for hydrogen remained.

Question 42

- (a) Based on your knowledge of diffusion, suggest any four factors which may affect the rate of diffusion. How each factor mentioned affects the rate of diffusion?
- (b) Two porous containers are filled with hydrogen and neon respectively. Under identical conditions, $\frac{2}{3}$ of hydrogen escapes in 6 hours. How long will it take for half the neon to escape? (You may use the following molar masses: H₂ = 2.02g/mol, Ne = 20.18g/mol).

Question 43

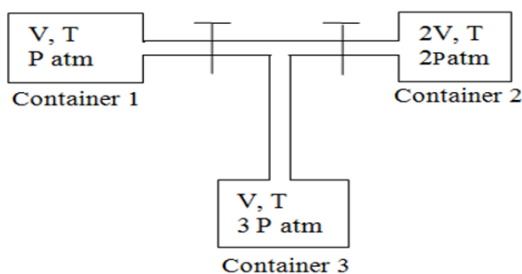
- (a) Some compounds are said to have 'abnormal' relative densities when determination is carried out experimentally. Result can either be higher or lower than the expected from their molecular formulae.
- What factor(s) lead to such abnormalities?
 - For each factor, give two examples of compounds whose vapour shows such abnormalities.
- (b) A container has two gases in it and one of them weighs 64g/mol. Given the following information; calculate the molecular mass of the other component.
- The mole fraction of unknown gas is 0.35
 - The total pressure inside the 1litre container is 1.6atm
 - The density of the gaseous mixture is 3.45g/L at 25°C

Question 44

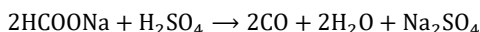
- (a) By using Amagat's curves, show how CO₂ deviates from ideal gas behaviour.
- (b) When an open flask containing air is heated from 27°C to 87°C, what percentage of the air in the flask is expelled? Assume that the volume of the flask and atmospheric pressure are constant.

Question 45

- (a) Aerosol cans will explode if heated. Explain.
- (b) When we open the taps given in the picture below, find the final pressure exerted by gases.

**Question 46**

- (a) According to Boyle's law; *pressure and volume are inversely proportional. However, when we fill air into a tyre, we are increasing both volume and pressure.* Give an explanation to eliminate this contradiction.
- (b) 0.964g sample of mixture of sodium methanoate and sodium chloride is analysed by adding sulphuric acid. The equation for the reaction for sodium methanoate with sulphuric acid is shown below.



The carbon monoxide formed measures 242mL when collected over water at 752mmHg and 22°C. Calculate the percentage of sodium methanoate in the original mixture. Given that: vapour pressure of water at 22°C is 19.8mmHg.

Question 47

A mixture of hydrogen gas, oxygen gas and 2mL of liquid water is present in a 0.5L rigid container at 25°C. The number of moles of hydrogen gas and the number of moles of oxygen gas is equal. The total pressure is 1146mmHg.

The mixture is sparked, and H₂ and O₂ react until one reactant is completely consumed.

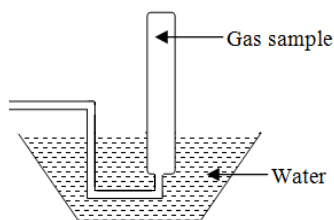
- Identify the reactant remaining and calculate the number of moles of the reactant remaining
- Calculate the total pressure in the container at the conclusion of the reaction if the final temperature is 90°C.
- Calculate the number of moles of water present as vapour in the container at 90°C

Given that:

- The vapour pressure of water at 25°C is 24mmHg
- The vapour pressure of water 90°C is 526mmHg

Question 48

A student collected a sample of hydrogen gas by the displacement of water as shown by the diagram below



The relevant data are given in the following table:

GAS SAMPLE DATA	
Volume of sample	90mL
Temperature	25°C
Atmosphere pressure	745mmHg
Vapour pressure of H ₂ O(25°C)	23.8mmHg

- Calculate the number of moles of hydrogen gas collected
- Calculate the number of molecules of water vapour in the sample gas
- Calculate the ratio of average speed of the hydrogen molecules to the average speed of the water vapour molecules in the sample.
- Which of the two gases, H₂ or H₂O, deviate more from ideal behaviour? Explain your answer.

Question 49

Represented above are five identical balloons, each filled to the same volume at 25°C and 1 atmosphere pressure with the pure gases indicated.

- Which balloon contains the greatest mass of gas? Explain
- Compare the average kinetic energies of the gas molecules in the balloons? Explain
- Which balloon contains the gas that would be expected to deviate most from the behaviour of an ideal gas? Explain
- Twelve hours after being filled, all the balloons have decreased in size. Predict which balloon will be the smallest. Explain your reasoning.

Question 50

- "Ideal gas law has crucial applications in various fields including in engineering." Name at least three objects made by engineers to support this claim.
- The atomic radius of sodium is 1.86×10^{-8} cm, and the molar volume of sodium is 23.68 cm³. If 68.52% of this volume is the actual volume occupied by sodium atoms, calculate the Avogadro's constant. (Volume of one sodium atom $\frac{4}{3}\pi r^3$).

Question 51

- Why basketball shrinks when left in cold surface overnight?
- When carbon dioxide gas is put in a sealed container at 701K and pressure of 10 atm and is heated to 1401K, some of the CO₂ decomposes to carbon monoxide and oxygen gas and the pressure rises to 22.5 atm. Calculate the mole percent of CO₂ that decomposes.

Question 52

Traditionally, high-flying aircraft and Formula 1 racing cars have had their tyres inflated with nitrogen gas instead of air. Recently, this practice has been extended to some other cars.

A car tyre is filled with nitrogen gas to a volume of 8.98dm^3 and a pressure of 207kPa at 20°C .

- (i) Using the ideal gas equation, calculate the mass of nitrogen gas, in grams, present in the car tyre under these conditions. Show your work clearly.
- (ii) During a car journey, the tyres become warm. Use the ideal gas equation to deduce the effect of that this has on the pressure in the tyres.
- (iii) One reason for the use of nitrogen gas in car tyres is that less gas is lost from the tyres during use because nitrogen molecules are larger than oxygen molecules. A suggested explanation for this is that nitrogen atoms are larger than oxygen atoms. Explain why a nitrogen atom is larger than an oxygen atom.

Question 53

- (a) Briefly explain the principle of Victor Meyer's method of determination of molecular mass of volatile substance.
- (b) It takes 22 hours for neon-filled balloon to shrink to half its original volume at s.t.p. If the same balloon is filled with helium, then how long it has taken for the balloon to shrink to one third of its original volume at s.t.p?

PART TWO SOLUTIONS

Two components liquid system

&

Colligative properties

Chapter 5

INTRODUCTION TO SOLUTION

Solutions are crucial to the processes that sustain life and to many other processes involving chemical reactions. We are coming across to solutions in everyday life; from soft drinks in 'Mangi shops', tea in the kitchen, to hydrochloric acid in the school laboratory. These solutions fall under category of substances called mixture. Therefore, in this context, if solution is the main course meal, then mixture is the great appetizer for our meal! So let us bring our yummy appetizer on the table; the mixture!

Mixture is the combination of two or more pure substances, whereby **pure substance** is the substance that has homogeneous and invariable chemical composition. It may exist in more than one phase but chemical composition is the same in all phases.

Pure substance may be an element or a compound. So the mixture may be combination of two or more different elements, two or more different compound or may be a combination of element(s) and compound(s).

Components of the mixture may be in different or in the same phase. This enables us to classify mixture into **heterogeneous** and **homogeneous mixture**.

Heterogeneous mixture

This is the mixture whose constituents are in different phase. A good example of this is the mixture of sand (solid phase) and water (liquid phase).

HOMOGENEOUS MIXTURE

This is the mixture whose constituents are in the same phase. A good example of this is the mixture of water and ethanol whereby both water and ethanol are in liquid phase.

For liquid – liquid homogenous mixture, the mixture can be classified into the following categories:

- Miscible mixture
- Partially miscible mixture
- Immiscible mixture

Miscible mixture

This is the homogeneous mixture whereby its components (constituents) tend to mix completely so that there is no formation of layers of the components.

This occurs when **intermolecular forces of attraction** in the pure liquids are equal to **intermolecular forces of attraction** in the solution. Thus for the mixture of two components, say A and B

A – – – – – A = B – – – – – B = A – – – – – B

(Intermolecular forces of attraction in liquid A) (Intermolecular forces of attraction in liquid B) (Intermolecular forces of attraction in the solution)

So from above it is clearly understood that: For intermolecular forces of attraction in pure liquids to be equal to intermolecular forces of attraction in the solution, the two intermolecular forces of attraction in the pure liquids (A and B) must be equal too, and hence two liquid components must be of the similar nature.

A good example of the miscible mixture is the mixture between:

- Benzene and Methylbenzene (toluene).
- Propan-1-ol and propan -2-ol
- Hexane and heptane
- Water and methanol

Gas – gas mixture is often completely miscible, why?

According to the kinetic theory of gases; gas consists of tiny (very small) molecules moving about in vacant space and thus when one gas is dissolved in another gas they form a homogeneous solution quite readily; in such a gaseous mixture, the components can be present to any (unlimited) extent and hence the mixture is completely miscible.

Partially miscible mixture

This is the homogeneous mixture where by its components tend to mix slightly. This occurs when intermolecular forces of attraction of the pure liquids do not differ much with intermolecular forces of attraction in the solution.

A good example of partially miscible mixture is the mixture between:

- Water and propanol
- Water and phenol
- Water and ether (ethyl ether)

Immiscible mixture

This is the homogenous mixture where by its components do not mix at all so that they tend to form separating layer.

This occurs when intermolecular forces of attraction in pure liquids differ much with intermolecular forces of attraction in the solution. Thus for the mixture of two components, say A and B:

$A - - - - - A \neq B - - - - - B \neq A - - - - - B$

So from above, it is clearly understood that; for intermolecular forces of attraction in pure liquids to be unequal to intermolecular forces of attraction in the solution, the two intermolecular forces of attraction in the pure liquids must be also different.

It should be understood that:

- Since all liquid – liquid mixtures are homogenous then all liquid – liquid mixtures are also solution (as we will see later solution is the uniform (homogeneous) mixture of two or more substances. Hence the same categories: Miscible, partially miscible and immiscible are commonly used as classification of solutions. So solutions are also classified into miscible solution, partially miscible solution and immiscible solution.
- Since all liquid – liquid mixture are solutions, their behaviour can be explained by the rule of dissolving which state that **“Like dissolve like”**. Thus when intermolecular forces of attraction of the two pure liquids are the same then the solution will be miscible while if the forces differ much their solution will be immiscible as shown earlier.

That is all about our appetizer; it is done! Take a breath; then let us bring our main dish on the table; the solution!

Meaning of solution

Solution is the uniform (homogeneous) mixture of two or more substances.

The important physical state to consider here is the final physical state of the solution and not the initial physical state of the components of the solution. The initial physical state may be different but the final physical state must be the same (uniform) for the mixture to be solution. For example, the mixture of table salt (solid) and water (liquid) is solution because the final physical state of the solution is liquid only. In this case water is able to convert the solid state of the salt into liquid state in the solution.

Components of solution may be termed as **solute and solvent**. Their meanings depend on whether their original physical states are the same or not.

If the original physical states of components of solution are different:

Solvent is the component (constituent) of the solution whose physical state is conserved in the solution. Example in the solution of table salt in water, water is solvent because the physical state of solution is liquid which is also the original physical state of water.

Solute is the component of the solution whose physical state is changed in the solution. Example in the solution of table salt and water, table salt is solute because its original solid physical state is changed into liquid in the solution

If the original physical states of components of solution are the same:

Solvent is the component with greater proportion (which is more concentrated).

Solute is the components with smaller proportion (which is less concentrated)

So generally, solvent and solute may be defined as follows:

Solvent is the component of the solution whose physical state is conserved in the solution or the component with greater proportion.

Solute is the component of the solution whose physical state is changed in the solution or the component with smaller proportion.

When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. The process is known as **dissolution**.

Characteristics of solution

Solutions exhibit these defining traits:

1. They are homogeneous (after a solution is made, it has the same composition at all points throughout; that is its composition is uniform).
2. The physical state of a solution is the same as that of the solvent.
3. The components of a solution are dispersed on a molecular scale (they consist of a mixture of separated solute particles each closely surrounded by solvent species).
4. The dissolved solute in a solution will not settle out or separate from the solvent.
5. The composition of a solution (concentration) can be varied continuously (within limits determined by the solubility of the components).

Dissolution process in terms of intermolecular forces

Two individual steps which must be carried out when a solute is dissolved in the solvent are explained below.

First step: The solute must be dispersed

This means that, the molecular units of the solute must be pulled apart through breaking its intermolecular forces.

- For example, if A is the solute, A-----A interactions (intermolecular forces) must be broken for it to be dissolved in a solvent. This requires energy to be absorbed (it is endothermic process).
- Greater strength of intermolecular forces means greater the amount of energy is required to break them making more difficult for the solute to dissolve and vice – versa.

Second step: The solute and solvent interacting each other (Solvation)

Whether this is favourable or not depends on the nature of the solute and solvent. For example, if our solute A is mixed with solvent B, then what is important in dissolving A in B is the strength of A----B interactions (intermolecular forces) compared to A-----A interactions.

- The formation of A-----B intermolecular forces is exothermic, so if A-----B intermolecular forces are stronger than A-----A intermolecular forces means that the heat evolved in forming

A-----B is greater than heat absorbed in breaking A-----A intermolecular forces, the overall process will be exothermic and hence the process of dissolving A in B will be energetically favourable.

- On the another hand, if A-----B intermolecular forces are weaker than A-----A intermolecular forces means that heat evolved in forming A-----B intermolecular forces is less than heat absorbed in breaking A-----A intermolecular forces making the overall process endothermic and hence the process of dissolving A in B will be energetically unfavourable.

You have to understand this:

In some cases, solutions do not form because the energy required to separate solute and solvent species is so much greater than the energy released by solvation.

Classification of solutions

We usually think of a solution as a liquid; that is a mixture of a gas, liquid, or solid solute in a liquid solvent with water as the first thing to come up in mind of many people after hearing the word 'solvent'. However, almost any gas, liquid, or solid can act as a solvent and actually, solutions can exist as gases and solids as well. Many alloys are solid solutions of one metal dissolved in another; for example, Tanzania 500-shilling coin contains nickel dissolved in steel (plated steel). Air is a gaseous solution, a homogeneous mixture of nitrogen, oxygen, and other gases. So in terms of their physical states, solution may be classified as:

- (i) Liquid solution
- (ii) Gas solution
- (iii) Solid solution

The three physical states of solution may occur in:

- Liquid – liquid solution
Example: ethanol in water
- Liquid – solid solution
Example: Salt (solute) in water (solvent)
- Liquid – gas solution
Example: Carbon dioxide (solute) in water (solvent)
- Solid – solid solution
Example: Alloy e.g. brass (an alloy of copper and zinc) or TZ 200-shilling coin (an alloy copper, nickel and zinc).
- Solid – Liquid solution
Example: Mercury (solute) in silver (solvent) commonly known as **silver amalgam**.
- Solid – Gas solution
Example: Hydrogen (solute) in palladium or platinum (solvent).
- Gas – gas solution
Example: Air

WAYS OF REPRESENTING CONCENTRATION OF SOLUTION

Composition of a solution can be described by expressing its **concentration** which can be defined as *the amount of the solute dissolved in a given amount of solution or solvent*. The concentration can be expressed either qualitatively which is the subjective measure or quantitatively which is objective measure. For example, qualitatively we can say that the solution is **dilute** (*contain very small amount of solute compared to the amount of solvent*) or it is **concentrated** (*contain very large amount of solute compared to that of solvent*). But in real life these kinds of description are subjective and thus they can add to lot of confusion and hence the need for objective approach which is a quantitative description of the solution. In this chapter, we are going to discuss various ways by which we can describe the concentration of the solution quantitatively.

Mass concentration

This is the mass of the solute dissolved in a unit volume of solution.

$$\text{That is: Mass concentration} = \frac{\text{Mass of solute}}{\text{Volume of solution}}$$

Mass concentration is commonly given in g/dm^3 ,

Other units are g/cm^3 , g/ml etc.

Relationship between mass concentrations of a solution components and density of the solution

$$\text{By definition: Density of solution} = \frac{\text{Mass of solution}}{\text{Volume of solution}}$$

But mass of solution = mass of solute + mass of solvent

$$\text{Then: Density of solution} = \frac{\text{mass of solute} + \text{mass of solvent}}{\text{volume of solution}} = \frac{\text{Mass of solute}}{\text{volume of solution}} + \frac{\text{Mass of solvent}}{\text{Volume of solution}}$$

$$\text{But } \frac{\text{mass of solute}}{\text{volume of solution}} = \text{mass concentration of solute}$$

$$\text{And } \frac{\text{mass of solvent}}{\text{volume of solution}} = \text{mass concentration of solvent}$$

Hence:

Density of solution = mass concentration of solute + mass concentration of solvent

Molar concentration (molarity)

This is number of moles of solute dissolved in a litre of solution.

$$\text{Thus Molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution in litres (or dm}^3\text{)}}$$

It is denoted by two square brackets, []

Its unit is mol/L (or mol/dm^3) or M where $1\text{M} = 1\text{mol/dm}^3$

The reader should understand that: A molar solution is commonly used to mean that: One mole of solute is dissolved in a litre of solution.

Remember: $1\text{dm}^3 = 1\text{Litre} = 1000\text{cm}^3$

Relationship between molarity and mass concentration

$$\text{From Molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution in dm}^3}$$

$$\text{But number of moles of solute} = \frac{\text{mass of solute}}{\text{molar mass of solute}}$$

$$\text{Then: Molarity} = \frac{\text{mass of solute}}{\text{volume of solution in dm}^3 \times \text{molar mass of solute}}$$

$$\frac{\text{mass of solute}}{\text{volume of solution in dm}^3} = \text{Mass of concentration in g/dm}^3$$

$$\text{Hence: Molarity} = \frac{\text{mass concentration in g/dm}^3}{\text{molar mass of solute in g/mol}}$$

Or mass concentration in $\text{g/dm}^3 = \text{molarity} \times \text{molar mass of solute in g/mol}$.

Molar concentration is the most common method of representing concentration; so when it is stated just 'concentration', it always implies molar concentration.

Molality

This is the number of moles of solute dissolved in 1kg of solvent.

Thus Molality = $\frac{\text{number of moles of solute}}{\text{mass of solvent in kg}}$

Unit of molarity is mol/kg or simply small letter *m*.

The term '**a molal solution**' is always used to indicate that: one mole of solute is dissolved in 1kg of solvent; that is the solution of 1mol/kg.

Molality versus molarity

Molality measure concentration of a solute in the solution as relative amount of the solute to the **mass** of the **solvent** whereas molarity is measured as the relative amount of the solute to the **volume** of the **solution**. Based on this general basic difference, there are number of facts can be deduced in comparing molality and molarity as explained below.

Molarity is temperature dependent while molality is not.

- Volume of the given mass of the solution increases with an increase in temperature. This means that the molarity also will decrease as the temperature increases.
- In contrast to the volume, mass of a solvent (or any other substance) does not vary with temperature. This means that molality of the solute in the solution remains constant on temperature change.
- The fact that molality is temperature independent is main reason of preferring it (molality) to the molarity in applications where physical properties of solution and effect of temperature on these properties is of importance.

However, molarity has the advantage over molality in that it is easier to measure the volume of a solution, using precisely calibrated volumetric flasks, than to weigh the solvent.

A molar solution is more concentrated than a molal solution.

Molarity is given by the following formula;

$$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution in dm}^3}$$

Whereas molality is given by the following formula;

$$\text{molality} = \frac{\text{number of moles of solute}}{\text{mass of solvent in kg}}$$

But density of water (most common solvent we will often meet with) is 1kg/dm³. That is 1kg of solvent is contained in 1dm³.

Thus numerical value of mass of solvent in kg = numerical value of volume of the solvent in dm³.

It follows that: Numerical value of molality = $\frac{\text{number of moles of solute}}{\text{Volume of solvent in dm}^3}$

Whereas, numerical value of molarity = $\frac{\text{number of moles of solute}}{\text{volume of solution in dm}^3}$

But volume of solution = volume of solvent + volume of solute

So it is clearly understood that: volume of solution > volume of solvent

Therefore, if;

Numerical value of molality of one solution = Numerical value of molarity of another solution;

Then the solution whose concentration is given in molarity must contain greater number of moles of solute for the two numerical values (of molality and molarity) to be equal and hence the solution is more concentrated. For example, 1M solution (a molar solution) contains greater amount of solute than 1m solution (a molal solution) and hence the former is more concentrated.

For given amount (number of moles) of solute and volume of solvent, numerical value of molality is greater than numerical value of molarity.

From the fact that;

$$\text{Numerical value of molality} = \frac{\text{number of moles of solute}}{\text{volume of solvent in dm}^3};$$

Numerical value of molarity = $\frac{\text{number of moles of solute}}{\text{Volume of solution in dm}^3}$;

And volume of solution > volume of solvent

It is clearly understood that if number of moles of solute is the same (kept constant)

the ratio, $\frac{\text{number of moles of solute}}{\text{volume of solvent in dm}^3}$ will be greater than the ratio, $\frac{\text{number of moles of solute}}{\text{volume of solution in dm}^3}$ and hence numerical value of molality will be greater than the numerical value of molarity.

However, the difference is not observed in very dilute solution!

For very dilute solution, volume of solute is negligible compared to the volume of the solvent and therefore; volume of solution = volume of solvent.

And hence numerical values of molality=numerical value of molarity if the solution is very dilute.

Normality

This is the number of equivalents of solute dissolved in one litre of the solution.

Thus: Normality = $\frac{\text{number of equivalents of solute}}{\text{volume of solution in litres (or dm}^3\text{)}}$

Its unit is N

Relationship between normality and molarity

From Normality = $\frac{\text{number of equivalents of solute}}{\text{volume of solution dm}^3}$

But number of equivalents of solute = $\frac{\text{mass of solute}}{\text{Equivalent weight of solute}}$

Then: Normality = $\frac{\text{mass of solute}}{\text{volume of solution in dm}^3 \times \text{equivalent weight of solute}}$

But $\frac{\text{mass of solute}}{\text{volume of solution in dm}^3} = \text{mass concentration of solute in g/dm}^3$

Thus: Normality = $\frac{\text{mass concentration in g/dm}^3}{\text{equivalent weight of solute}}$

For acid-base reaction:

Equivalent weight = $\frac{\text{molar mass}}{\text{acidity or basicity}}$

Then: Normality = $\frac{\text{mass concentration in g/dm}^3 \times \text{Basicity or Acidity}}{\text{molar mass of solute}}$

But $\frac{\text{mass concentration in g/dm}^3}{\text{molar mass of solute}} = \text{molarity}$

Hence for acid – base reaction

Normality = Molarity × Basicity (or Acidity)

For redox reactions:

Equivalent weight = $\frac{\text{molar mass}}{\text{number of electrons transferred}}$

Then from Normality = $\frac{\text{mass concentration in g/dm}^3}{\text{equivalent weight of solute}}$

It becomes:

Normality = $\frac{\text{mass concentration in g/dm}^3 \times \text{number of electrons transferred}}{\text{Molar mass of solute}}$

But $\frac{\text{mass concentration in g/dm}^3}{\text{molar mass of solute}} = \text{Molarity}$

Hence for redox reactions: Normality = Molarity $\times$ Number of electrons transferred

The term '**A normal solution**' is used to express the solution of 1N

Definition of equivalent weight

This is the mass of a compound required to give (or react with) one mole (Avogadro's number) of fundamental entity in a reaction we might consider.

Relationship between normality of acid and base in acid – base reaction

For Acid – base reaction

$$\frac{M_a V_a}{M_b V_b} = \frac{n_a}{n_b} \dots\dots\dots (i)$$

Where;

M_a is the molarity of acid

M_b is the molarity of base

V_a is the volume of acid

V_b is the volume of base

n_a is the stoichiometric coefficient of acid in a balanced chemical equation for the reaction

n_b is the stoichiometric coefficient of base in a balanced chemical equation for the reaction

Then:

$$M_a n_b V_a = M_b n_a V_b \quad (\text{By rearranging equation (i) above})$$

But n_b = Basicity of acid

And n_a = Acidity of acid

So $M_a n_b = N_a$ (Normality for acid)

And $M_b n_a = N_b$ (Normality for base)

Hence: $N_a V_a = N_b V_b$

Similarly, for redox reaction;

$$N_o V_o = N_r V_r$$

Where N_o and N_r is the normality of oxidising and reducing agent respectively

V_o and V_r is the volumes of oxidising and reducing agents respectively.

*The number of electrons transferred, basicity of acid or acidity of base collectively are known as **equivalent factor**.*

Hence regardless to whether the reaction is redox or acid – base reaction, the normality and molarity are related by the following equation:

$$\text{Normality} = \text{molarity} \times \text{equivalent factor}$$

Mass percentage $\left(\% \left(\frac{m}{m} \text{ or } \frac{w}{w} \right) \right)$

This is the mass of solute in grams dissolved in 100g of solution.

$$\text{Thus } \% \left(\frac{m}{m} \right) = \frac{\text{mass of solute in g}}{\text{mass of solution in g}} \times 100\%$$

The mass percentage is the most common method of representing concentration as percentage, so whenever we talk (or you asked to find) just percentage without any extra information, the implication will always be mass percentage.

Relationship between mass percentage and mass concentration

$$\text{From } \% \left(\frac{m}{m} \right) = \frac{\text{mass of solute in g}}{\text{mass of solution in g}}$$

Where $\% \left(\frac{m}{m} \right)$ has been converted to fraction by dividing the percentage by 100 so that there is no need of multiplying the right hand side of the equation by 100 as shown on original formula.

But mass of solution = Density of solution $\times$ volume of solution

$$(\text{From Density} = \frac{\text{mass}}{\text{volume}}; \text{mass} = \text{Density} \times \text{volume}).$$

Then:

$$\% \left(\frac{m}{m} \right) = \frac{\text{mass of solute in g}}{\text{volume of solution} \times \text{Density of solution}}$$

$$\text{But } \frac{\text{mass of solute in g}}{\text{volume of solution}} = \text{mass concentration}$$

$$\text{Then } \% \frac{m}{m} = \frac{\text{mass concentration}}{\text{Density of solution}}$$

$$\text{Hence: Mass concentration} = \text{Density of solution} \times \% \left(\frac{m}{m} \right)$$

Where mass percentage, $\% \left(\frac{m}{m} \right)$ must be converted to fraction by dividing the percentage by 100.

Parts per million (ppm)

This is the mass solute dissolved one million grams of the solution

$$\text{Thus ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

This method of representation of concentration is useful when the concentration is extraordinary dilute.

ppm can also express in $\frac{m}{v}$ (mass to volume) ratio.

In $\frac{m}{v}$ ratio, ppm is defined as mass of solute in grams dissolved in 10^6 cm^3 .

$$\text{That is ppm} \left(\frac{m}{v} \right) = \frac{\text{mass of solute in g}}{\text{volume of solution in cm}^3} \times 10^6$$

Numerically; ppm in $\frac{m}{v} = \text{ppm in } \frac{m}{m} \text{ (or } W/W \text{) if the solvent is water}$

Mass - volume percentage $\left(\% \left(\frac{m}{v} \right) \right)$

This is the mass of solute in grams dissolved in 100 cm^3 of the solution

$$\text{Thus } \% \left(\frac{m}{v} \right) = \frac{\text{mass of solute in g}}{\text{volume of solution in cm}^3} \times 100\%$$

Mole fraction (X)

This is the ratio of number of number of moles of solute to the total number of moles of all components in the solution

$$\text{Thus } X_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$\text{Where } X_{\text{solute}} + X_{\text{solvent}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} + \frac{n_{\text{solvent}}}{n_{\text{solute}} + n_{\text{solvent}}} = \frac{n_{\text{solvent}} + n_{\text{solute}}}{n_{\text{solvent}} + n_{\text{solute}}} = 1$$

$$\text{Hence: } X_{\text{solute}} + X_{\text{solvent}} = 1$$

Also with mixture of two components, say A and B;

$$X_A = \frac{n_A}{n_A + n_B} \text{ And } X_B = \frac{n_B}{n_A + n_B}$$

$$\text{Then } \frac{X_A}{X_B} = \frac{n_A}{n_A + n_B} \times \frac{n_A + n_B}{n_B} = \frac{n_A}{n_B}$$

$$\text{Thus } \frac{X_A}{X_B} = \frac{n_A}{n_B}$$

And hence ratio of mole fractions of the two components is equal to the ratio of their number of moles.

Dilution

The reciprocal of concentration is known as **dilution** and can be defined as: *the volume of solution in litres which contain one mole of solute.*

$$\text{Thus Dilution} = \frac{\text{Volume of solute in litres (dm}^3\text{)}}{\text{Number of moles of solute}}$$

$$\text{Or Dilution} = \frac{1}{\text{Molarity}}$$

Its unit is $\text{dm}^3\text{mol}^{-1}$ or M^{-1}

Dilution is also known as **molar volume** (as opposed to molar concentration).

DILUTION PRINCIPLE

Dilution principle may be stated as:

Concentration of the solution containing fixed mass (or number of moles) of the solute varies inversely to its volume.

That is $M \propto \frac{1}{V}$ or $MV = \text{constant}$ (n is constant)

From which $M_1V_1 = M_2V_2 = M_3V_3 = \dots\dots\dots = M_nV_n$

To have better understanding this, suppose we have the following:

M_c = Molar concentration of concentrated solution.

M_d = Molar concentration of dilute solution.

V_c = Volume of the concentrated solution used to prepare the diluted solution of concentration, M_d

V_d = Volume of dilute solution obtaining after mixing pure water and the concentrated solution

($V_d = V_c + V_{H_2O}$)

Using $[] = \frac{n}{V}$ or $n = V[]$

Number of moles of the solute in the concentrated solution = M_cV_c

Number of moles of the solute in the diluted solution = M_dV_d

Since the dilution is done by adding pure water (which has no solute in it), number of moles of solute in the concentrated solution and diluted solution remains constant and hence;

$M_cV_c = M_dV_d$ (mathematical form of dilution principle)

So in other words, dilution principle may be stated as: *If the concentrated solution is diluted by adding more solvent, the number of moles of solute remains constant.*

Generally, if two solutions (containing the same kind of the solute) say solution 1 and solution 2 with their respective concentrations M_1 and M_2 are mixed by taking V_1 as the volume of solution 1 and V_2 as the volume of solution 2, the new concentration of the solution mixture can be found as follows:

Number of moles of the solute in solution 1 = M_1V_1

Number of moles of the solute in solution 2 = M_2V_2

Total number of moles of the solute in the solution mixture = $M_1V_1 + M_2V_2$

Total volume of the solution mixture = $V_1 + V_2$

So the concentration of the solute in the solution mixture

$$= \frac{\text{Total number of moles of solute in the mixture}}{\text{Volume of the mixture}} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

Hence **the concentration of the mixture** = $\frac{M_1V_1 + M_2V_2}{V_1 + V_2}$

If M_3 represent the concentration of the mixture,

and V_3 represent the volume of the mixture = $V_1 + V_2$.

The above formula becomes: $M_3 = \frac{M_1V_1 + M_2V_2}{V_3}$

Or $M_3V_3 = M_1V_1 + M_2V_2$

In actual sense, the dilution principle is the special case for the above generalisation where;

M_1 represents molar concentration of concentrated solution, M_c

V_1 represents volume of concentrated solution, V_c

M_2 represents molar concentration solute in pure water = 0

V_2 represents volume of pure water, V_{H_2O}

M_3 represents molar concentration of the diluted solution, M_d

V_3 represents volume of diluted solution ($V_c + V_{H_2O}$)

Then, as $M_2V_2 = 0$ (Pure water has zero concentration of the solute)

The above formula ($M_3V_3 = M_1V_1 + M_2V_2$) becomes;

$M_dV_d = M_cV_c$ which is the dilution principle

WORKED EXAMPLES

Example 1

A common salt solution contains 10g of salt per 100cm³ of the solution. What is:

- Mass concentration of the salt
- Molarity

Solution

$$(i) \text{ Mass concentration} = \frac{\text{mass of solute in g}}{\text{volume of solution in dm}^3} = \frac{10\text{g}}{0.1\text{dm}^3} = 100\text{g/dm}^3$$

So mass concentration is 100g/dm³

(ii) A common salt is NaCl whose molar mass is 58.5g/mol

$$\text{Using Molarity} = \frac{\text{mass concentration in g/dm}^3}{\text{molar mass of solute in g/mol}} = 100/58.5 \text{ M} = 1.71\text{M}$$

Hence mass concentration of the salt is 1.71M

Example 2

What is the mole fraction and molality of HCl in concentrated hydrochloric acid which contains 36%

$\left(\frac{m}{m}\right)$ HCl?

Solution

Mass of HCl in 100g of solution is 36g

So mass of water in the solution = $(100 - 36)\text{g} = 64\text{g}$

$$n_{\text{HCl}} = \frac{m_{\text{HCl}}}{M_{\text{HCl}}} = 36/36.5 \text{ moles} = 0.986 \text{ moles}$$

$$n_{\text{w}} = \frac{m_{\text{w}}}{M_{\text{w}}} = \frac{64}{18} \text{ moles} = 3.556 \text{ moles}$$

$$\text{Then } X_{\text{HCl}} = \frac{n_{\text{HCl}}}{n_{\text{HCl}} + n_{\text{w}}} = \frac{0.986}{0.986 + 3.556} = 0.22$$

Hence mole fraction of HCl is 0.22

$$\text{Molality} = \frac{\text{number of moles of HCl (solute)}}{\text{mass of water (solvent) in kg}} = \frac{0.986}{0.064} \text{ mol/kg} = 15.4 \text{ mol/kg}$$

Hence molality of HCl is 15.4 mol/kg

Example 3

10g of common salt were dissolved in 100g of water, what is the mass percentage of the solute?

Solution

Mass of solute (common salt) = 10g

Mass of solution = mass of water + mass of common salt = $(100 + 10)\text{g} = 110\text{g}$

$$\text{Using } \% \left(\frac{m}{m} \right) = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% = \frac{10}{110} \times 100\% = 9.09\%$$

So mass percentage of the solute is 9.09%

Example 4

How would you prepare 1 Litre of 0.9% $\left(\frac{m}{v} \right)$ sodium chloride solution?

Solution

0.9% $\left(\frac{m}{v} \right)$ sodium chloride means:

Mass of NaCl in 100cm³ of its solution is 0.9g

So mass of NaCl in 1000cm³ (1L) of its solution will be = $\frac{0.9}{100} \times 1000\text{g} = 9\text{g}$

Hence the solution can be prepared by mixing 9g of NaCl in 1Litre of solution.

Example 5

Sulphuric acid solution containing 571.6g of H₂SO₄ per dm³ of solution at 20°C has density of 1.3294g/ml. calculate

- (i) Molarity of sulphuric acid
- (ii) Percentage of mass of H₂SO₄
- (iii) Mole fraction of the solution components
- (iv) Normality of the acid solution
- (v) Molality of hydrochloric acid

Solution

$$(i) \text{ Molarity} = \frac{\text{mass concentration in g/dm}^3}{\text{molar mass of the H}_2\text{SO}_4(\text{solute})} = \frac{571.6}{98} = 5.83\text{M}$$

Molarity of sulphuric acid is 5.83M

$$(ii) \text{ Using: Mass concentration} = \text{Density} \times \% \left(\frac{\text{m}}{\text{m}} \right)$$

$$\text{Then } \% \left(\frac{\text{m}}{\text{m}} \right) = \frac{\text{mass concentration}}{\text{Density}} \times 100\%$$

$$\text{But density} = 1.3294\text{g/ml} = 1329.4\text{g/L}$$

$$\text{Then mass percentage} = \frac{571.6}{1329.4} \times 100\% = 43\%$$

$$\text{So mass percentage of H}_2\text{SO}_4 \text{ is } 43\% \left(\frac{\text{m}}{\text{m}} \right)$$

(iii) Mass of solution in 1L of solution is 1329.4g

$$\text{Mass of H}_2\text{SO}_4 \text{ in 1L of the solution} = 571.6\text{g}$$

$$\text{Thus mass of water in 1l of the solution} = (1329.4 - 571.6)\text{g} = 757.8\text{g}$$

$$\text{Number of moles of H}_2\text{SO}_4 = \frac{571.6}{98} \text{ mol} = 5.83\text{moles}$$

$$\text{Number of moles of water} = \frac{757.8}{18} \text{ mole} = 42.1 \text{ moles}$$

$$\text{Moles fraction of H}_2\text{SO}_4 = \frac{\text{number of moles of H}_2\text{SO}_4}{\text{Total number of moles of solution}} = \frac{5.83}{5.83+42.1} = 0.12$$

Mole fraction of H₂SO₄ is 0.12

$$\text{Mole fraction of water} = 1 - \text{mole fraction of H}_2\text{SO}_4 = 1 - 0.12 = 0.88$$

(iv) Normality of acid = Molarity × Basicity

$$\text{But Basicity of H}_2\text{SO}_4 = 2$$

$$\text{Then Normality of the acid solution} = 2 \times 5.83\text{N} = 11.66\text{N}$$

$$(v) \text{ Molality} = \frac{\text{number of moles of solute (H}_2\text{SO}_4\text{)}}{\text{mass of solvent(water) in kg}}$$

But number of moles of H₂SO₄ in 757.8g or 0.7578kg of water is 5.83moles

$$\text{Then Molality of H}_2\text{SO}_4 = \frac{5.83}{0.7578} \text{ mol/kg} = 7.69\text{mol/kg}$$

Hence Molality of the acid is 7.69mol/kg

Example 6

You want to prepare 100cm³ of 2M solution of sulphuric acid from a stock of 18M solution of the acid. How much of the concentrated acid have to dilute with water to 100cm³?

Solution

$$\text{By dilution law: } M_c V_c = M_d V_d \text{ or } V_c = \frac{M_d V_d}{M_c}$$

$$\text{Where: } M_d = 2\text{M}, V_d = 100\text{cm}^3, M_c = 18\text{M}$$

$$\text{Then } V_c = \frac{2 \times 100}{18} \text{ cm}^3 = 11.11\text{cm}^3$$

Hence volume of concentrated acid required is 11.11cm³. (In the example, 11.11cm³ of concentrated solution must be mixed with (100 – 11.11) cm³ or 88.89cm³ of distilled water)

Example 7

Find the concentration of the mixture obtained by mixing 100mL of 0.2M HCl and 150cm³ of 0.1M HCl.

Solution

$$\text{Concentration of the mixture} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2} = \frac{(100 \times 0.2) + (150 \times 0.1)}{(100 + 150)} = 0.14M$$

Thus the concentration of the solution mixture is 0.14M

Example 8

450g of 30% ($\frac{m}{m}$) hydrochloric acid are being mixed with 150g of 20% ($\frac{m}{m}$) hydrochloric acid. Which concentration will the mixture have?

Solution

$$\text{Mass of HCl in 450g of 30\% } \left(\frac{m}{m}\right) \text{ HCl} = \frac{30}{100} \times 450g = 135g$$

$$\text{Mass of HCl in 150g of 20\% } \left(\frac{m}{m}\right) \text{ HCl} = \left(\frac{20}{100}\right) \times 150g = 30g$$

$$\text{Total mass of HCl} = (135 + 30)g = 165g$$

$$\text{Total mass of solution} = (450 + 150)g = 600g$$

$$\% \frac{m}{m} \text{ HCl in the mixture} = \frac{\text{Total mass of HCl}}{\text{Total mass of solution}} \times 100\% = \frac{165g}{600g} \times 100\% = 27.5\%$$

Hence mass percentage of hydrochloric acid in the mixture is 27.5% ($\frac{m}{m}$)

Example 9

Dilute 10g of 65% mass – percentage of nitric acid so that a 12% mass – percentage of the acid will be formed.

Solution

$$\text{Mass of HNO}_3 \text{ in 10g of 65\% } \left(\frac{m}{m}\right) \text{HNO}_3 = \frac{65}{100} \times 10g = 6.5g$$

Let mass of water to be added = xg

So total mass of solution after dilution = (10 + x)g

$$\text{Then using: } \% \left(\frac{m}{m}\right) = \frac{\text{mass of HNO}_3 \text{ (solute)}}{\text{mass of solution}} \times 100\% = \frac{6.5}{10+x} \times 100 = 12$$

$$= \frac{650}{10+x} = 12 \text{ Then } 650 = 120 + 12x$$

$$12x = 530 \text{ or } x = 44.17g$$

Hence 44.17g of water is required for dilution

Example 10

Dilute 65% ($\frac{m}{m}$) nitric acid to 12%

Solution

Let mass of 65% ($\frac{m}{m}$) HNO₃ taken be xg

And mass of water used for dilution be yg

$$\text{Then mass of 65\% } \left(\frac{m}{m}\right) \text{ HNO}_3 \text{ taken will be } \frac{65x}{100} = 0.65x$$

And total mass of solution after dilution will be (x + y)g

$$\text{Using } \%(\text{m}/\text{m}) = \frac{\text{mass of HNO}_3(\text{solute})}{\text{mass of solution}} \times 100\% = \frac{0.65x}{x+y} = \frac{12}{100}$$

$$\text{or } 0.65x = 0.12x + 0.12y$$

$$0.53x = 0.12y$$

$$\frac{y}{x} = \frac{0.53}{0.12} = \frac{53}{12}$$

Hence 53 parts of water should be mixed with 12 parts of 65% HNO_3

Example 11

The partial molar volumes of propanone (CH_3COCH_3) and trichloromethane (CHCl_3) in a mixture in which the mole fraction of CHCl_3 is 0.4693 are 74.166 and $80.235\text{cm}^3\text{mol}^{-1}$ respectively. What is the volume of a solution of total mass 1kg ?

Solution

Let volume of propanone (in cm^3) used be V_p and volume of trichloromethane (in cm^3) used be V_t

Using number of moles of each component = $\frac{\text{Partial volume}}{\text{Molar volume}}$

$$\text{Then } n_p = \frac{V_p}{74.166}$$

$$\text{And } n_t = \frac{V_t}{80.235}$$

$$\text{It follows that: } \frac{n_p}{n_t} = \frac{80.235V_p}{74.166V_t}$$

$$\text{But } \frac{n_p}{n_t} = \frac{x_p}{x_t} = \frac{1-0.4693}{0.4693} = 1.13083$$

$$\text{Thus } 1.13083 = \frac{80.235V_p}{74.166V_t} \text{ or } V_p = 1.04529V_t \dots \dots \dots (i)$$

Also using $m = nM_r$:

$$m_p = n_p \times \text{molar mass of } \text{CH}_3\text{COCH}_3$$

$$m_p = \frac{V_p}{74.166} \times 58 = 0.78203V_p$$

$$m_t = n_t \times \text{molar mass of } \text{CHCl}_3$$

$$m_t = \frac{V_t}{80.235} \times 119.5 = 1.48937V_t$$

$$\text{But } m_p + m_t = 1000\text{g}$$

$$\text{Thus } 0.78203V_p + 1.48937V_t = 1000 \rightarrow (ii)$$

Solving (i) and (ii) simultaneously gives;

$$V_t = 433.4972\text{cm}^3$$

$$V_p = 453.13029\text{cm}^3$$

$$\text{Therefore } V_{\text{Soln}} = V_t + V_p = (433.4972 + 453.13029)\text{cm}^3 = 886.62749\text{cm}^3$$

Hence the volume of the solution is 886.627cm^3

DIGGING DEEPER EXERCISE 5

EXERCISE 5A: BINDER QUESTIONS

Question 1

- (a) What does the term solution used for?
- (b)
 - (i) How many types of solutions are formed?
 - (ii) Write briefly about each type with an example.
- (c) Give an example of solid solution in which the solute is a gas.

Question 2

Show that for very dilute solutions, molality $\cong$ molarity.

Question 3

Is molarity or molality dependent on temperature? Explain your answer.

Question 4

0.05M NaOH Solution in water has density of 1.112g/mL. Express the concentration in:

- (a) Mass percent
- (b) Molality
- (c) Mole fraction

Question 5

An antifreeze solution is prepared from 222.6g of ethylene glycol ($C_2H_6O_2$) and 200g of water.

- (a) Calculate the molality of the solution.
- (b) If the density of the solution is 1.072g/mL, then what shall be the molarity of the solution?

EXERCISE 5B: REAL QUESTIONS

Question 6

The following are substances which we are coming across to them in daily life. Identify the solute and solvent in each:

- (i) Seawater
- (ii) 50/50 mixture of ethylene glycol and water (antifreeze mixture used to cool car engine)
- (iii) Air
- (iv) Carbonated water
- (v) Bronze

Question 7

Give a daily life example of substance fulfilling the following scenarios: (In each case, clearly identify solute and solvent).

- (i) Liquid solution in which the solute is a solid.
- (ii) Solid solution in which both solute and solvent are solids.
- (iii) Liquid solution in which the solute is a gas.
- (iv) Gas solution in which the solute is a liquid.
- (v) Gas solution in which the solute is solid.

Question 8

A sample of drinking water was found to be severely contaminated with chloroform ($CHCl_3$) supposed to be a carcinogen. The level of contamination was 15ppm.

- (i) Express this in percent by mass.
- (ii) Determine the molality of chloroform in the water sample.

Question 9

If the density of sample of water from lake **Nyasa** is 1.25g/mL and contains 92g of Na^+ ions per kg of water. Calculate the molality of Na^+ ions in the lake **Nyasa**.

Question 10

Nalorphene ($C_{19}H_{21}NO_3$), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5mg. Calculate the mass of $1.5 \times 10^{-3}m$ aqueous solution required for the above dose.

EXERCISE 5C: HOT QUESTIONS**Question 11**

The sap in a maple tree can be described approximately as a 3% (by mass) solution of sucrose (molecular weight = 342.2948g/mol) in water. If the density of the sap is 0.010g/mL, and assuming the sap consists only of sucrose and water, calculate the molarity of sucrose in the sap.

Question 12

A solution of glucose in water is labeled 10%w/w. What would be the molality of the solution and mole fraction of each component in the solution? If the density of solution is 1.2g/mL, then what shall be the molarity of the solution?

Question 13

A solution is prepared by mixing 300g of 25% solution and 400g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

Question 14

Concentrated sulphuric acid ($18.4MH_2SO_4$) has density of 1.84g/mL. After dilution with water to 5.2M, the solution has density of 1.38g/mL

- (a) Calculate the volume percentage of concentrated acid needed to make 1L or 5.2 MH_2SO_4
- (b) Determine the mass percentage of H_2SO_4 in the original concentrated solution
- (c) What is the molarity of the 5.2 MH_2SO_4 solution?

Question 15

Fish, like all animals, need a supply of oxygen, which they obtain from oxygen dissolved in the water. The minimum oxygen concentration needed to support most fish is around 5ppm($\frac{m}{v}$). How many moles of O_2 per litre of water, does this correspond to?

Question 16

Calculate the molarity of a 60% ($\frac{w}{w}$) solution of ethanol (C_2H_5OH) in water whose density is 0.8937g/mL.

Question 17

Two solutions of a substance (non-electrolyte) are mixed in the following manner: 480mL of 1.5M the first solution is mixed with 520mL of 1.2M of second solution. What the molarity of the final mixture?

Chapter 6

RAOULT'S LAW OF VAPOUR PRESSURE

INTRODUCTION

To understand the Raoult's law of vapour pressure, we must first understand the term accompanied with the law; vapour pressure. So in our today's wonderful meal, vapour pressure is our starter we must consume first; otherwise without this highly needed appetizer, the main course could be hot enough to burn your mouth and make your tongue tingling! And here it is.....!

At a particular temperature, substances have a tendency to form some vapour. This vapour actually behave like any gas and thus they exert pressure called **vapour pressure**. The tendency of the substance to form vapour at given temperature is what we call volatility.

So **vapour pressure** (also known as **vapour tension**) of a substance is *the pressure exerted by volatile component of the substance formed over its surface at a given temperature*.

And vapour pressure of a **liquid** is the pressure exerted by volatile component of the liquid formed over its surface at given temperature.

When the temperature is increased, the number of vapour (gas) particles and their velocity are also increased and eventually the vapour pressure is also increased and hence the vapour pressure is said to increase with an increase in temperature; that is the vapour pressure of the substance is temperature dependent. In two 'dots', the increase in temperature do two things to increase vapour pressure:

- It increases concentration (number) of vapour particles.
- It increases velocity of vapour particles.

The two factors, increases frequency of collision (the increase in velocity, increases collision intensity as well) between vapour particles and walls of the container and hence greater vapour pressure.

Vapour pressure as saturated vapour pressure

When a liquid is kept in a closed container, the following things occur with respect to evaporation:

- Firstly, liquid particles (molecules) will appear to escape to the upper part of the container as vapour.
- The vapour will then collide with walls in the upper part of the container and lid as well where it will condense to the liquid again. In other words, the process of evaporation is reversible physical process.
That is $\text{liquid} \rightleftharpoons \text{vapour}$
- At the beginning of the evaporation process, there is no vapour to condense and thus the rate of evaporation of the liquid will be greater than the rate of condensation of vapour at the initial stage of the evaporation. More vapour means more vapour pressure; so at these initial stages of the evaporation, the vapour pressure tends to increase.
- The process of evaporation (in the closed container) will proceed (and thus the vapour pressure continues to increase) until the rate of evaporation of the liquid is equal to the rate of condensation of the vapour.
- When this occurs, the physical process, $\text{liquid} \rightleftharpoons \text{vapour}$, is said to be at equilibrium.
- At this point of the physical equilibrium, the pressure of that vapour is said to be **saturated** hence the term **saturated** (or **saturation**) **vapour pressure** (or **equilibrium vapour pressure** if one pays attention on the fact that physical equilibrium is formed when the saturated vapour pressure is attained).

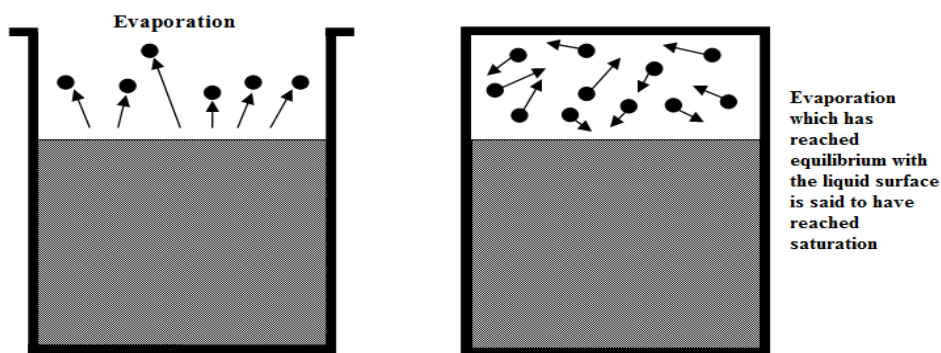


Figure 6.1 Saturated vapour pressure

By definition:

Saturated vapour pressure of a liquid at given temperature is the pressure of the vapour in equilibrium with excess liquid at that temperature.

Note:

When we are talking about **vapour pressure** the actual implication is usually **saturated vapour pressure**. So the terms vapour pressure and saturated vapour pressure are always used interchangeable although there is a subtle difference between the two.

Vapour pressure and boiling point

If the liquid is open to the air, its vapour pressure is seen as a partial pressure along with the other constituents of the air.

- The temperature at which vapour pressure is equal to the atmospheric pressure is called the **boiling point**. At boiling point, vapour pressure of the liquid is equal to the external pressure.

If the liquid has higher vapour pressure, then it needs lower temperature to increase its vapour pressure to the external pressure value and hence lower boiling point of the liquid. So higher vapour pressure implies lower boiling point and vice-versa.

- On another hand, increasing external pressure implies that the liquid will need higher temperature to increase its vapour pressure so as to balance with the external pressure and hence higher boiling point of the liquid. So higher external pressure implies higher boiling point and vice-versa.

RAOULT'S LAW

Consider a binary solution containing two liquids A and B which are completely miscible with each other in all proportions. In such solutions, the terms, solute and solvent, can be interchanged for the two components and the vapour formed over the liquid solution surface will constitute of both A and B molecules with vapour pressure of solution coming from both components (A and B). Raoult's law describes relationship between partial vapour pressure of each component (in the vapour mixture) and their respective concentration (mole fraction) in the liquid solution.

According to the law, the partial vapour pressure a particular component varies directly proportional to its mole fraction in the liquid solution with vapour pressure of pure component as the constant for proportionality.

That is $P_A \propto X_A$ and $P_B \propto X_B$

Introducing constant for proportionality which are P_A° and P_B° respectively

Hence:

$$P_A = X_A P_A^\circ \text{ and } P_B = X_B P_B^\circ$$

Where P_A and P_B are partial vapour pressures exerted in the solution by liquids A and B respectively. X_A and X_B are mole fractions of **liquid** A and B respectively.

P_A° and P_B° are vapour pressures of **pure** liquids A and B respectively.

Therefore, **Raoult's law of vapour pressure** can be stated as follows: *Partial vapour pressure of a particular constituent (component) in a solution which contains two or more volatile miscible liquids is the product of its mole fraction and its vapour pressure of the pure liquid at given temperature.*

Raoult's law is only applicable for solution whose intermolecular forces between the components in the solution are similar to those intermolecular forces between individual components.

- The solution behaving in such way is termed as ideal solution. So in other words, Raoult's law is applicable for **ideal solutions** only. It is equivalent to ideal gas law for ideal gases.

Vapour pressure of solution from Raoult's law and Dalton's law

Raoult's help us to know partial vapour pressure exerted by a particular liquid component in the solution. Once a vapour has been formed, the vapour being a gas obeys all gas laws. So we may combine Raoult's law and Dalton's law of vapour pressure to get vapour pressure of the ideal solution as shown below:

Consider the solution which contains two volatile miscible liquids, say A and B:

Then by Raoult's law;

$$P_A = X_A P_A^\circ \text{ and } P_B = X_B P_B^\circ$$

But by Dalton's law of partial pressures:

$P_{\text{soln}} = P_A + P_B$; where P_{soln} = vapour pressure of the solution

Hence $P_{\text{soln}} = X_A P_A^\circ + X_B P_B^\circ$

Recall: $X_A + X_B = 1$

So if A is less volatile than B i.e. $P_A^\circ < P_B^\circ$

Then $P_A^\circ < P_{\text{soln}} < P_B^\circ$

(Vapour pressure of solution must be between P_A° and P_B°)

It should be understood that:

The vapour composition of the solution can be obtained by using the fact that:

$$X_A^V = \frac{P_A}{P_{\text{soln}}} \text{ and } X_B^V = \frac{P_B}{P_{\text{soln}}}$$

Where X_A^V and X_B^V are mole fractions in vapour phase for liquids A and B respectively.

But $P_A = X_A^L P_A^\circ$ and $P_B = X_B^L P_B^\circ$

$$\text{Then } X_A^V = \frac{X_A^L P_A^\circ}{P_{\text{soln}}} \text{ and } X_B^V = \frac{X_B^L P_B^\circ}{P_{\text{soln}}}$$

Since A is less volatile, $P_B^\circ > P_A^\circ$

And $P_B^\circ > P_{\text{soln}}$ while $P_A^\circ < P_{\text{soln}}$

So from $X_A^V = \frac{X_A^L P_A^\circ}{P_{\text{soln}}}$, it becomes $\frac{P_A^\circ}{P_{\text{soln}}} < 1$ and hence $X_A^V < X_A^L$

While from $X_B^V = \frac{X_B^L P_B^\circ}{P_{\text{soln}}}$, $\frac{P_B^\circ}{P_{\text{soln}}} > 1$ and hence $X_B^V > X_B^L$

Therefore, the vapour composition of less volatile component (liquid A) is less than its liquid composition while the vapour composition of more volatile component (liquid B) is greater than its liquid composition.

Hence the solution which obeys Raoult's law (**ideal solution**) boils in such a way that the vapour formed is richer in one component which more volatile thus enabling the separation of components of the solution by **fractional distillation**. This conclusion is similar to **Konowaloff's rule** which can be stated as follows: *When an ideal solution is boiled at given temperature, the vapour phase is always richer in the more volatile component as compared to the liquid solution phase.*

WORKED EXAMPLES ON RAOULT'S LAW

Example 1

Two pure liquids A and B have vapour pressures of $1.5 \times 10^4 \text{ Pa}$ and $3.5 \times 10^4 \text{ Pa}$ respectively. If a mixture of A and B obeys Raoult's law, calculate the mole fraction of A and B if the solution has a total vapour pressure of $2.9 \times 10^4 \text{ Pa}$ at 20°C .

Solution

By Dalton's law of vapour pressure, total vapour pressure of solution is given by,

$$P_{\text{soln}} = P_A + P_B$$

$$\text{But from Raoult's law: } P_A = X_A P_A^0; \text{ and } P_B = X_B P_B^0$$

$$\text{Then } P_{\text{soln}} = X_A P_A^0 + X_B P_B^0$$

$$\text{But } X_A + X_B = 1 \text{ or } X_B = 1 - X_A$$

$$\text{So } P_{\text{soln}} = X_A P_A^0 + (1 - X_A) P_B^0$$

$$P_{\text{soln}} = X_A P_A^0 - X_A P_B^0 + P_B^0$$

$$\text{Or } X_A = \frac{P_{\text{soln}} - P_B^0}{P_A^0 - P_B^0} = \frac{(2.9 - 3.5) \times 10^4}{(1.5 - 3.5) \times 10^4} = 0.3$$

$$X_B = 1 - X_A = 1 - 0.3 = 0.7$$

Hence: Mole fraction of A is 0.3

Mole fraction of B is 0.7

Example 2

Calculate the vapour pressure of solution containing 50g of heptanes and 38g of octane at 20°C . The vapour pressure of pure liquids at 20°C are heptane 473Pa, octane 140Pa.

Solution

$$n_H = \frac{m_H}{M_H} = \frac{50}{100} \text{ mol} = 0.5 \text{ mol}$$

$$n_O = \frac{m_O}{M_O} = \frac{38}{114} \text{ mol} = 0.333 \text{ mol}$$

$$X_H = \frac{n_H}{n_H + n_O} = \frac{0.5}{0.5 + 0.333} = 0.6$$

$$X_O = 1 - X_H = 1 - 0.6 = 0.4$$

Since octane and heptanes are miscible, their solution must obey Raoult's law. So by combining Raoult's law and Dalton's law of vapour pressure: $P_{\text{soln}} = X_H P_H^0 + X_O P_O^0$

$$P_{\text{soln}} = (0.6 \times 473) + (0.4 \times 140) = 339.8 \text{ Pa}$$

Hence the vapour pressure of the solution is 339.8Pa

Example 3

Two pure liquids A and B have vapour pressure of 17000Nm^{-2} and 35000Nm^{-2} at 25°C respectively. An equimolar mixture of A and B has vapour pressure of 26000Nm^{-2} at 25°C . Calculate the vapour pressure of a mixture containing four moles of A and one mole of B at 25°C .

Solution

Checking whether the solution obey Raoult's law or not:

Since $n_A = n_B$ (equimolar mixture of A and B)

$$\text{Then } X_A = X_B = \frac{1}{2}$$

$$\text{So } X_A P_A^0 = \frac{1}{2} \times 17000\text{Nm}^{-2} = 8500\text{Nm}^{-2}$$

$$\text{And } X_B P_B^0 = \frac{1}{2} \times 35000\text{Nm}^{-2} = 17500\text{Nm}^{-2}$$

$$\text{Then } X_A P_A^0 + X_B P_B^0 = (8500 + 17500)\text{Nm}^{-2} = 26000\text{Nm}^{-2}$$

That is; $P_{\text{soln}} = X_A P_A^0 + X_B P_B^0$ and hence the solution of A and B obeys Raoult's law.

For 4 moles of A and 1 mole of B

$$X_A = \frac{n_A}{n_A + n_B} = \frac{4}{4 + 1} = 0.8$$

$$X_B = 1 - X_A = 1 - 0.8 = 0.2$$

As the solution obeys Raoult's law:

$$\begin{aligned} P_{\text{soln}} &= X_A P_A^0 + X_B P_B^0 = (0.8 \times 17000) + (0.2 \times 35000) \\ &= (13600 + 7000)\text{Nm}^{-2} = 20600\text{Nm}^{-2} \end{aligned}$$

Hence the vapour pressure of the solution is 20600Nm^{-2}

The reader should note that:

Not all solutions obey Raoult's law, so the extra care is needed before application of Raoult's law. This confirms necessity of checking whether the solution obeys Raoult's law or not because in the above example there is no any other information we can use to deduce the fact.

Example 4

Hexane and heptanes are totally miscible and form an ideal two components system. If the vapour pressure of the pure liquids are 56000Nm^{-2} and 24000Nm^{-2} respectively at 50°C . Calculate:

- The total vapour pressure
- The mole fraction of heptanes in the vapour above an equimolar mixture of hexane and heptane

Solution

Since the solution is ideal, it obeys Raoult's law.

$$\text{Then } P_{\text{soln}} = X_{\text{hexane}} P_{\text{hexane}}^0 + X_{\text{heptane}} P_{\text{heptane}}^0$$

But as $n_{\text{hexane}} = n_{\text{heptane}}$ (equimolar mixture of hexane and heptane)

$$\text{It follows that } X_{\text{hexane}} = X_{\text{heptane}} = \frac{1}{2}$$

$$\text{So } P_{\text{soln}} = \frac{1}{2} \times 56000\text{Nm}^{-2} + \frac{1}{2} \times 24000\text{Nm}^{-2}$$

$$P_{\text{soln}} = 40000\text{Nm}^{-2}$$

(a) Thus the vapour pressure of the solution is 40000Nm^{-2}

From (a) above;

$$P_{\text{heptane}} = X_{\text{heptane}} P_{\text{heptane}}^{\circ} = \frac{1}{2} \times 24000\text{Nm}^{-2} = 12000\text{Nm}^{-2}$$

$$\text{And } P_{\text{soln}} = 40000\text{Nm}^{-2}$$

$$\text{Then } X_{\text{heptane}}^V = \frac{P_{\text{heptane}}}{P_{\text{soln}}} = \frac{12000}{40000} = 0.3$$

(b) Hence the mole fraction of heptanes in the vapour is 0.3

Example 5

10g of methanol (CH_3OH) give an ideal solution when mixed with 50g of ethanol ($\text{C}_2\text{H}_5\text{OH}$). If the vapour pressure of methanol and ethanol at the same temperature are 6265Pa and 2933Pa respectively. Calculate the:

- Partial pressure exerted by each component in the mixture.
- The composition of the vapour.

Solution

$$n_{\text{methanol}} = \frac{m_{\text{methanol}}}{M_{\text{methanol}}} = \frac{10}{32} \text{ moles} = 0.3125\text{mol}$$

$$n_{\text{ethanol}} = \frac{m_{\text{ethanol}}}{M_{\text{ethanol}}} = \frac{50}{46} \text{ moles} = 1.1\text{mol}$$

$$X_{\text{methanol}} = \frac{n_{\text{methanol}}}{n_{\text{methanol}} + n_{\text{ethanol}}} = \frac{0.3125}{0.3125 + 1.1} = 0.22$$

$$X_{\text{ethanol}} = 1 - X_{\text{methanol}} = 1 - 0.22 = 0.78$$

Since the solution is ideal, then it obeys Raoult's law.

$$\text{Then } P_{\text{soln}} = X_{\text{methanol}} P_{\text{methanol}}^{\circ} + X_{\text{ethanol}} P_{\text{ethanol}}^{\circ}$$

$$\begin{aligned} P_{\text{soln}} &= (0.22 \times 6265) + (0.78 \times 2933) \\ &= 1378.3\text{Pa} + 2287.74\text{Pa} = 3666.04\text{Pa} \end{aligned}$$

$$\text{Then } X_{\text{methanol}}^V = \frac{P_{\text{methanol}}}{P_{\text{soln}}}$$

$$\text{But } P_{\text{methanol}} = X_{\text{methanol}} P_{\text{methanol}}^{\circ} = 1378.3\text{Pa}$$

$$\text{So } X_{\text{methanol}}^V = \frac{1378.3}{3666.04} = 0.376 \text{ or } 37.6\%$$

$$\text{And } X_{\text{ethanol}}^V = 1 - X_{\text{methanol}}^V = 1 - 0.376 = 0.624 \text{ or } 62.4\%$$

Hence the vapour composition is 37.6% and 62.4% by mole of methanol and ethanol respectively.

Example 6

Liquid Y and Z are completely miscible. A certain mixture of the two liquids boils at 410K when pressure is $1.63 \times 10^5\text{Nm}^{-2}$. If the vapour pressure of Y at this temperature is $1.15 \times 10^5\text{Nm}^{-2}$ and that of Z is $6.04 \times 10^5\text{Nm}^{-2}$. Calculate the mole fraction of Y:

- In the liquid mixture
- In the vapour mixture

Solution

Since the solution is completely miscible, it obeys Raoult's law:

$$\text{Then } P_{\text{soln}} = X_Y P_Y^{\circ} + X_Z P_Z^{\circ}$$

But $X_Y + X_Z = 1$

Or $X_Z = 1 - X_Y$

So $P_{\text{soln}} = X_Y P_Y^0 + (1 - X_Y) P_Z^0$

$P_{\text{soln}} = X_Y (P_Y^0 - P_Z^0) + P_Z^0$

Or $X_Y = \frac{P_{\text{soln}} - P_Z^0}{P_Y^0 - P_Z^0} = \frac{(1.63 - 6.04) \times 10^5}{(1.15 - 6.04) \times 10^5} = 0.9$

Hence mole fraction of Y in the liquid mixture is 0.9

Then $P_Y = X_Y P_Y^0 = 0.9 \times 1.15 \times 10^5 \text{ Nm}^{-2} = 1.035 \times 10^5 \text{ Nm}^{-2}$

$P_Z = X_Z P_Z^0 = (1 - X_Y) P_Z^0 = 0.1 \times 6.04 \times 10^5 \text{ Nm}^{-2} = 6.04 \times 10^4 \text{ Nm}^{-2}$

$P_{\text{soln}} = P_Y + P_Z = 1.035 \times 10^5 \text{ Nm}^{-2} + 6.04 \times 10^4 \text{ Nm}^{-2}$

$= 1.639 \times 10^5 \text{ Nm}^{-2}$

It follows that: $X_Y^V = \frac{P_Y}{P_{\text{soln}}} = \frac{1.035 \times 10^5}{1.639 \times 10^5} = 0.63$

Hence mole fraction of Y in the vapour mixture is 0.63

Example 7

- (a) Calculate the composition of the mixture AB which at 760mmHg boils at 88°C (the saturated vapour pressure of A and B at 88°C are 957mmHg and 378mmHg respectively). Assume the mixture of A and B obeys Raoult's law.
- (b) Calculate the composition of the vapour obtained when the liquid mixture (a) above is boiled.

Solution

At boiling point;

Vapour pressure of the solution = Atmospheric pressure

But the atmospheric pressure is 760mmHg (Given)

So the vapour pressure of solution, $P_{\text{soln}} = 760 \text{ mmHg}$

As the solution Obey Raoult's law:

$P_{\text{soln}} = X_A P_A^0 + X_B P_B^0$

But $X_B = 1 - X_A$

Then $P_{\text{soln}} = X_A P_A^0 + (1 - X_A) P_B^0$

$P_{\text{soln}} = X_A (P_A^0 - P_B^0) + P_B^0$

Therefore: $X_A = \frac{P_{\text{soln}} - P_B^0}{P_A^0 - P_B^0} = \frac{760 - 378}{957 - 378} = 0.66$ or 66%

Then $X_B = 1 - X_A = 1 - 0.66 = 0.34$ or 34%

(a) Hence the composition of the mixture is 66% and 34% by mole of A and B respectively

$P_A = X_A P_A^0 = 0.66 \times 957 \text{ mmHg}$
 $= 631.62 \text{ mmHg}$

Then $X_A^V = \frac{P_A}{P_{\text{soln}}} = \frac{631.62}{760} = 0.831$ or 83.1%

And $X_B^V = 1 - X_A^V = 1 - 0.831 = 0.169$ Or 16.9%

(b) Hence the composition of the vapour is 83.1% and 16.9% by mole of A and B respectively.

Example 8

Benzene and toluene form a nearly ideal solution. At 80°C, the vapour pressure of pure benzene (Mwt = 78g/mol) is 753torr and that of toluene (Mwt = 92g/mol) is 290torr. The following questions refer to a solution that contains equal weight of the two liquids.

- Calculate the partial pressure of each component that would be in equilibrium with the solution at 80°C.
- At what atmospheric pressure will this solution boil at 80°C?
- What will be the composition of the liquid that condenses when this vapour is cooled?

Solution

- Let mass of each component be m (the two components weighs equal).

Then number of moles of benzene, $n_b = \frac{m}{78}$

And number of moles of toluene, $n_t = \frac{m}{92}$

So in the liquid mixture: $X_b = \frac{n_b}{n_b + n_t} = \frac{\frac{m}{78}}{\frac{m}{78} + \frac{m}{92}} = \frac{46}{85}$

And $X_t = 1 - X_b = 1 - \frac{46}{85} = \frac{39}{85}$

By Raoult's law: $P_t = P_t^\circ X_t = \frac{290 \times 39}{85} \text{ torr} = 133 \text{ torr}$

And $P_b = P_b^\circ X_t = \frac{753 \times 46}{85} \text{ torr} = 407.5 \text{ torr}$

Hence:

Partial pressure of toluene is 133torr

Partial pressure of benzene is 407.5torr

- The solution will boil when the vapour pressure of the solution (P_{soln}) is equal to the atmospheric pressure.

But by Dalton's law of partial pressure: $P_{\text{soln}} = P_t + P_b = (133 + 407.5) \text{ torr} = 540.5 \text{ torr}$

Hence the atmospheric pressure required to boil the solution is 540.5torr

- Mole fraction of toluene in the vapour phase, $X_t^v = \frac{P_t}{P_{\text{soln}}} = \frac{133 \text{ torr}}{540.5 \text{ torr}} = 0.246$

And $X_b^v = 1 - X_t^v = 1 - 0.246 = 0.754$

When the vapour is condensed, the composition the condensed liquid does not change compared to the composition of the vapour.

That is; liquid composition = composition of vapour which has been condensed to get the liquid

Hence the composition of the distillate (condensed liquid) will be 0.246 and 0.754 for toluene and benzene respectively by the mole fraction.

Example 9

A solution is prepared by mixing 5.81g acetone (molar mass 58.1g/mol) and 11.9g chloroform (molar mass 119.4 g/mol). At this solution has a total vapour pressure of 260torr. The vapour pressures of pure acetone and pure chloroform at are 345 and 293 torr, respectively.

- Is this an ideal solution?
- Rationalise the answer stated in (i) above.

Solution

$$\text{Using; } n = \frac{m}{M_r}$$

$$n_{\text{Acetone}} = \frac{5.81\text{g}}{58.1\text{gmol}^{-1}} = 0.1\text{mol}$$

$$n_{\text{Chloroform}} = \frac{11.9\text{g}}{119.4\text{gmol}^{-1}} = 0.1\text{mol}$$

$$\text{Using; Mole fraction, } X = \frac{n}{n_T}$$

$$X_{\text{Acetone}} = \frac{0.1\text{mol}}{(0.1 + 0.1)\text{mol}} = 0.5$$

$$\text{And } X_{\text{Chloroform}} = 1 - X_{\text{Acetone}} = 1 - 0.5 = 0.5$$

According to Raoult's law;

$$\begin{aligned} \text{Ideal } P_{\text{soln}} &= X_{\text{Acetone}} P_{\text{Acetone}}^{\circ} + X_{\text{Chloroform}} P_{\text{Chloroform}}^{\circ} \\ &= 0.5 \times 345\text{Pa} + 0.5 \times 293\text{Pa} = 319\text{Pa} \end{aligned}$$

But the real $P_{\text{soln}} = 260\text{Pa}$ which is less than the ideal P_{soln} (319Pa).

- Since the given real pressure is not equal to ideal pressure determined by Raoult's law, the solution is not ideal.
- As the real pressure of the solution is less than that predicted by Raoult's law, the solution shows negative deviation from Raoult's law. The negative deviation is explained by presence of intermolecular hydrogen bonds in the solution which are stronger intermolecular forces than dipole-dipole forces present in pure acetone and chloroform.

IDEAL AND NON-IDEAL SOLUTIONS**Ideal solutions**

A solution which obeys Raoult's law is said to be **ideal**. The **ideal solution** has intermolecular forces of attraction which are equal to intermolecular forces of attraction in pure liquids (solvents) before their mixing.

That is for the solution which contains of two liquids, say A and B. If the solution is ideal then:

$$A \dots \dots \dots A = B \dots \dots \dots B = A \dots \dots \dots B$$

(Intermolecular force of attraction in the pure liquid A) (Intermolecular force of attraction in the pure liquid B) (Intermolecular force of attraction in the solution)

Ideal solutions obey Raoult's law and are formed when the two liquids are of the same nature i.e. either **both are polar liquids** or **both are non- polar liquids** thus becoming **miscible liquids**.

So **an ideal solution** can be defined as *a mixture of substances (most common, liquid substances) of similar chemical structures and polarities.*

- For example, both liquid hexane and liquid heptane are hydrocarbon and non – polar molecules and thus their mixture is the ideal solution.

Other examples of ideal solution are:

- Solution of methanol in water (both are polar liquids)
- Solution of benzene and toluene (both are non- polar liquids)

Formation ideal solution in terms of intermolecular forces

During the mixing process, molecules of A try to get in between molecules of B. So energy is required to separate B and B, and A and A by breaking B -----B intermolecular forces and A-----A intermolecular forces respectively.

- However, energy is released as different molecules of A and B come together in forming A -----B interactions; (remember formation of any bond is exothermic process while the breaking of the bond is endothermic process).
- Since intermolecular forces A-----A, B-----B and A-----B are similar, the same energy absorbed in breaking A-----B and B-----B intermolecular forces will be released in forming A-----B and thus there is no energy change ($\Delta H = 0$) in the mixing process. And also because no change in strength of intermolecular forces, no volume change ($\Delta v = 0$) will be observed in the process.

Characteristics of ideal solution

1. Intermolecular forces of attraction in pure liquids are equal to intermolecular forces of attraction in the solution.
2. Obey Raoult's law at any concentration. That is $P_{\text{soln}} = X_A P_A^0 + X_B P_B^0$ as $P_A = X_A P_A^0$ and $P_B = X_B P_B^0$ for the solution which consist of liquid A and B. Thus the vapour pressure of ideal solution always lies between vapour pressures of the pure liquids.

$$P_A^0 < P_{\text{soln}} < P_B^0 \text{ (if A is less volatile than B)}$$
3. Its formation is not accompanied with change in energy. That is formation of the ideal solution is neither endothermic nor exothermic.
4. Its formation is not accompanied with change in volume.
 That is $V_{\text{soln}} = V_A + V_B$ for the solution which consist of liquid A and B with respective volume of V_A and V_B
5. Its boiling point always lies between boiling points of the pure liquids.

$$T_B < T_{\text{soln}} < T_A \text{ if A is less volatile than B}$$
6. Its components can be separated by simple fractional distillation.

Non- ideal solutions

Non ideal solution is the solution whose intermolecular forces of attraction in pure liquids are not equal to intermolecular forces of attraction in the solution.

That is for the non-ideal solution which consists of two liquids, say A and B, then:



Unlike ideal solution, non- ideal solution does not obey Raoult's law.

However, it should be noted that:

Non- ideal solution may be converted to nearly ideal solution by making the solution more dilute, why?

Reason:

In very dilute solution there are much more solvent-solvent forces of attraction than solvent-solute forces of attractions (as number of solvent molecules is too large compared to number of solute molecular) and hence intermolecular forces of attraction in the solution become almost equal to intermolecular forces of attraction in pure liquids.

Characteristics of non- ideal solution

1. Intermolecular forces of attraction in the pure liquids are not equal to intermolecular forces of attraction in the solution.
2. It does not obey Raoult's law.
 That is $P_{\text{soln}} \neq X_A P_A^0 + X_B P_B^0$ as $P_A \neq X_A P_A^0$ and $P_B \neq X_B P_B^0$
 Thus the vapour pressure of the non-ideal solution does not always lie between the vapour pressures of the pure liquids.

3. Its formation is accompanied with change in energy. That is, heat energy is either evolved or absorbed during formation of non-ideal solution.
4. Its formation is accompanied with change in volume
That is $V_{\text{soln}} \neq V_A + V_B$
5. Its boiling point does not always lie between the boiling points of pure liquids.
6. Its components cannot be separated by simple fractional distillation.

CLASSIFICATION OF NON-IDEAL SOLUTIONS

Depending on deviation of vapour pressure of the solution from that predicted from Raoult's law, non-ideal solution can be classified into the following categories:

- Non-ideal solution with positive deviation
- Non-ideal solution with negative deviation.

Non-ideal solution of positive deviation

This is the solution whose vapour pressure is greater than that predicted by Raoult's law.

As the vapour pressure decreases with an increase in intermolecular forces of attraction;

Non-ideal solution with positive deviation has intermolecular forces of attraction which are less than intermolecular forces of attraction of at least one of the pure liquids. This is attained when **non-polar liquid** is mixed to **polar liquid**. In which the non-polar tends to weaken forces in the polar liquid and hence the intermolecular forces of attraction in the solution become smaller than intramolecular forces of attraction in the polar liquid.

Since non-ideal solution of positive deviations are formed by mixing non-polar and polar liquids, the solutions are always **immiscible** (or **partially miscible solution**).

A good example of non-ideal solution with positive deviation is the liquid mixture of hexane and ethanol.

In mixing hexane and ethanol, hexane molecules get in between the ethanol molecules.

As the result of the mixing, many hydrogen bonds between ethanol molecules are broken up. Since there are only weak Van der Waals forces between different molecules, the total intermolecular forces in the solution are reduced and the vapour pressure of the solution is higher than expected.

Other examples of non-ideal solutions with positive deviation are:

- Solution of ethanol and water (partially miscible solution)
- Solution of benzene and ethanol (partially miscible solution)
- Solution of phenol and water (partially miscible)
- Solution of Chlorobenzene and water (immiscible solution)

Formation of non-ideal solution of positive deviation in terms of intermolecular forces

If A and B form non-ideal solution with positive deviation, then A-----B intermolecular forces are weaker than A-----A and B-----B intermolecular forces. This means that it requires more energy to break the interactions in the pure liquids (A-----A, and B-----B interactions) than energy released in forming A-----B interactions in the solution and hence the process of mixing the two liquids becomes endothermic in overall. The endothermic process of making non-ideal solution with positive deviation is witnessed by the solution being colder than pure liquids before the mixing. Due to weaker intermolecular forces in the solution the total volume increases, that is $V_{\text{soln}} > V_A + V_B$.

Characteristics of non-ideal solution of positive deviation

1. Intermolecular forces of attraction in the solution are less than intermolecular forces of attraction of at least one of the pure liquid.
2. The vapour pressure of the solution is greater than that which would be predicted by Raoult's law.
That is $P_{\text{soln}} > X_A P_A^0 + X_B P_B^0$ as $P_A > X_A P_A^0$ and $P_B > X_B P_B^0$

- Its formation is endothermic, that is heat is absorbed during formation of non-ideal solution with positive deviation.
- The volume of the solution is greater than the summation of volume.
That is, $V_{\text{soln}} > V_A + V_B$
- The boiling point of the solution is less than the ideal boiling point.
- Its components cannot be separated by fractional distillation.

Non- ideal solution of negative deviation

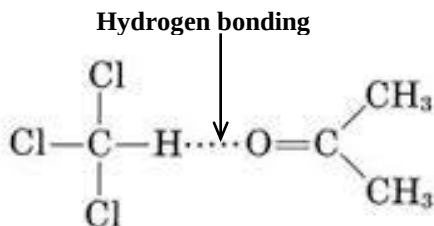
This is the solution whose vapour pressure is less than that predicted by Raoult's law.

In non- ideal solution with negative deviation, the intramolecular forces of attraction in the solution is greater than intermolecular forces of attraction of either of the pure liquid. Thus for the solution which consist of two liquids say A and B; if the solution is non- ideal with negative deviation, then:

$$A \dots \dots \dots B > A \dots \dots \dots A \text{ and } A \dots \dots \dots B > B \dots \dots \dots B$$

A good example of non – ideal solution with negative deviation is liquid mixture of trichloromethane (CHCl_3) and propanone (CH_3COCH_3).

- In pure liquids, trichloromethane and propanone have weak Van der Waals forces in each.
- After mixing, hydrogen bonds between trichloromethane and propanone molecules are formed. These hydrogen bonds in the solution are stronger than Van der Waals forces of pure liquids.



Non-ideal solutions of negative deviation are more commonly formed when there is a chemical reaction between the liquids. Are always formed when strong mineral acids are mixed with water, for example:

- Solution of hydrochloric acid in water.
- Solution of hydrobromic acid in water.
- Solution of hydroiodic acid in water.
- Solution of nitric acid in water.
- Solution of sulphuric acid in water.

In pure components, water has intermolecular hydrogen bonds while acids may have dipole-dipole forces (for example, in pure HCl and HBr) or intermolecular hydrogen bonds (for example, in HNO_3 and H_2SO_4). In the acid-water mixture, the acid ionises resulting to formation of ion-ion interactions in the solution. These ion-ion interactions are stronger than hydrogen bonds or dipole-dipole forces in the pure components and hence negative deviation for the solution.

Formation of non-ideal solution of negative deviation in terms of intermolecular forces

If A and B form non ideal solution with negative deviation, then A-----B intermolecular forces are stronger than A-----A and B-----B intermolecular forces. This means that it requires less energy to break the interactions in the pure liquids (A-----A, and B-----B interactions) than energy released in forming A-----B interactions in the solution and hence the process of mixing the two liquids become exothermic in overall. The exothermic process of making non – ideal solution is with negative deviation is witnessed by the solution being warmer than pure liquids before the mixing. Due to stronger intermolecular forces in the solution the total volume decreases, that is $V_{\text{soln}} < V_A + V_B$.

Characteristics of non-ideal solution of negative deviation

1. Intermolecular forces attraction in the solution is greater than those of all pure liquids.
2. The vapour pressure of the solution is less than that predicted by Raoult's law.
That is, $P_{\text{soln}} < X_A P_A^\circ + X_B P_B^\circ$ as $P_A < X_A P_A^\circ$ and $P_B < X_B P_B^\circ$
3. Its formation is exothermic (heat is evolved during formation of non-ideal solution with negative deviation)
4. The volume of the solution is less than the summation of volume of its constituent liquids.
That is $V_{\text{soln}} < V_A + V_B$
5. The boiling point of the solution is greater than the ideal boiling point.
6. Its components cannot be separated by fractional distillation.

GRAPHS OF VAPOUR PRESSURE OF SOLUTION AGAINST MOLE FRACTION OF COMPONENTS IN IDEAL AND NON-IDEAL SOLUTIONS**Graphs for ideal solutions**

If A is more volatile than B ($P_A^\circ > P_B^\circ$) and the solution between A and B obeys Raoult's law;

Then $P_A = X_A P_A^\circ$ (The graph of P_A against X_A is the straight line which passes through the origin and has positive slope which is equal to P_A° . It is in the general form of straight line equation, $y = mx$ with $y = P_A$, $m = P_A^\circ$ and $x = X_A$)

And $P_B = X_B P_B^\circ$ (Again the graph of P_B against X_B is the straight line which passes through the origin and has positive slope which is equal to P_B°).

Where:

P_A and P_B are partial vapour pressures of A and B respectively;

X_A and X_B are mole fractions for A and B respectively;

P_A° and P_B° are vapour pressure of pure A and pure B respectively.

Then by Dalton's law of partial pressure: $P_{\text{soln}} = P_A + P_B$

Substituting $P_{\text{soln}} = X_A P_A^\circ + X_B P_B^\circ$

But $X_B = 1 - X_A$

It follows that: $P_{\text{soln}} = X_A P_A^\circ + (1 - X_A) P_B^\circ$

Or $P_{\text{soln}} = X_A P_A^\circ + P_B^\circ - X_A P_B^\circ$

Or $P_{\text{soln}} = X_A (P_A^\circ - P_B^\circ) + P_B^\circ$

The final equation corresponds to the equation of the straight line graph of P_{soln} (on y - axis) against X_A (on x - axis) with following features;

1) Slope of the line = $P_A^\circ - P_B^\circ$

This can easily be deduced by equating terms of the equation, $P_{\text{soln}} = X_A (P_A^\circ - P_B^\circ) + P_B^\circ$ with the general equation of straight line which is $y = mx + c$ where $y = P_{\text{soln}}$, $x = X_A$,
 $m = P_A^\circ - P_B^\circ$ and $c = P_B^\circ$

Also since $P_A^\circ > P_B^\circ$ (A is more volatile than B), $P_A^\circ - P_B^\circ$ gives positive number and thus the line has positive slope.

Be careful!

The line has positive slope if and only if the graph of P_{soln} is constructed versus moles fraction of more volatile component (in this case, X_A).

If the graph of P_{soln} against mole fraction of less volatile component (X_B) is constructed the line will have negative slope as per the following equation;

$P_{\text{soln}} = X_B (P_B^\circ - P_A^\circ) + P_A^\circ$ and $c = P_A^\circ$

2) y – intercept = P_B° .

As shown in (i) above, $c = P_B^\circ$. This is the vapour pressure of pure B (less volatile component) and is obtained when $X_A = 0$ (when there is no A at all, there is only B).

That is from;

$$P_{\text{soln}} = X_A(P_A^\circ - P_B^\circ) + P_B^\circ$$

When $X_A = 0$; $P_{\text{soln}} = P_B^\circ$ (when there is no A in the solution, the vapour pressure of the 'solution' is the pressure of pure B).

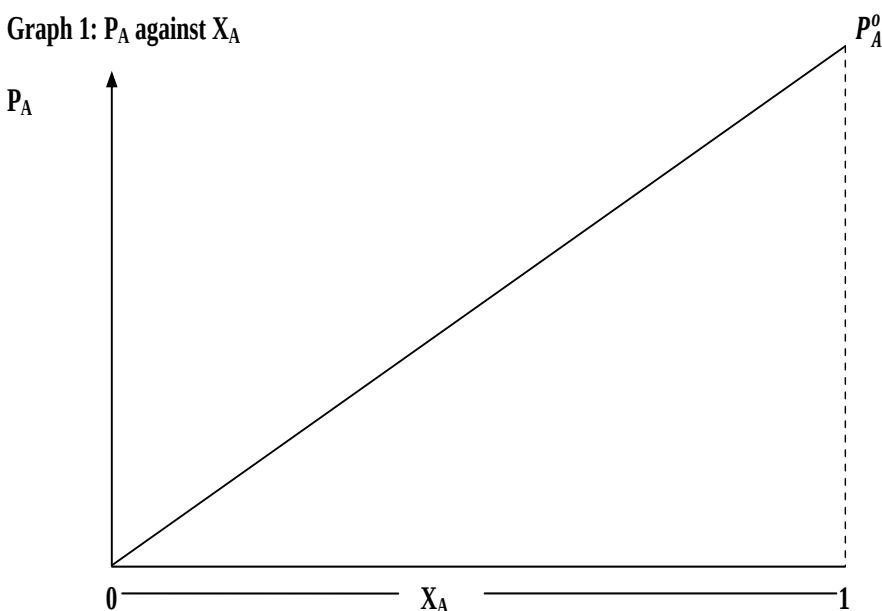
By similar argument, vapour pressure of pure A can be found if $X_A = 1$ (there is only A in the 'solution').

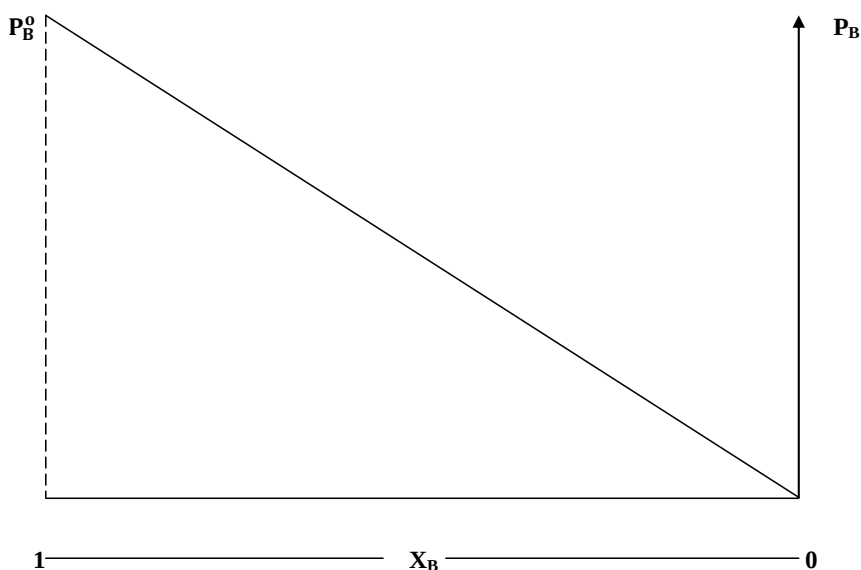
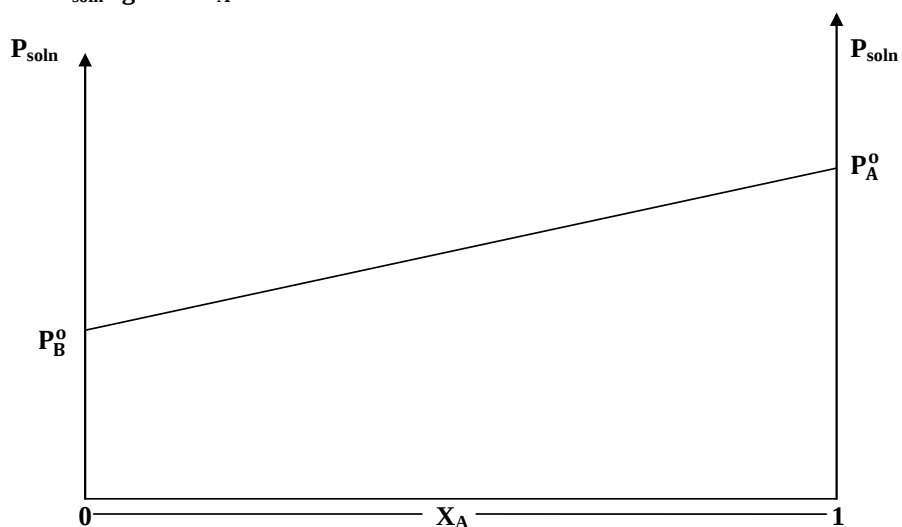
That is from;

$$P_{\text{soln}} = X_A(P_A^\circ - P_B^\circ) + P_B^\circ$$

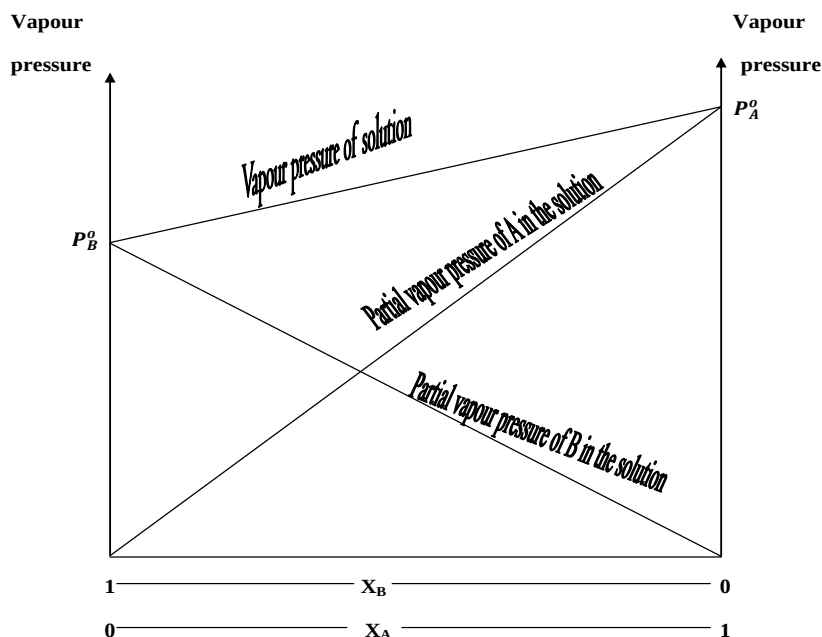
When $X_A = 1$; $P_{\text{soln}} = P_A^\circ - P_B^\circ + P_B^\circ = P_A^\circ$

Graph 1: P_A against X_A



Graph 2: P_B against X_B Graph 3: P_{soln} against X_A 

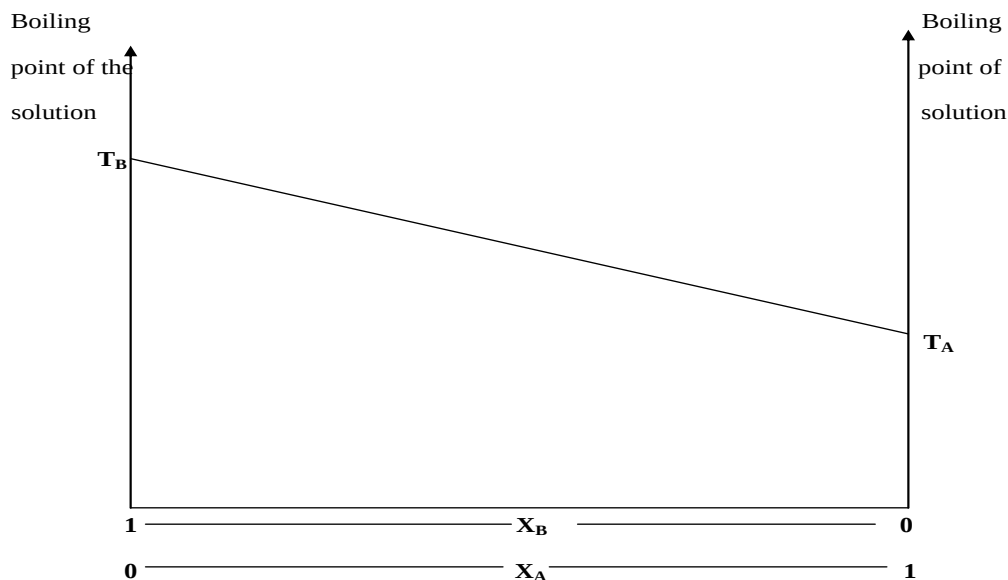
Combining **graph 1,2 and 3** gives more detailed of graph vapour pressure of solution against mole fraction of its components which show variation of partial pressure of each component in the solution as follows:



It should be noted that

The graph of boiling point of solution against mole fraction of its components can be derived from the graph of vapour pressure of the solution (**Graph 3**) by using the fact that the liquid which has higher vapour pressure (more volatile liquid which is A in this case) has lower boiling point and vice versa. This can be done as follows:

A graph of boiling point of ideal solution against mole fraction of its components



Where:

- A is more volatile than B (A has higher vapour pressure and lower boiling point than B).
- T_A is the boiling point of the pure liquid A.
- T_B is the boiling point of the liquid B.

Example 10

Below is the equation of line which is obtained after constructing the graph of vapour pressure (in mmHg) of the ideal solution (a solution which obeys Raoult's law) against mole fraction of one of the two components of the solution.

$$P = 200X + 400$$

Where P represent vapour pressure of the solution

X is the mole fraction of the component

Find the following:

- (i) Vapour pressure of the solution when the mole fraction of **another** component of the solution is 0.2.
- (ii) Vapour pressure of pure component which is less volatile
- (iii) Vapour pressure of pure component which is more volatile

Solution

- (i) $X + \text{mole fraction of another component} = 1$

$$X = 1 - \text{mole fraction of another component} = 1 - 0.2 \text{ or } X = 0.8$$

$$\text{Substituting } P = (200 \times 0.8 + 400)\text{mmHg} = 560\text{mmHg}$$

Hence the vapour pressure of the solution is 560mmHg

- (ii) Since the given equation of the line suggests the positive slope for the line, X is the mole fraction of more volatile component of the solution.

Then, the vapour pressure of pure component which is less volatile will be obtained when there is no component which is more volatile in the solution; that is $X = 0$

So substituting $X = 0$ in $P = 200X + 200$, gives;

$$P = 200 \times 0 + 400 \text{ or } 400\text{mmHg}$$

Hence vapour pressure of the pure component which is less volatile is 400mmHg

- (iii) Vapour pressure of the pure component which is more volatile is obtained when $X=1$ (there is only pure component which is more volatile in the 'solution').

Substituting $X = 1$ in $P = 200X + 200$ gives;

$$P = 200 \times 1 + 400 \text{ or } 600\text{mmHg}$$

Hence vapour pressure of the pure component which is more volatile is 600mmHg

Example 11

Liquid M and N forms two components ideal solution when they are mixed together. The graph of vapour pressure of the solution against mole fraction of M was found to obey the following equation:

$$P = -150X + 600 \quad (\text{At } 10^\circ\text{C})$$

Where P is the vapour pressure of the solution in mmHg;

X is the mole fraction M.

Find the following:

- (i) Mole fraction of N when the vapour pressure of the solution is 495mmHg
- (ii) Vapour pressure of pure component which is less volatile
- (iii) Vapour pressure of pure component which is more volatile
- (iv) The amount of atmospheric pressure needed to boil the solution with mole fraction of M, 0.1 at 10°C

Solution

(i) If $P = 495$;

$$495 = -150X + 600; \text{ from which } X = 0.7 = X_M$$

$$\text{But } X_M + X_N = 1$$

$$\text{From which } X_N = 1 - X_M = 1 - 0.7 = 0.3$$

Hence the vapour pressure of N is 0.3

(ii) Since the graph has negative slope, M is less volatile component, (remember that the graph was for the vapour pressure of the solution against mole fraction of M).

And when $X=1$, there is only pure M (less volatile) in the 'solution'.

$$\text{Substituting } X = 1 \text{ in } P = -150X + 600 \text{ gives; } P = -150 \times 1 + 600 \text{ or } 450 \text{ mmHg}$$

Hence the vapour pressure of the pure component which is less volatile is 450 mmHg

(iii) When $X = 0$, there is pure N (more volatile) in the 'solution'.

$$\text{Then } P = -150 \times 0 + 600 \text{ or } 600 \text{ mmHg}$$

Hence the vapour pressure of the pure component which is more volatile is 600 mmHg

(iv) The solution is said to boil, if the vapour pressure of the solution is equal to the atmospheric pressure

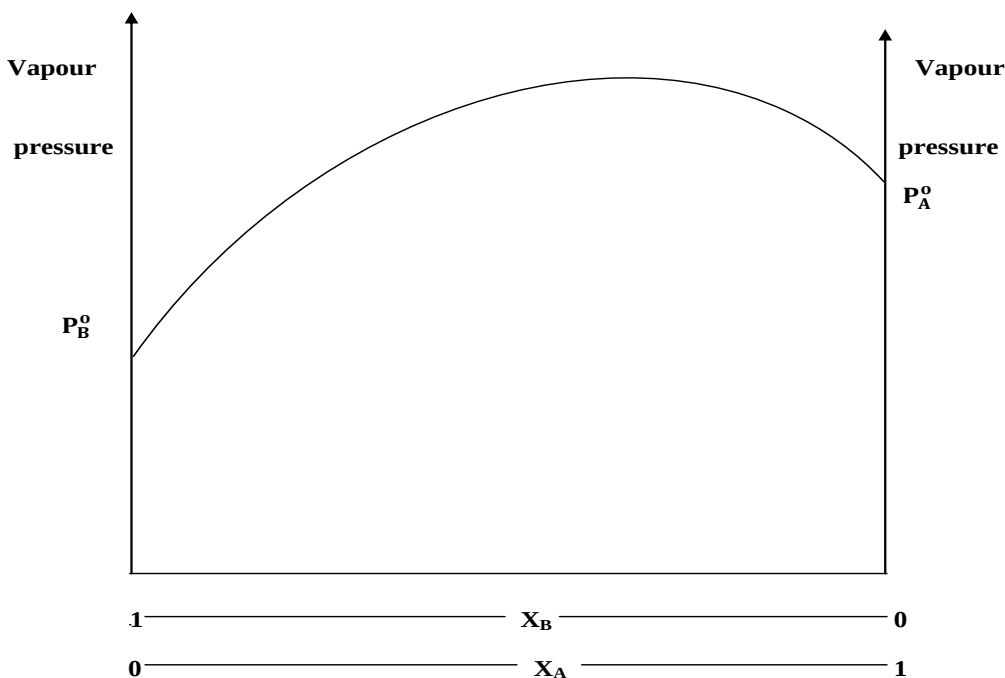
$$\text{When mole fraction of } M = 0.01; X = 0.01 \text{ and } P = -150 \times 0.1 + 600 \text{ or } 585 \text{ mmHg}$$

So if the atmospheric pressure = 585 mmHg, the solution will boil at 10°C .

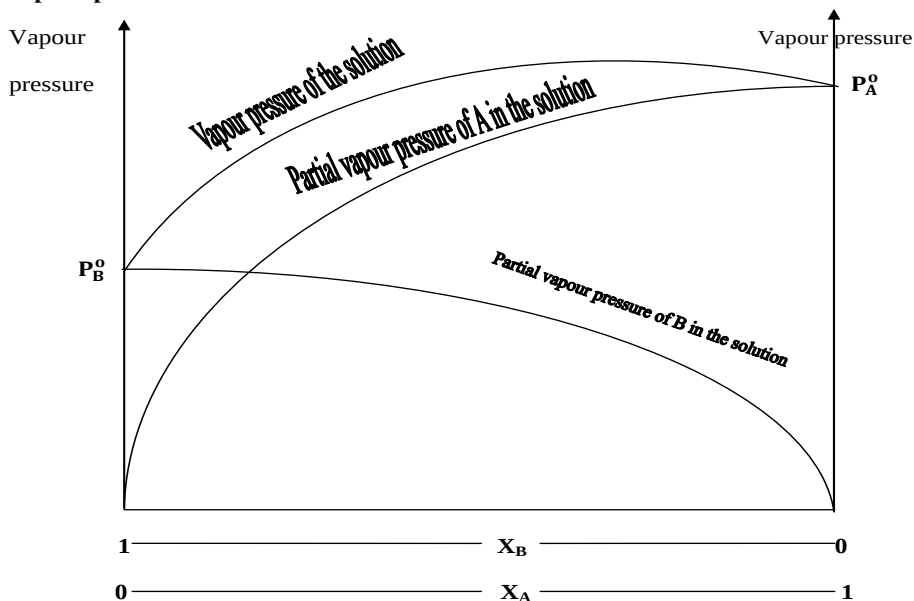
Hence the amount of atmospheric pressure required is 585 mmHg.

Graphs for vapour of non-ideal solution of positive deviation

Graph I: Without showing how partial vapour pressures of each components vary in the solution.

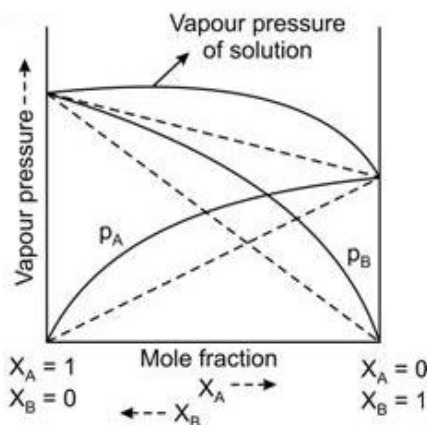


Graph II: Showing how partial vapour pressure of each component constitute to the vapour pressure of the solution



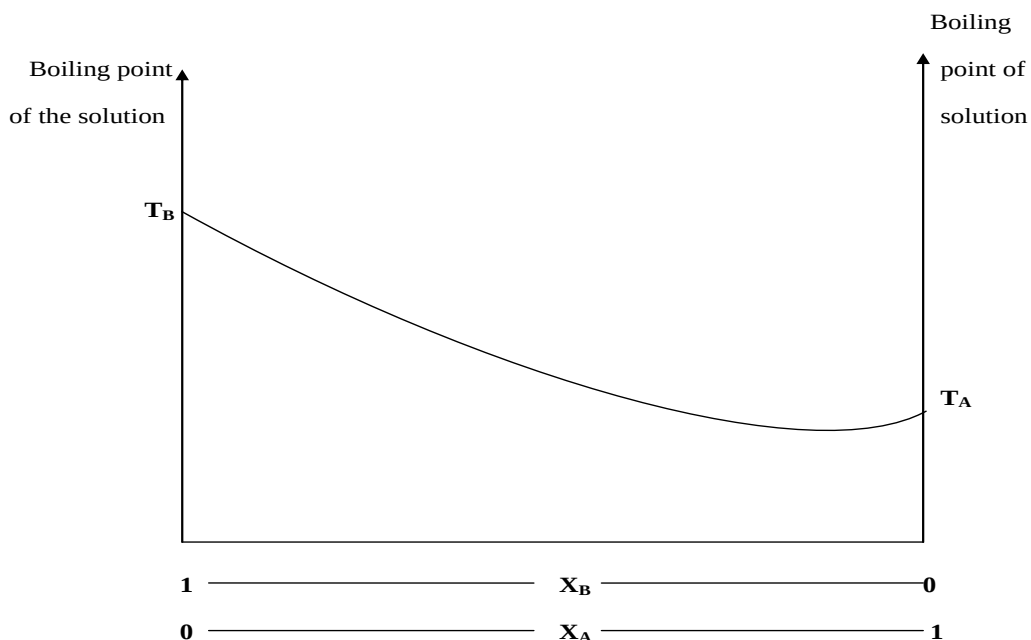
It should be noted that:

- Above graphs (see **graph I**) for non-ideal solution with positive deviation shows the maximum, hence the name **maximum vapour pressure mixture** for non-ideal solution with positive deviation.
- If straight lines are drawn between (0 and P_B^0) to show variation of partial pressure of B against its mole fraction for **ideal solution** and another straight line for the same aim for liquid A. And finally in the same graph the straight line can be drawn between P_B^0 and P_A^0 to show **vapour pressure of ideal solution** against mole fraction of its components. In each case the straight lines will pass below the curved lines verifying that vapour pressure of non-ideal solution with positive deviation is always greater than that of ideal solution.



Graph of boiling point of non-ideal solution with positive deviation can be derived from the graph of vapour pressure of the solution as follows:

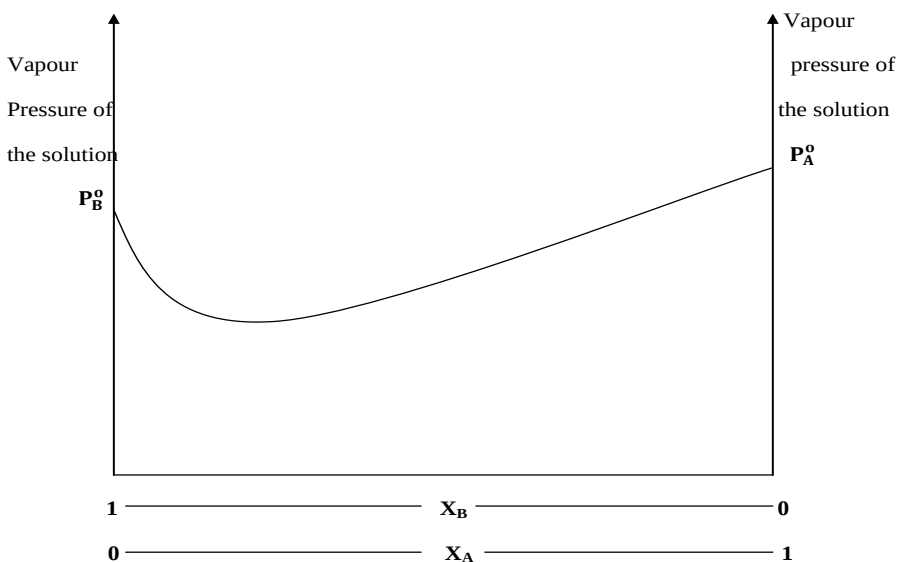
A graph of boiling point of non-ideal solution with positive deviation against mole fraction of its components



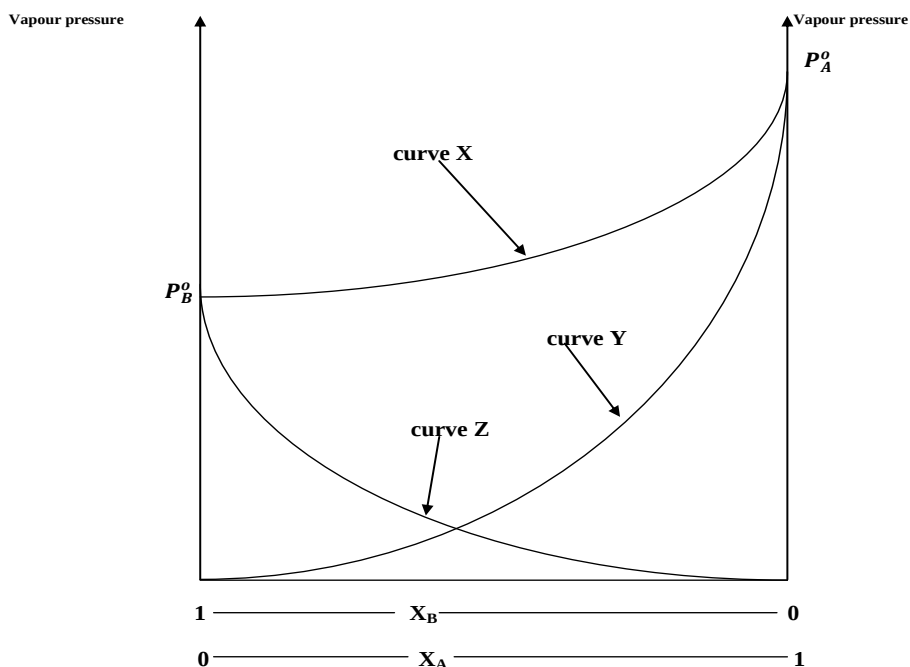
Where T_A and T_B are boiling points of pure A and B respectively, so from the above graph of boiling point of the non-ideal solution with positive deviations versus mole fraction of its components, it is clearly understood that; while the graph of the vapour pressure shows maximum, the graph of boiling point shows **minimum** and hence non-ideal solution with positive deviation are also known as **minimum boiling mixture**.

Graphs for non-ideal solution of negative deviation

Graph A: Without showing variations of partial vapour pressure of components in the solution.



Graph B: Showing how partial vapour pressure of each component constitute to the vapour pressure of the solution



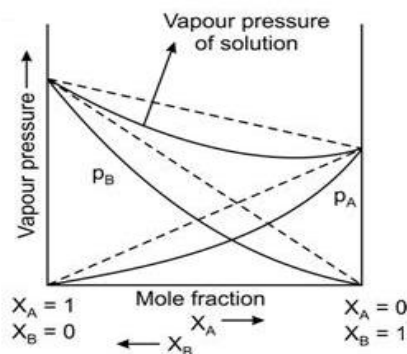
Where curve **X** represent vapour pressure of the solution

curve Y represent partial vapour pressure of A in the solution

curve Z represent partial vapour pressure of B in the solution

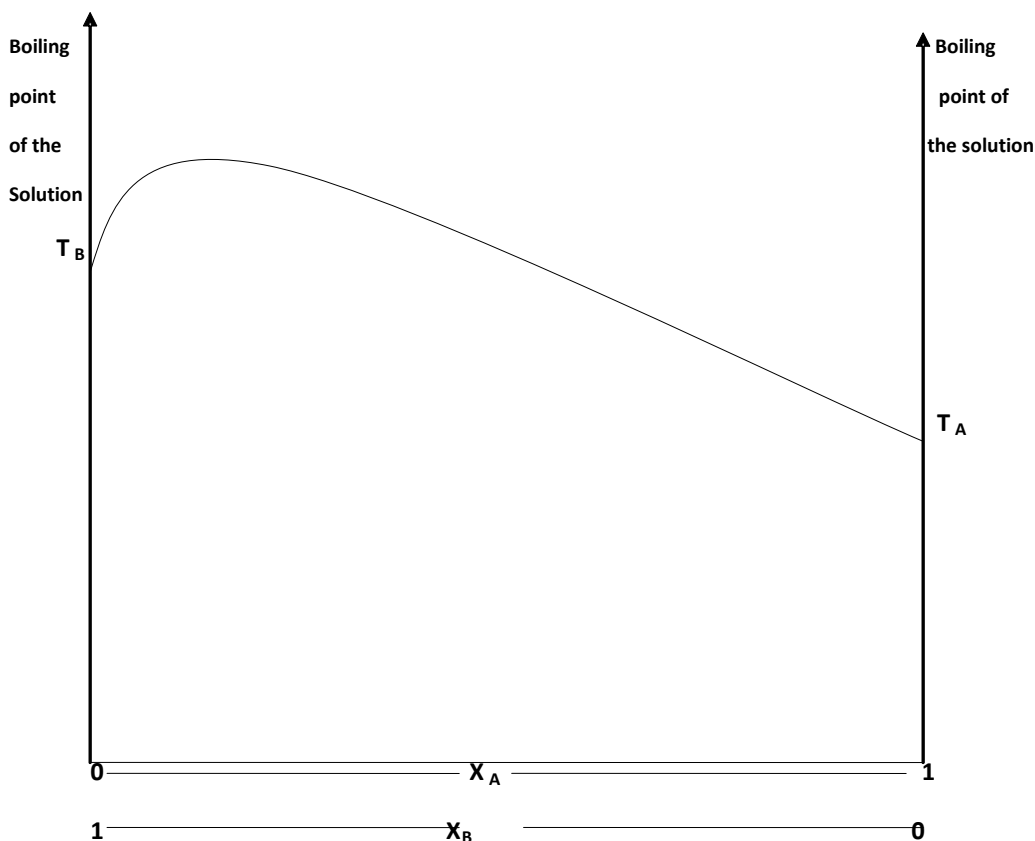
The reader should note that:

- Graph of vapour pressure of non-ideal solution with negative deviation shows minimum hence the name, **minimum vapour pressure mixture** for non-ideal solution with negative deviation.
- If straight lines are drawn between (0 and P_B^0) to show variation of partial pressure of B against its mole fraction for **ideal solution** and another straight line for the same aim for liquid A. And finally in the same graph the straight line can be drawn between P_B^0 and P_A^0 to show **vapour pressure of ideal solution** against mole fraction of its components. In each case the straight lines will pass above the curved lines verifying that vapour pressure of non-ideal solution with negative deviation is always smaller than that of ideal solution.



Graph of boiling point of non-ideal solution with negative deviation can be derived from the graph of the vapour pressure of the solution (**graph A**) as follows:

A graph of boiling point for non-ideal solution with negative deviation versus mole fraction of its components



Where T_A and T_B are boiling points of pure A and B respectively

So from the above graph it is clearly understood that; while the graph of vapour pressure of non-ideal solution with negative deviations shows minimum, the graph of boiling point of the solution shows maximum and hence **non-ideal solutions with negative deviation are also known as maximum boiling mixture.**

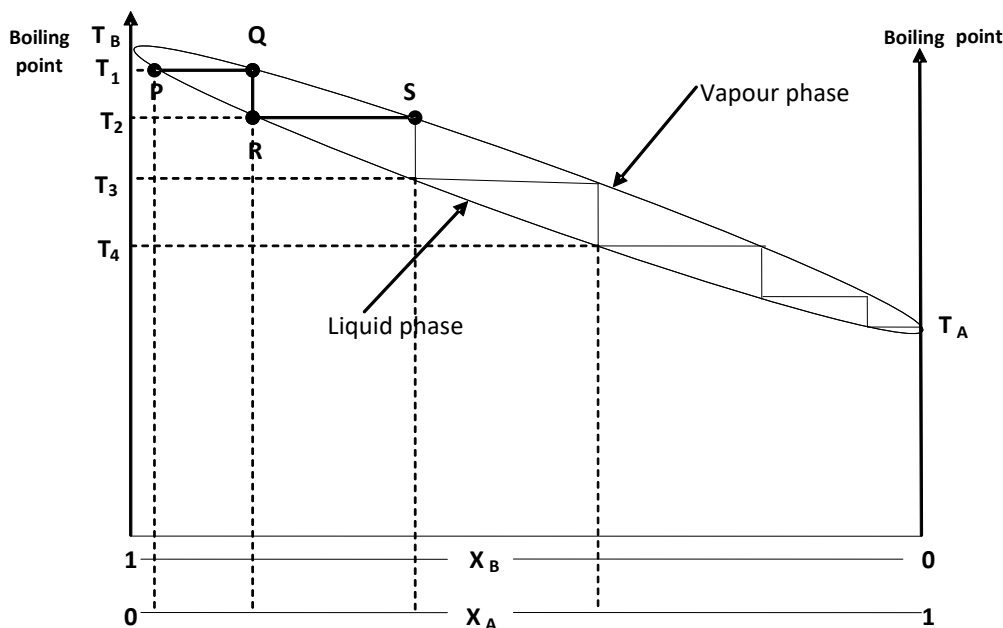
BEHAVIOUR OF IDEAL SOLUTIONS ON DISTILLATION

The important character about ideal solution in distillation is that; the vapour composition of the solution is continuously changing compared to its liquid composition on successive distillation and condensation. This makes possible to separate components of ideal solution by **fractional distillation.**

Ideal solution boils in such a way that, the vapour formed is richer in one component which is more volatile. So on successive distillation and condensation:

- Pure component which **more volatile** is found in the **collector** as the **distillate.**
- Pure component which **less volatile** remains in the **distillation flask** as the **residue.**

The above facts can be illustrated graphically as follows:

A graph to illustrate boiling point –composition relation of ideal solution in the distillation

Where T_A and T_B are boiling points of pure A and B respectively

Explanation of the behaviour shown by the graph:

- When liquid **P** is distilled at T_1 the Vapour **Q** is formed whose composition (mole fraction) of **A** (which is more volatile component) is greater than its liquid composition.
- When vapour **Q** is condensed, the liquid **R** (with the same composition as that of **Q**) is formed which boils at relative lower temperature, T_2 . On distilling liquid **R**, the vapour **S** is formed in which composition (mole fraction) of A which is more volatile component continue to increase and so on.
- Finally, pure A is found on collector as distillate and pure B remains in the distillation flask as residue.

It should be noted that:

In drawing graphs of boiling point versus composition so as to show behaviour of solution (ideal or non-ideal) in distillation, **the curve of vapour phase must be drawn above the curve of liquid phase** while for the graph of vapour pressure versus composition to show the same behaviour, **the curve of vapour phase must be drawn below the curve of liquid phase**.

Example 12

Explain how a mixture of methanol and water behaves on fractional distillation?

Solution

The mixture of methanol and water is the ideal solution, methanol being more volatile. Thus the solution will boil in such a way that, the vapour formed is richer in methanol (more volatile). So on successive distillation and condensation pure methanol will be collected as distillate in the collector and pure water remains in the distillation flask as residue and hence the solution (mixture) can be separated into its pure components by fractional distillation.

The student should understand that:

When you are asked to explain the behaviour of certain solution on distillation, you are required to give three important information which answer the following questions:

- Vapour formed is richer in what component?
- What distillate in the collector?
- What residue in the distillation flask?

BEHAVIOUR OF NON –IDEAL SOLUTION ON DISTILLATION

Unlike ideal solutions whose vapour composition is continuously changing on successive distillation and condensation until pure components are obtained; the vapour composition of non-ideal solution is not continuously changing (compared to its liquid composition) on successive distillation and condensation. Once the solution has attained **azeotropic composition**, the liquid and vapour composition become in equilibrium, thus making the boiling point of the solution (**azeotropic mixture**) to remain constant, hence non –ideal solution cannot be separated into its pure components by fractional distillation.

Definitions terms

Azeotropic mixture or **azeotrope** is the constant boiling point mixture whose vapour and liquid composition remains unchanged on distillation. The mixture is also known as **constant boiling point mixture**

Azeotropic composition is the proportion of components of the solution required to form the constant boiling point mixture whose composition does not change on distillation. That is azeotropic composition is the proportion (composition) of the solution components which are required for formation of azeotropic mixture of particular solution.

It is good to understand that:

- Azeotropic mixture of non–ideal solution with positive deviation, has minimum boiling of the solution, that is the boiling point of the solution is less than either of the two components (azeotropic mixture is the minimum point on the boiling point graph of non-ideal solution with positive deviation) and hence such azeotrope is known as **minimum boiling azeotrope**.
- Azeotropic mixture of non–ideal solution with negative deviation has maximum boiling point of the solution, that is the boiling point of the solution is greater than either of the pure component (azeotropic mixture is the maximum point on the boiling point graph of non-ideal solution with negative deviation) and hence such azeotrope is known as **maximum boiling azeotrope**.

Behaviour of non–ideal solution with positive deviation on distillation**General behaviour:**

Non ideal solution with positive deviation boils in such a way that **the vapour formed attains azeotropic composition**.

What is going to be collected as residue depends on the composition of the solution which is distilled and not in volatility of components of the solution like in ideal solution. But to insist the fact; the vapour formed must attain the azeotropic composition and **hence the distillate which is found in the collector must be azeotropic mixture**. (Regardless to volatility or solution composition).

To have better understanding of the concept consider ethanol-water system which forms non–ideal solution of positive deviation. Ethanol boils at 78°C while water boils at 100°C and their solution form azeotropic mixture when ethanol (alcohol) is 96% by moles.

What happen when the solution containing less than 96 %(e.g. 50%) of ethanol is distilled?

General behaviour for ethanol – water system is that; the solution boils in such a way that the vapour formed attains 96% of ethanol (azeotropic composition). To do this, more ethanol (which is more volatile) should vapourise and on successive distillation and condensation, azeotropic mixture will be found in collector as distillate and the pure water remains in the distillation flask as residue.

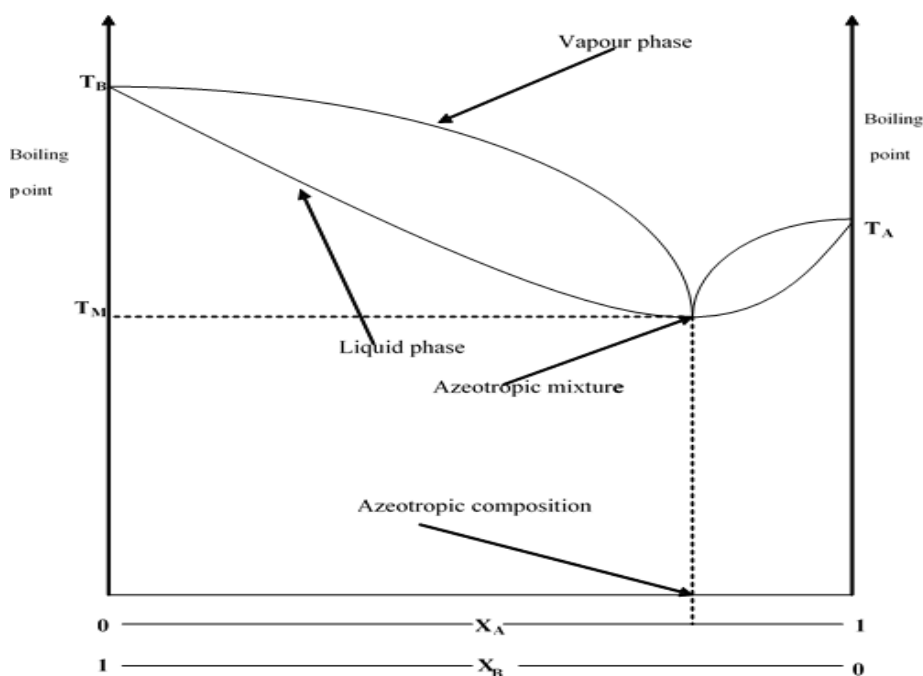
So we cannot get pure ethanol directly from fractional distillation. To get pure ethanol from the azeotropic mixture, a suitable dehydrating agent like calcium oxide, CaO , is introduced into the distillate so as to eliminate water which is only 4%

What happens when the solution containing greater than 96%(e.g. 98%) of ethanol is distilled?

In this case solution will boil in such a way that the vapour formed is richer in water (which is less volatile!) until ethanol in the collector is reduced to 96%. So successive distillation and condensation finally gives azeotropic mixture in collector as distillate and the residue in the distillation flask will be ethanol (which is more volatile!)

CONCLUSION

Non ideal solution with positive deviation cannot be separated into its pure components by fractional distillation. One pure component may be obtained in the distillation flask as residue (the substance obtained depends on composition of the solution) but the distillate in the flask must be azeotropic mixture.

Graph (i): To illustrate boiling point –composition relation of non-ideal solution with positive deviation

Where:

T_A is the boiling point of pure A

T_B is the boiling point of pure B

T_M is the boiling point of the azeotropic mixture (**azeotropic point**)

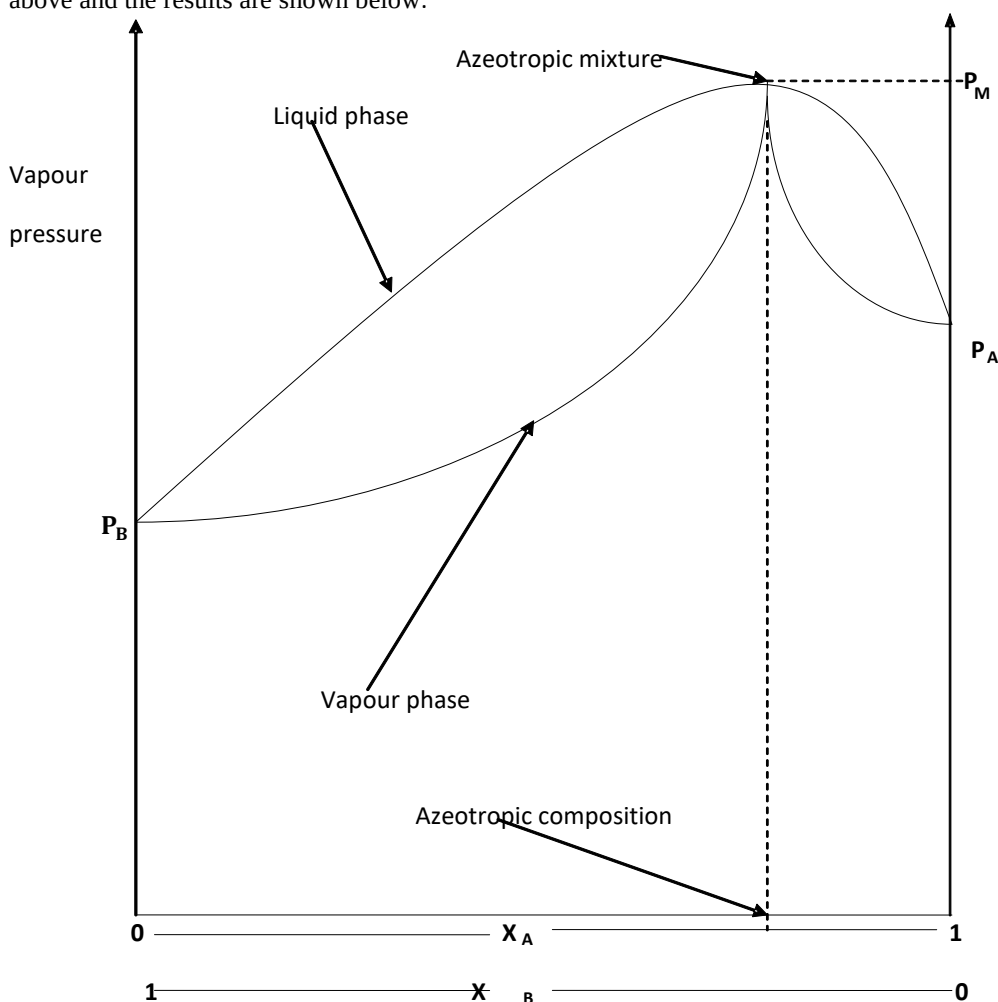
The boiling point of azeotropic mixture is known as **azeotropic point**.

Derivation of the graph of vapour pressure – composition relation for non-ideal solution with negative deviation from the corresponding graph of boiling point – composition to show behaviour of the solution in the distillation

As the vapour pressure of the solution varies inversely to its boiling point, the following points must be taken into consideration in deriving the graph:

- The vapour pressure of a component with greater boiling point must be smaller than that of another component and vice-versa.
- The curve to show liquid phase must be drawn above the curve which show vapour phase.
- The graph shows maxima and the azeotropic mixture is found at the maximum point of the graph.

Using above three facts, graph for vapour pressure – composition can be derived from **Graph(i)** above and the results are shown below:



Where:

P_A is the vapour pressure of pure A

P_B is the vapour pressure of pure B

P_M is the vapour pressure of azeotropic mixture

Example 13

A (Boiling point is 90°C) and B (Boiling point is 60°C) form the solution whose azeotropic mixture is obtained when A is 60% and the mixture boils at 55°C

- (i) Explain how solution which contains 40% of A will behave on distillation.
- (ii) Explain how the solution which contains 20% of B will behave on distillation.

Solution

- (i) The solution will boil in such a way that the vapour formed is richer in A until its percentage in the collector (vapour phase) is 60%. Finally, after successive distillation and condensation the filtrate in the collector will be azeotropic mixture which contains 60% of A and the residue in the distillation flask will be pure B.
- (ii) The solution will boil in such a way that the vapour formed is richer in B until its percentage in the vapour phase (collector) is 40% (so A is 60%). Finally after successive distillation and condensation the filtrate in the collector will be azeotropic mixture which contains 60% of A and the residue in the distillation flask will be pure A.

Remember three important information are required in answering these kinds of questions, and here are mentioned again!

- The vapour formed is richer in what component?
- What is the distillate in the collector?
- What is the residue in the distillation flask?

Behaviour of non – ideal solution with negative deviation on distillation**General behaviour:**

Non ideal solution with negative deviation boils in such a way that, **the residue which remains in the distillation flask attains azeotropic composition.**

Hence in non-ideal solution with negative deviation, **the residue must be azeotropic mixture** but the pure component which collected as filtrate depends on the composition of the solution and not on the volatility of the components of the solution. As in the positive deviation, non –ideal solution with negative deviation cannot be separated into its pure components by fractional distillation. The better understanding of the concept can be obtained in answering **example** below:

Example 14

Liquid A has boiling point of 90°C and B has boiling point of 60°C . When A and B are mixed together they form non- ideal solution whose azeotropic mixture is obtained when A is 60% and the mixture (azeotropic mixture) boils at 98°C . Explain how the solution will behave on distillation if the solution contain:

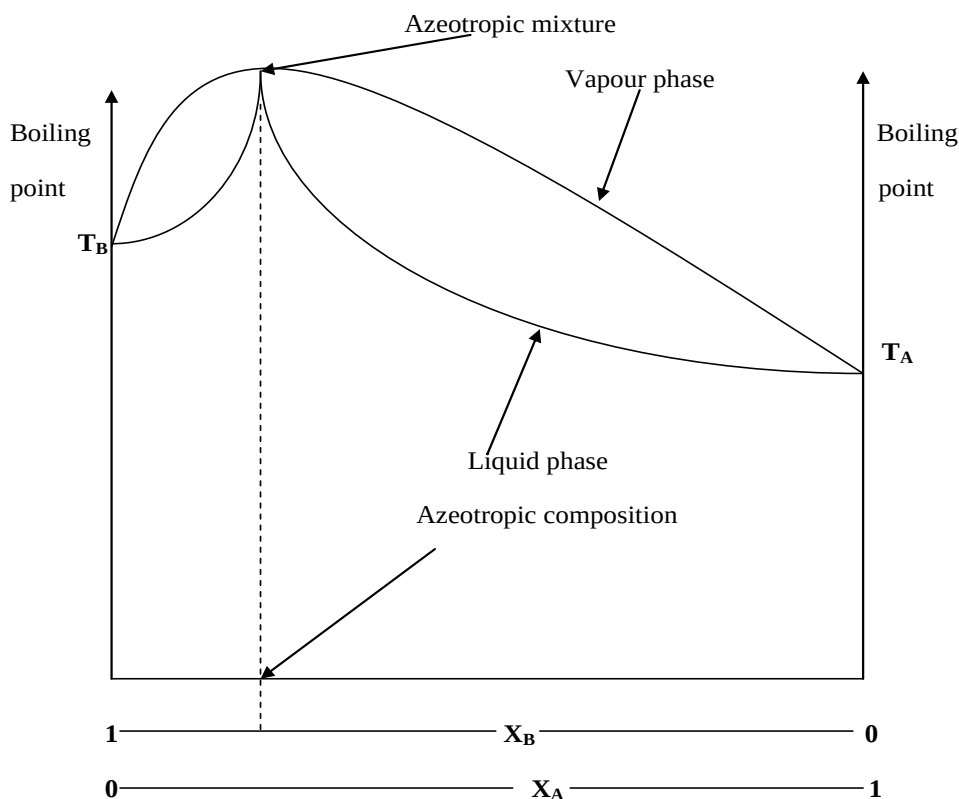
- (i) 40% of A
- (ii) 80% of A

Solution

Since the boiling point of the azeotropic mixture than of either of the two liquids, then the solution of A and B is the non-ideal solution with negative deviation. Thus:

- (i) The solution will boil in such a way that the vapour formed is richer in B until the percentage of A in the distillation flask reaches 60%. Finally, after successive distillation and condensation the filtrate in the collector will be pure B and the residue in the distillation flask will be azeotropic mixture which contain 60% of A.
- (ii) The solution will boil in such a way that the vapour formed is richer in A until its percentage in the distillation flask decreases to 60%. Finally, after successive distillation and condensation the filtrate in the collector will be pure A and the residue in the distillation flask will be azeotropic mixture which contain 60% of A.

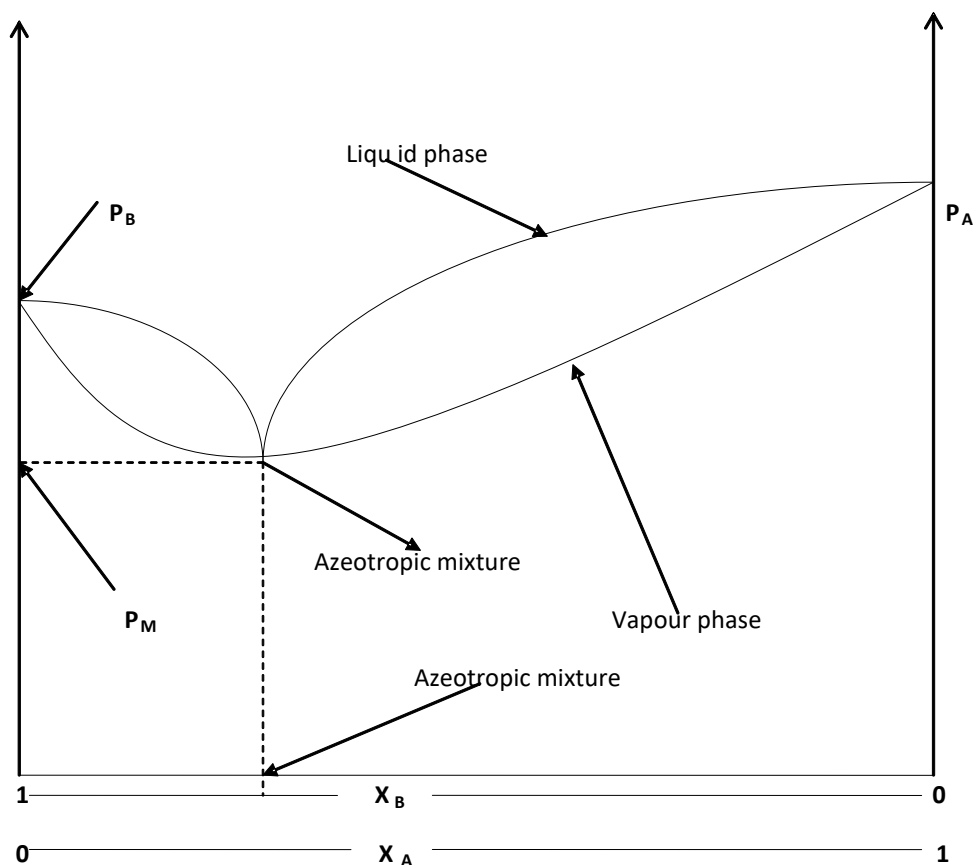
Graph(ii): To illustrate boiling point –composition relation of non ideal solution with negative deviation



Where

T_A and T_B are boiling points of pure A and B respectively.

The graph of vapour pressure – composition can be derived from above graph (**Graph (ii)**) as follows:



Where: P_A and P_B are vapour pressures of pure A and B respectively

P_M is the vapour pressure of azeotropic mixture

Table 6.1 Summary of differences between ideal and non-ideal solutions

IDEAL SOLUTIONS		NON – IDEAL SOLUTIONS			
		OF POSITIVE DEVIATION		OF NEGATIVE DEVIATION	
01	Obey Raoult's law at all concentrations	01	Do not obey Raoult's law	01	Do not obey Raoult's law
02	Neither heat is evolved nor absorbed during dissolution; $\Delta H_{\text{mix}} = 0$	02	Heat is absorbed during dissolution; $\Delta H_{\text{mix}} > 0$	02	Heat is evolved during dissolution; $\Delta H_{\text{mix}} < 0$
03	Total volume of solution is equal to the sum of individual volumes of components; $\Delta V_{\text{mix}} = 0$	03	Volume is increased after dissolution; $\Delta V_{\text{mix}} > 0$	03	Volume is decreased after dissolution; $\Delta V_{\text{mix}} < 0$
04	$P_{\text{soln}} = X_A P_A^0 + X_B P_B^0$	04	$P_{\text{soln}} > X_A P_A^0 + X_B P_B^0$	04	$P_{\text{soln}} < X_A P_A^0 + X_B P_B^0$
05	Intermolecular forces in pure liquid are equal to the intermolecular forces in the solution	05	Intermolecular forces in the solution are weaker than intermolecular forces of at least one of the pure component	05	Intermolecular forces in the solution are greater than all of pure components.

Methods of separating azeotropic mixture

As we have seen, components of azeotropic mixture cannot be separated by normal fractional distillation. It requires modified technique to achieve the separation. There are various methods which can be employed; but in this book we are going to discuss briefly three important methods which are azeotropic distillation, chemical method and molecular sieving. The choice of method and reagent to be used, depends on the composition of the azeotrope.

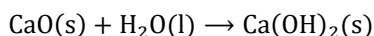
1. Azeotropic distillation

This is done by adding third component (volatile component) to the azeotrope so as to obtain new azeotrope with lower boiling point. For example, benzene may be added as third component in the ethanol-water azeotrope so as to get anhydrous alcohol (ethanol).

In our example, after adding benzene in ethanol-water azeotrope containing about 96% ethanol with boiling point of about 78°C, new ternary azeotrope (ethanol-water-benzene azeotrope) with boiling point of about 65°C (much lower than the original 78°C) is formed. On distillation, the new azeotrope is vapourised, leaving behind anhydrous alcohol.

2. Chemical method:

This involve adding another substance that reacts and remove one component. For example, calcium oxide (quicklime) or concentrated sulphuric acid can be used to eliminate water from water containing azeotrope. For sulphuric acid; it eliminates water due to its hygroscopic nature while calcium oxide; it eliminates water as per reaction:



3. Molecular sieving (adsorption)

Molecular sieves like activated charcoal and silica gel are generally used for adsorbing and eliminating unwanted substances (gas or liquid) with a very low concentration. They have small pores which allow to carry (adsorb) only small molecules like water leaving larger molecules like ethanol.

VAPOUR PRESSURE OF COMPLETELY IMMISCIBLE LIQUIDS MIXTURE

Unlike in liquid-liquid miscible solution where by the vapour pressure exerted by one component in the solution is affected by another component as the vapour pressure of the component is concentration dependent; in immiscible solution each component exerts pressure independently.

Thus if A and B are immiscible with their respective pressure of pure components of P_A^0 and P_B^0 . Then their respective partial pressures in the mixture (solution) remain unchanged.

That is partial pressures of A and B in the solution remains P_A^0 and P_B^0 respectively and hence according to Dalton's law of partial pressures: $P_{\text{soln}} = P_A^0 + P_B^0$

So it is clearly understood that the vapour pressure of immiscible solution is greater than either of the two components and hence its boiling point is less than either of the two. For example, the boiling point of bromobenzene, which is immiscible to water, is 156°C and that of pure water is 100°C, but a mixture of the two boil at 95°C (61°C below normal boiling point of bromobenzene!).

STEAM DISTILLATION

The fact, that a system of immiscible liquids starts boiling at temperatures less than the normal boiling points of both the liquids, has been applied in steam distillation. The steam distillation is a process of purifying organic liquids which have high boiling points and are immiscible with water.

By steam distillation means that the distillation is carried in a current of steam. A mixture of water and a high boiling (organic) liquid is heated by means of a current of steam. It is the steam that produces the required heat for the distillation.

Steam distillation is more preferred for temperature sensitive materials like natural aromatic compounds. Many organic compounds tend to decompose at high sustained temperature.

- Separation by normal distillation would then not be an option, so water or steam is introduced into the distillation apparatus (flask).
- The water vapour carries small amount of the vapourised compounds to the condensation flask, where the condensed liquid phase separated, and allowing easy collection.
- This process effectively allows for distillation at lower temperature, reducing the deterioration of the desired products.
- If the substances to be distilled are very sensitive to heat, steam distillation may be applied under reduced pressure, thereby reducing the operating temperature further.

To have better understanding of how steam distillation is carried out and its importance, consider hypothetical organic liquid **A** which is contaminated with some impurities, for example inorganic compounds. Also suppose the organic compound **A** has the following properties:

- Its boiling point is high, say 180°C
- Its decomposition temperature is lower than its boiling temperature, say 140°C
- It is immiscible water

Now suppose that our task is to separate the liquid **A** from inorganic compounds (impurities) so as to get pure **A**. We may think one of the following options.

First option: Normal distillation

If we employ this method, it will require 180°C (boiling temperature of **A**) for **A** to be distilled.

- However this temperature is above the decomposition temperature (140°C); so the decomposition of **A** into smaller molecules will occur in preference to its boiling.
- So in actual sense, the distillation of the mixture of **A** and impurities will end up with fragments which are formed after decomposition of liquid **A** and not pure liquid **A**.

Conclusion

This option is not successful because it ends up with decomposition products of **A** and not pure **A** as intended.

Second option: Steam distillation

This option solves the problem that occurred in the first option. It is the successful option which will end up with getting pure **A** as explained below.

Firstly, water is introduced into the distillation flask containing impure **A**

- Because the water – **A** mixture immiscible, each component of the mixture will exert its vapour pressure independently and therefore the vapour pressure of the mixture will be greater than either of the two components.

$$P_{\text{mixture}} = P_{\text{A}}^{\circ} + P_{\text{H}_2\text{O}}^{\circ}$$

- Since the vapour pressure of the mixture is greater than either of the pure component, the boiling point of the mixture will be lower than either of the two components. This is the general rule for behaviour of immiscible liquids in boiling, that: *Agitated mixture of immiscible liquids will boil at temperature lower than the boiling point of either of the pure liquids.*
- So the mixture will boil at temperature which is below the boiling temperature of the pure water (water has lower boiling point than **A**, so if the boiling temperature of the mixture is lower than both of the two components, it has to be below the boiling temperature of water). Numerically the boiling point of the mixture (at 1atm) will be less than 100°C, say 95°C, which is below the temperature needed to decompose **A**.

Then steam is blown through the mixture and the water and **A** turn to vapour.

- The **steam** can be generated by heating water in another container (flask).
- As the hot **steam** passes through the mixture it condenses, releasing heat. This heat will be enough to boil the mixture of water and **A** (at 95°C) provided that the volume of the mixture is not too

large (if the volume of the mixture is too large, it is suggested to heat the distillation flask as well to avoid having to use so much steam that large amount of steam will be condensed as well resulting to too large volume of liquid in the distillation flask).

The vapour formed after passing steam (or even heating) into the distillation flask is then condensed and collected.

- The collected vapour will consist of both **water** and **A**.
- Because they (water and A) are immiscible, they will form two layers which can be separated easily by separating funnel so as to get pure **A**.

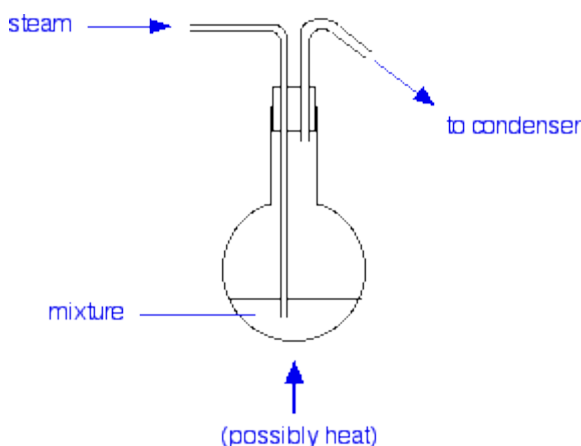


Figure 6.2 Simplified diagram for steam distillation apparatus

Generally, steam distillation is done in preference to ordinary distillation in the following cases:

- 1) For purification of an organic liquid when the impurities are difficult to be removed by other methods.
- 2) When the given impure is decomposed at high temperature and must, therefore, be distilled at a temperature lower than its boiling point.
- 3) In separating compounds from others not volatile in it.

Composition of distillate in the steam distillation

Up to this point, I have no doubt that you are familiar with Raoult's law. The law applies for ideal solutions only. That is the law applies for solution which contains totally miscible liquids like methanol and ethanol, benzene and toluene or hexane and heptane. In these solutions, the partial vapour pressure exerted by a particular constituent in the solution is concentration dependent, that is; it is affected by another constituent in the solution. And this is clearly explained by Raoult's law whereby the partial vapour pressure exerted by the constituent varies directly proportional to its mole fraction.

In **immiscible solution**, the liquids do not mix so that each constituent (liquid component) of the solution exerts pressure independently. So for immiscible solution which consist of two liquids, say A and B such that each liquid exerts vapour pressure of P_A and P_B respectively in the solution.

$$\text{Then } P_A V = n_A RT \dots\dots\dots (i)$$

$$\text{And } P_B V = n_B RT \dots\dots\dots (ii)$$

Then taking $\frac{(i)}{(ii)}$ gives

$$\frac{P_A}{P_B} = \frac{n_A}{n_B} \text{ (Unlike in miscible solution where by partial vapour pressure depend on mole fraction of the liquids)}$$

Hence for immiscible liquid solution: $\frac{P_A}{P_B} = \frac{n_A}{n_B}$

But $n_A = \frac{m_A}{M_A}$ and $n_B = \frac{m_B}{M_B}$

Thus from $\frac{P_A}{P_B} = \frac{n_A}{n_B}$, it follows that: $\frac{P_A}{P_B} = \frac{m_A M_B}{m_B M_A}$ or $\frac{m_A}{m_B} = \frac{P_A M_A}{P_B M_B}$

If the component B is water; then the last formula becomes: $\frac{m_A}{M_{H_2O}} = \frac{P_A M_A}{P_{H_2O} M_{H_2O}}$

The above final result provides the ratio of masses of the distillate (A and water) in the collector.

Conditions for steam distillation to be applicable

For purification by steam distillation, an impure compound must meet the following criteria:

1. Must be immiscible in water (so that it becomes possible to be separated from the distillate by using separating funnel).
2. Must be chemically non-reactive with water.
3. Should not decompose at the temperature of steam.
4. The impurities should be non-volatile
5. Should have relatively high molecular mass (so as to give a reasonable amount of distillate).
6. Should have a fairly high vapour pressure at temperature close to 100°C (so as to give reasonable amount of distillate).

The reader should understand that:

The last two conditions (5 and 6) can easily be deduced from the equation derived in the previous section by using the fact that: as the equation: $\frac{m_A}{m_{H_2O}} = \frac{P_A M_A}{P_{H_2O} M_{H_2O}}$ suggests; in order for the mass of A to be large in the distillate (**efficient steam distillation**), the product on numerator of right hand side of the equation must be large too so that m_A becomes large compared to m_{H_2O} . This requires P_A and M_A to be fairly large so that the product $P_A M_A$ becomes large compared to $P_{H_2O} M_{H_2O}$.

Industrial applications of steam distillation

Apart from non-industrial application like **determination of molar mass of non-volatile substances**, steam distillation procedures are used in various industrial activities as outlined below:

1. Extraction of essential oils

This is the main industrial application of steam distillation. Essential oils (were called essential because they were thought to represent the very essence of odour and flavour) like rose oil and garlic oil are produced by different methods of steam distillations either in a small scale or in the large scale (industrial level).

2. Separation of fatty acids from mixtures

Steam distillations used for purification of fatty acids and also for determination of a certain amount of fatty acids in a compound.

3. Checking quality of food materials

Steam distillations used in various industrial processes to check quality and impurity level in certain foods.

4. Juice analysis

Amount of volatile acids in certain juices and wines is estimated by using steam distillation.

5. Flavour extraction

A partial modification technique of steam-distillation has been used for the isolation of dairy flavour from dairy products.

Advantages and disadvantages of steam distillation

As we have seen in the previous section, the process of steam distillation is one of various methods that allows you to extract the essential oil from plants. This technique of oil extraction is the main method used in the fragrance and essential oil industry because it has the advantage of being the most efficient and cost-effective and it does not change chemical composition of the plant oils. However, the process requires some skill and investment in equipment. To assemble the facts together, below are advantages and disadvantages of steam distillation.

Advantages:

1. Thermal decomposition can be avoided (Because distillation occurs at a temperature below the boiling point of either that of the component or that of water).
2. There is no need for subsequent separation steps.
3. It used for distillation of organic compounds with very high boiling point like oils (therefore it is used in oil production in industrial scale).
4. It used to determine the relative molecular mass of a substance.
5. Requires less fuel for the steam boiler for extraction of oils.

Disadvantages:

1. It is not a complete separation method (since the distillate will be a mixture of water and the organic liquid, thus another method of separation is required such as a separating funnel).
2. The liquid mixture with small difference in boiling points cannot be separated (since both evaporate at the same temperature and are converted to vapour).

Example 15

Bromobenzene distills in steam at 95°C. The vapour pressure of bromobenzene and water at 95°C are $1.59 \times 10^4 \text{ Nm}^{-2}$ and $8.5 \times 10^4 \text{ Nm}^{-2}$ respectively. Calculate the percentage by mass of bromobenzene in distillate.

Solution

The molar mass of bromobenzene ($\text{C}_6\text{H}_5\text{Br}$) is 157g/mol.

Let mass percentage of bromobenzene be y

Then mass of water in 100g of the distillate will be $(100 - y)$

$$\text{So using: } \frac{m_b}{m_{\text{H}_2\text{O}}} = \frac{P_b M_b}{P_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}}}$$

$$\frac{y}{100-y} = \frac{1.59 \times 10^4 \times 157}{8.5 \times 10^4 \times 18} = 1.63$$

$$y = 163 - 1.63y \text{ or } 2.63y = 163; y = 62\%$$

Hence the percentage by mass of bromobenzene in distillate is 62%

Example 16

An aromatic compound Z was steam distilled at 98.6°C and one atmosphere pressure. The distillate was found to contain 25.5grams of water and 7.4 grams of aromatic compound Z. Given that the saturated vapour pressure of water at 98.6°C is 720mmHg. Calculate the relative molecular mass of the aromatic compound.

Solution

$$\text{Using: } \frac{m_Z}{m_{\text{H}_2\text{O}}} = \frac{P_Z M_Z}{P_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}}} \text{ or } M_Z = \frac{m_Z \times P_{\text{H}_2\text{O}} \times M_{\text{H}_2\text{O}}}{m_{\text{H}_2\text{O}} \times P_Z}$$

But 1 atmosphere = 760mmHg

And at boiling point; total vapour pressure of solution = atmospheric pressure

$$\text{Then } P_Z + P_{\text{H}_2\text{O}} = 760$$

$$\text{or } P_Z = 760 - P_{\text{H}_2\text{O}} = (760 - 720) \text{ mmHg} = 40 \text{ mmHg}$$

$$\text{Then } M_Z = \frac{7.4 \times 720 \times 18}{25.5 \times 40} \text{ g/mol} = 94 \text{ g/mol.}$$

Hence molecular weight of the aromatic compound is 94g/mol.

Example 17

Chlorobenzene which is soluble in water, steam distilled at 91°C under atmospheric pressure of 101300Pa. A sample of the steam distillate contains 23.7g of Chlorobenzene for every 10g of water. Calculate the vapour pressure of water and chlorobenzene.

Solution

$$\text{Using } \frac{m_c}{m_{\text{H}_2\text{O}}} = \frac{P_c M_c}{P_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}}}$$

$$\text{But } P_c + P_{\text{H}_2\text{O}} = 101300 \text{ Pa}$$

$$P_{\text{H}_2\text{O}} = 101300 - P_c$$

$$\text{Then } \frac{m_c}{m_{\text{H}_2\text{O}}} = \frac{P_c M_c}{(101300 - P_c) M_{\text{H}_2\text{O}}}$$

Molar mass of chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$) is 112.5g/mol

Molar mass of water (H_2O) is 18g/mol.

And it is given that:

$$\text{Mass of chlorobenzene } (m_c) = 23.7 \text{ g}$$

$$\text{Mass of water } (m_{\text{H}_2\text{O}}) = 10 \text{ g}$$

$$\text{Then } \frac{23.7}{10} = \frac{112.5 P_c}{18(101300 - P_c)}$$

$$2.37 = \frac{6.25 P_c}{(101300 - P_c)}$$

$$240081 - 2.37 P_c = 6.25 P_c$$

$$P_c = 27851.6 \text{ Pa and } P_{\text{H}_2\text{O}} = (101300 - 27851.6) \text{ Pa} = 73448.4 \text{ Pa.}$$

Hence the vapour pressure of water is 73448.4Pa

And the vapour pressure of chlorobenzene is 27851.6Pa

Example 18

When chlorobenzene is steam distilled at 100kPa, the boiling point of the mixture is 91°C. At this temperature, the vapour pressure of chlorobenzene is 29kPa. What is the mass of the distillate that contains 100g of chlorobenzene?

Solution

$$\text{Using } \frac{m_w}{m_c} = \frac{P_w M_w}{P_c M_c}$$

$$\text{Where } P_w = 100 - P_c = (100 - 29) \text{ kPa} = 71 \text{ kPa}$$

$$\text{Substituting } \frac{m_w}{100 \text{ g}} = \frac{71 \text{ kPa} \times 18 \text{ g mol}^{-1}}{29 \text{ kPa} \times 112.5 \text{ g mol}^{-1}}$$

$$\text{From which } m_w = 39.17 \text{ g}$$

$$\text{Mass of distillate} = m_w + m_c = (39.17 + 100) \text{ g} = 139.17 \text{ g}$$

DIGGING DEEPER EXERCISE 6

EXERCISE 6A: BINDER QUESTIONS

Question 1

What is boiling point of liquid? How it is affected by external pressure?

Question 2

- (a) What is the vapour pressure?
- (b) Why vapour pressure of liquid is also known as saturated vapour pressure?
- (c) How does the vapour pressure vary with temperature?

Question 3

When liquid A is mixed with liquid B to form a solution at room temperature, the solution becomes warm to the touch. Does this suggest a positive or negative deviation from Raoult's law? Explain.

Question 4

Why in constructing boiling temperature of the solution against composition curve, liquid phase curve lies below the vapour phase curve while in the vapour pressure of solution against composition curve, the vapour phase curve lies below the liquid phase curve.

Question 5

In a binary solutions obeying Raoult's law, can the liquid and the vapour phases have the same composition? Explain.

Question 6

- (i) What are immiscible liquids.
- (ii) Outline two important characteristics of immiscible liquid system.

Question 7

For each system, compare the intermolecular interactions in the pure liquids with those in the solution to decide whether the solution will be approximately ideal solution, non-ideal solution with positive deviation or non-ideal solution with negative deviation:

- (i) cyclohexane and ethanol
- (ii) methanol and acetone
- (iii) n-hexane and isooctane

Question 8

For each of the following liquid mixture; classify the mixture as ideal solution, non-ideal solution with positive deviation or non-ideal solution with negative deviation:

- (i) Benzene and n-hexane
- (ii) Trichloromethane and acetone
- (iii) Ethylene glycol and carbon tetrachloride
- (iv) Acetic acid and propanol

Question 9

List down at least three differences between fractional distillation and steam distillation.

Question 10

Components of azeotropic mixture cannot be separated by simple distillation. However, there are other ways which can be employed to separate the mixture. Suggest any three methods that can be used to separate azeotropic mixture.

Question 11

When two volatile liquids are mixed to form solution, the heat change for the process may be either be zero, positive or negative. Explain clearly each of the three scenarios.

Question 12

Explain the behaviour of ideal solution on fractional distillation.

Question 13

Explain why the concept of ideal solution is just ideal.

Question 14

Why is an increase in temperature observed on mixing chloroform and acetone?

Question 15

Predict the deviation from Raoult's law when two liquids are mixed and the heat of the solution is small. Give an explanation to support your prediction.

Question 16

Why are deviations from the ideal behaviour predicted by Raoult's law more common for solutions of liquids than are deviations from the ideal behaviour predicted by the ideal gas law for solutions of gases?

Question 17

A mixture of chlorobenzene and bromobenzene forms nearly ideal solution but a mixture of chloroform and acetone does not. Why?

Question 18

Why all gas-gas solutions are considered to be ideal?

Question 19

A 'solution' is made by dissolving ice in water. Is the solution ideal or non-ideal? Explain.

Question 20

At 20°C, the vapour pressure of toluene is 0.0289atm and the vapour pressure of benzene is 0.0987atm. Equal chemical amounts of toluene and benzene are mixed and form an ideal solution. Calculate the mole fraction of benzene and toluene in the vapour in equilibrium with this solution.

Question 21

100g of liquid A(molar mass 140g/mol) was dissolved in 100g of liquid B (molar mass 180g/mol).The vapour pressure of pure liquid B was found to be 500torr.Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475torr.

Question 22

Two liquids, A and B, form an ideal solution. The solution boils at 22°C and 0.255atm. The vapour pressure of pure A is 0.192atm at 22°C and the vapour pressure of B is 0.311 atm, also at 22 °C. Determine the mole fraction of each solution component.

EXERCISE 6B: REAL QUESTIONS

Question 23

Volatile hydrocarbons are not used in the brakes of automobile as lubricants, but non-volatile hydrocarbons are used as lubricants. Explain.

Question 24

Is steam distillation used to isolate limonene from lemon? Explain.

Question 25

Compared to other methods, steam distillation is said to be cheap. Give two reasons to support this statement.

Question 26

Mention any three real life examples of substances which can be separated by steam distillation.

Question 27

Steam distillation is used commercially to separate important organic compounds like fatty acids. In the separation of the fatty acid, the steam distillation is usually undertaken under reduced pressure; explain why.

Question 28

Which type of deviation is shown by the solution formed by mixing kerosene oil and alcohol? Explain.

Question 29

According to Boyle's; if the volume of container is doubled then the pressure exerted by a gas will be halved, provided that temperature and the amount of the gas remains constant. Now you're shifting 1L of water kept in 10L bucket into 20L bucket at the same temperature, will vapour pressure halve? Explain.

Question 30

In the water-ethanol azeotropic mixture calcium oxide and not concentrated sulphuric acid is used as dehydrating agent to remove water from the mixture while in the nitric acid-water azeotrope, the acid is preferred to the oxide. Explain.

Question 31

Liquid ammonia bottles are cooled in ice before opening the seal. Explain.

Question 32

Mr. Akilikubwa, the laboratory technician, performed an experiment for determining boiling point of ethoxyethane, $(C_2H_5O)_2O$, trichloromethane, $CHCl_3$, and their mixture. He observed the boiling point of ethoxyethane-trichloromethane mixture is higher than of either ethoxyethane or trichloromethane. Explain this observation in terms of the intermolecular forces present in the pure liquids and in the mixture.

Question 33

You are given with the following: 50 mL of liquid labelled **X** which has boiling point of $83^\circ C$ and 50 mL of water and you are instructed to mix the two liquids. You found that the mixture is miscible with volume of 95 mL.

- What will happen to the boiling point of the mixture? Explain.
- What is the possible identity of liquid **X**?

Question 34

Your great friend **Kipute** argued to you that; *"Without a doubt, I'm sure you know that, one of important characteristics of compounds is that compounds have fixed composition, aren't you?"* She paused a little bit, hands on her waist, then she continued; *"Now, azeotrope has fixed composition like compounds. However, the azeotrope is usually regarded as a mixture and not as a compound. I can't make sense, how this comes?!"* What could be your response?

Question 35

The vapour pressure of pure benzene is 750 torr and the vapour pressure of toluene is 300 torr at a certain temperature. You make a solution by pouring "some" benzene with "some" toluene. You then place this solution in a closed container and wait for the vapor to come into equilibrium with the solution. Next, you condense the vapour. You put this liquid (the condensed vapour) in a closed container and wait for the vapour to come into equilibrium with the solution. You then condense this vapour and find the mole fraction of benzene in this vapour to be 0.714. Determine the mole fraction of benzene in the original solution assuming the solution behaves ideally.

EXERCISE 6C: HOT QUESTIONS**Question 36**

Azeotropes can be said to be similar to compounds. Justify.

Question 37

Fractional distillation of a particular liquid binary mixture leaves behind a liquid consisting of both components in which the composition does not change as the liquid is boiled off. Is this behaviour characteristic of a maximum or a minimum boiling point azeotrope? Explain.

Question 38

Components of binary mixture of two liquids **A** and **B** were being separated by distillation. After sometime, separation of components stopped and composition of vapour phase became same as that of liquid phase. Both components start coming in the distillate. Explain why this happened.

Question 39

At 20°C, the vapour pressure of toluene is 0.0289atm and the vapour pressure of benzene is 0.0987atm. Equal chemical amounts (equal number of moles) of toluene and benzene are mixed and form an ideal solution. Calculate the mole fraction of benzene and toluene in the vapour in equilibrium with this solution

Question 40

Calculate the boiling point (at 1atm) of a solution containing 116g of acetone (Mwt=58) and 72g of water (Mwt = 18) by using data in the following table.

Table 6.2 Vapour pressure of acetone and water

Temperature (°C)	Vapour pressure (atm) acetone	Vapour pressure (atm) water
60	1.14	0.198
70	1.58	0.312
80	2.12	0.456
90	2.81	0.694

Question 41

Benzene and toluene form a nearly ideal solution. At 80°C, the vapour pressure of pure benzene (Mwt = 78.1) is 753torr and that of toluene (Mwt = 92.1) is 290torr. The following questions refer to a solution that contains equal weights of the two liquids

- Calculate the partial pressure of each component that would be in equilibrium with the solution at 80°C
- At what atmospheric pressure will this solution boil at 80°C?
- What will be the composition of the liquid that condenses when this vapour is cooled?

Question 42

Benzene and toluene are both mainly non-polar compounds. If instead of toluene, an equivalent chemical amount of a polar compound like benzoic acid were dissolved in benzene, how would you expect the partial pressure of benzene above the solution to deviate from the partial pressure of benzene above an ideal solution (if at all)? Explain

Question 43

What role does the molecular interaction play in a boiling point of a solution of alcohol and water?

Question 44

Ethyl benzoate is liquid with a boiling point of 213°C. It is virtually insoluble in water

- The vapour pressures of water and ethyl benzoate at 50°C are

Ethylbenzoate	0.2kPa
Water	12.25kPa

- What would be the total vapour pressure of an equimolar mixture of the two liquids at 50°C?
- What would be the effect on the total vapour pressure if you increased the proportion of water so that there were 3 moles of water to 1 mole of ethylbenzoate?
- The vapour pressures of water and ethyl benzoate at 99°C are:

Ethyl benzoate 2.34kPa
Water 97.76kPa

What can you say about the boiling of the mixture at atmosphere pressure (101.325kpa)?

Question 45

Bromobenzene (Molecular mass: 157g/mol) steam distills at 95 °C. Its vapour pressure at 95 °C is 120mmHg.

- (i) What is the vapour pressure of water at 95 °C in atm?
- (ii) How many grams of bromobenzene would steam distill with 20.0 grams of water?

Question 46

30.0mL of pentane (density = 0.626g/mL, vapour pressure = 511torr) and 45.0mL of hexane (density = 0.655g/mL, vapour pressure = 150torr) are mixed at 25.0 °C to form an ideal solution.

- (i) Calculate the vapour pressure of this solution.
- (ii) Calculate the composition (in mole fractions) of the vapour in contact with this solution.

Question 47

Butanone ($\text{CH}_3\text{CH}_2\text{COCH}_3$) has a vapour pressure of 100torr at 25°C. At the same temperature, propanone (CH_3COCH_3) has a vapour pressure of 222torr. What mass of propanone must be mixed with 190g of butanone to give a solution with a vapour pressure of 135torr at 25°C?

Question 48

At 333 K, substance A has a vapour pressure of 1atm and substance B has a vapour pressure of 0.2atm. A solution of A and B is prepared and allowed to equilibrate with its vapour. The vapour is found to have equal moles of A and B. What was the mole fraction of A in the original solution?

Question 49

20.772g of a volatile solute is dissolved in 495g of water to form an ideal solution. This solute does not react with water nor dissociate in solution. The pure solute displays, at 60 °C, a vapour pressure of 14.94torr. At 60 °C the vapor pressure of this solution is determined to be 147.34 torr. Calculate the molar mass of this volatile solute. (The vapor pressure of water at 60 °C is 149.4torr.)

Question 50

Compound A and benzene are miscible. At 60 °C, compound A has a vapour pressure of 96mmHg. Benzene has a vapor pressure of 395mmHg at 60 °C. A 50:50 mixture by mass of benzene and A has a vapour pressure of 281 mmHg. Calculate the molar mass of A?

Question 51

The vapour pressure above a solution of two volatile miscible components is 745torr and the mole fraction of component B in the vapor is 0.59. Calculate the mole fraction of B in the liquid if the vapour pressure of pure B is 637torr.

Chapter 7

COLLIGATIVE PROPERTIES

INTRODUCTION

Many solution properties depend on the nature (the chemical identity) of the solute. For example; $0.1\text{M}\text{H}_2\text{SO}_4$ is acidic while $0.1\text{M}\text{KOH}$ is basic or $0.1\text{M}\text{HCl}$ is more acidic than $0.1\text{M}\text{CH}_3\text{COOH}$. Also solution of table salt conducts electricity while that of table sugar does not. Properties like electrolytic conductivity, surface tension, viscosity, density and many more, are all properties of solution which depend on chemical identity of the solute. However, there are a few solution properties that depend only upon the amount of solute species, regardless of their identities. These properties include the vapour pressure, the freezing point, the boiling point and the osmotic pressure. These properties are changed as the amount of solute in given amount of the solvent is changed and they actually change altogether at the same time (adding solute in the solvent change all of the mentioned properties). Because they tied together in this way, they are referred to as the **colligative properties**. (The Latin 'co ligare' means **to bind together** is the source of the German 'kolligative' which resulted to the 'colligative').

Colligative properties are properties of solution which depend on relative amount of solute and solvent and not on the nature of the solute.

Colligative properties are observed when **non-volatile solutes** are dissolved in **very dilute solution**, why? (The bolded words are conditions for colligative properties to be observed).

When the solution is made very dilute, the solution behaviour become very close to **ideal behaviour** i.e. the solution become **ideal** thus making possible for the solution to obey Raoult's law as the law holds for ideal solution only. This is due to the fact that, the solute being non-volatile while the solvent is volatile liquid, the two differ much on strength of their intermolecular forces. The only way to make the solution ideal despite the large difference in their intermolecular forces is by making the solution very dilute.

Also the solute must be non-volatile so that it does not form vapour; that is, its partial vapour pressure at boiling point of the solution is zero.

Four important colligative properties to be studied in this chapter are:

- Lowering of vapour pressure
- Boiling point elevation
- Freezing point depression
- Osmotic pressure

Understanding the amount of solute present in the solution

As we have seen, colligative properties depend merely upon the amount of solute present in the solution. So if our task is to find what exactly resides deep inside colligative properties, then comprehensive understanding of the amount of the solute is crucial tool which we must acquire for digging colligative properties deeper! To acquire this pick-axe, we need to have detailed answers to the following questions:

- 1) What is the amount of solute?
- 2) How is the amount of solute in the solution related to the amount of the substance dissolved?
- 3) What factors are considered in comparing the amount of solute in the solution?

We are going to answer those three questions, one after another so as to get our pick-axe for digging deeper colligative properties in our hand!

What is the amount of solute?

The amount of solute reflects the number of solute particles. It is expressed as the number of moles of solute particles (of course per given amount of solvent or solution).

- This can be in terms of mole fraction (in vapour pressure lowering), molality (in boiling point elevation and freezing point depression) or molar concentration (in osmotic pressure).

Thus in dealing with the amount of solute, the amount must be in moles. So in colligative properties perspective, whenever the amount of solute is mentioned, the implication is the number of moles of solute particles.

How is the amount of solute in the solution related to the amount of substance dissolved?

Firstly, let us ensure that we have common understanding on the key terms in the above question.

In this context:

Amount of substance dissolved: This is the amount of substance taken in mixing with solvent.

- It reflects the amount of solute before making the solution.

Amount of solute in the solution: This is the actual amount of solute present in the solution.

- It reflects the amount of solute after making the solution. And this is the amount which accounts for observed colligative properties (not the former).

Now, there is a sub-question here; *is the amount of substance dissolved necessary equal to the amount in the solution?*

The answer is no! The amount of solute before making the solution is **not** necessary equal to the amount of solute after making the solution.

- In case of soluble covalent compounds (most of organic compounds), the situation is simple; the two amounts are always equal. But in case of inorganic compounds and slightly soluble substances (or insoluble substances) the situation is tricky!

To have better understanding of this, consider the following three scenarios:

First scenario: Glucose is dissolved in aqueous solution.

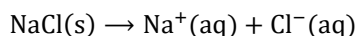
Glucose is the covalent soluble substance. So when certain amount of glucose is dissolved in the solution, the amount of solute in the solution will remain the same.

- Thus 0.1mol of glucose dissolved in 1L of the solution will give colligative properties which correspond to 0.1mol of solute in 1L of the solution as well. This is simple, nothing's strange!

Second scenario: Sodium chloride is dissolved in aqueous solution.

Here the trick comes! Sodium chloride is highly soluble ionic compound. It dissolves in water, and during the dissolution process, it ionises to give its constituent ions.

- Thus, if 0.1mol of NaCl is dissolved in 1L of the solution, it will give 0.2mol of solute (assuming complete ionisation) as per equation



Before making the solution 0.1mol 0 0

After making the solution 0 0.1mol 0.1mol

Total amount of solute after making the solution = (0.1 + 0.1)mol = 0.2mol

Hence, if 0.1mol of NaCl is dissolved in 1L of the solution, it will give colligative properties which correspond to 0.2mol of solute in 1L of the solution.

- In this case, although the concentration of NaCl will be noted as 0.1M; but in reality the effective concentration will be 0.2M and this effective concentration is the one that accounts for colligative properties.

Third scenario: Iodine is dissolved in aqueous solution.

Here iodine is covalent molecule with very low solubility in water. Let us have hypothetical situation whereby 0.1mol of iodine is dissolved in 1L of solution in which only 0.02mol of it actually dissolves, leaving 0.08mol of it undissolved.

- Thus, in this scenario, although 0.1mol of iodine was dissolved in the solution, the observed colligative properties will correspond to 0.02mol of solute in 1L of the solution.

To conclude.....!

Colligative properties are determined by dissolved amount of solute present in the solution which is not necessary equal to the amount of the substance dissolved.

What factors are considered in comparing the amount of solute in the solution?

To do the comparison of amount of colligative properties, we must be able to compare amounts of solute in the solution whereby greater amount of the solute means greater colligative properties. To understand this, it is important to study three factors associated with it.

1. Concentration

For similar compounds, larger concentration means greater amount of the solute in the solution which in turn means greater colligative properties. For example:

- 0.2M Glucose has greater amount of solute in the solution than 0.1M Urea.
- 0.2M NaCl has greater amount of solute in the solution than 0.1M KCl.

2. Number of ions per formula unit

For salts (ionic compounds), larger number of ions per formula unit means more solute particles are formed after dissolving it in the solution and hence greater amount of solute in the solution (which in turn means higher colligative properties). For example:

- 0.1M $\text{Ca}(\text{NO}_3)_2$ has greater amount of solute in the solution than 0.1M NaNO_3 because the former has three ions per formula unit while the latter has two ions per formula unit.
- 0.1M $\text{Ca}(\text{NO}_3)_2$ has greater amount of solute in the solution than 0.2M Glucose though the latter has greater concentration because the former having three ions per formula unit has effective concentration of $0.1\text{M} \times 3 = 0.3\text{M}$ while the latter being covalent its effective concentration remains to be 0.2M.

3. Ability of a compound to undergo ionisation in the solution.

Salts which are more ionic, have greater ability of ionising in the solution to give greater amount of solute in the solution. For example; 0.1M KCl has greater amount of solute in the solution than 0.1M LiCl because the former being more ionic (KCl has smaller degree of polarisation), its ionisation is closer to completion than the latter.

Understand this!

Salts with higher degree of polarisation (salts with smaller sized and higher charged cations) have lower ability to undergo ionisation in the solution due to the following reasons:

- 1) Their cations firmly hold their anions (smaller sized and higher charged cations have stronger attraction to anions) making difficult for their ionic bonds to break (therefore decreasing the chance of forming ions in the solution).

- 2) Even after forming ions by difficulty, the ions (cations and anions) tend to recombine by the same reason of strong attraction between them and the phenomenon is known as **ion pairing** (this ion pairing makes chance of forming ions in the solution even narrower).

That is all about our tool! After getting our pick-axe, now it is the time of digging our colligative properties, one after another!

LOWERING OF VAPOUR PRESURE

The colligative properties really depend on the escaping tendency of solvent molecules from the liquid phase. When non-volatile solute is dissolved in a certain solvent, there is decrease (lowering) in vapour pressure of the solvent in the solution due to the following reasons:

- Concentration of solvent is lowered.
- Reduction of the chance of solvent molecules to escape into the air (as some surface of the solvent is covered by non-volatile solute).

Consider a non-volatile solute is dissolved in a liquid solvent to form very dilute solution:

By Raoult's law: $P_{sv} = X_{sv}P_{sv}^0$ (We are applying Raoult's law because the solution is very dilute)

and $P_{su} = X_{su}P_{su}^0$

Where:

P_{sv} and P_{su} are partial vapour pressures exerted in solution by solvent and non-volatile solute respectively.

P_{sv}^0 and P_{su}^0 are vapour pressures of pure solvent and pure non-volatile solute respectively.

X_{sv} and X_{su} are mole fractions in the solution for solvent and non-volatile solute respectively.

By combining Raoult's law and Dalton's law of partial pressures: $P_{soln} = X_{sv}P_{sv}^0 + X_{su}P_{su}^0$

But for non-volatile solute, $P_{su}^0 = 0$ (We are using this condition because the solute is non-volatile).

Then $P_{soln} = X_{sv}P_{sv}^0$

But $X_{sv} = 1 - X_{su}$ ($X_{sv} + X_{su} = 1$)

The $P_{soln} = (1 - X_{su})P_{sv}^0$ or $P_{soln} = P_{sv}^0 - X_{su}P_{sv}^0$ Or $X_{su}P_{sv}^0 = P_{sv}^0 - P_{soln}$

But $P_{sv}^0 - P_{soln} =$ Lowering in the vapour pressure of the solvent, ΔP

It follows that: $\Delta P = X_{su}P_{sv}^0$

But P_{sv}^0 is constant at given temperature

Hence $\Delta P \propto X_{su}$

The final result is another form of Raoult's law which is known as **Raoult's law of lowering in vapour pressure** which states that:

When a non-volatile solute is dissolved in the solvent at given temperature, the lowering of the vapour pressures of the solvent in the solution varies directly proportional to the mole fraction of the solute.

Also from: $\Delta P = X_{su}P_{sv}^0$ or $X_{su} = \frac{\Delta P}{P_{sv}^0}$

Where $\frac{\Delta P}{P_{sv}^0}$ is the relative lowering in vapour pressure and the result is known as **Raoult's law of relative lowering in vapour pressure** which states that:

When a non-volatile solute is dissolved in a solvent at given temperature, the relative lowering of vapour pressure of solvent in the solution is equal to the mole fraction of the solute.

Very important to understand that:

The last two forms of Raoult's law (Raoult's law of lowering in vapour pressure and Raoult's law of relative lowering in vapour pressure) are derived from more general form of Raoult's law which is the **Raoult's law of (partial) vapour pressure**. So when you are asked to state just 'Raoult's law' you **must** state the **Raoult's law of vapour pressure** discussed in the previous chapter (**chapter 6**).

Calculations of molar mass of a solute from Raoult's law of relative lowering in vapour pressure

From Raoult's law of relative lowering in vapour pressure; $X_{su} = \frac{\Delta P}{P_{sv}^0}$, but $X_{su} = \frac{n_{su}}{n_{su} + n_{sv}}$

For very dilute solution (**The lowering in vapour pressure is colligative property which holds for dilute solutions only i.e. for ideal solution only which is the condition for Raoult's law to be true**): $n_{sv} \gg n_{su}$

Such that: $n_{sv} + n_{su} \approx n_{sv}$

And it becomes: $X_{su} = \frac{n_{su}}{n_{sv}}$

Thus from: $X_{su} = \frac{\Delta P}{P_{sv}^0}$

It follows that: $\frac{n_{su}}{n_{sv}} = \frac{\Delta P}{P_{sv}^0}$

But $n_{su} = \frac{m_{su}}{M_{su}}$ and $n_{sv} = \frac{m_{sv}}{M_{sv}}$

Then $\frac{n_{su}}{n_{sv}} = \frac{m_{su}M_{sv}}{m_{sv}M_{su}} = \frac{\Delta P}{P_{sv}^0}$

Hence: $M_{su} = \frac{m_{su} \times M_{sv} \times P_{sv}^0}{m_{sv} \times \Delta P}$

Where: m_{su} and m_{sv} are masses of non- volatile solute and solvent respectively

M_{sv} is the molar mass of the solvent

P_{sv}^0 is the vapour pressure of pure solvent

ΔP is the lowering in vapour pressure of solvent in the solution i.e. $\Delta P = P_{sv}^0 - P_{soln}$

Example 1

The vapour pressure of 1% urea solution at 38°C is 49.85 mmHg. If the vapour pressure of pure water is 50 mmHg and 250 mmHg at 38°C and 72°C respectively. Calculate the vapour pressure of 1% urea at 72°C.

Solution

Mass of urea in 100g of its solution is 1g (1% urea)

So mass of water in 100g of the solution = $(100 - 1)g = 99g$

Molar mass of water is 18g/mol.

At 38°C $P_{soln} = 49.85 \text{ mmHg}$

$$P_{sv}^0 = 50 \text{ mmHg}$$

So $\Delta P = P_{sv}^0 - P_{soln} = (50 - 49.85) \text{ mmHg} = 0.15 \text{ mmHg}$

Using: $M_{su} = \frac{m_{su} \times M_{sv} \times P_{sv}^0}{m_{sv} \times \Delta P}$

$$M_{su} = \frac{1 \times 18 \times 50}{99 \times 0.15} \text{ g/mol} = 60.6 \text{ g/mol}$$

Hence molar mass of urea is 60.6g/mol

At 72°C; $P_{sv}^0 = 250\text{mmHg}$

Then: $60.6 = \frac{1 \times 18 \times 250}{99 \times \Delta P}$

But $\Delta P = P_{sv}^0 - P_{soln}$

Or $P_{soln} = P_{sv}^0 - \Delta P = (250 - 0.75)\text{mmHg} = 249.25\text{mmHg}$

Therefore, the vapour pressure of 1% urea at 72°C is 249.25mmHg.

Alternative solution

Using: $\frac{\Delta P}{P_{sv}^0} = X_{urea}$

At 38°C: $P_{sv}^0 = 50\text{mmHg}$, $P_{soln} = 49.85\text{mmHg}$

So $\Delta P = P_{sv}^0 - P_{soln} = (50 - 49.85)\text{mmHg} = 0.15\text{mmHg}$

Then $X_{urea} = \frac{0.15}{50} = 0.003$

At 72°C: $\Delta P = P_{sv}^0 X_{urea}$

Where $P_{sv}^0 = 250\text{mmHg}$

Then $\Delta P = 250 \times 0.003\text{mmHg} = 0.75\text{mmHg}$

Using $P_{soln} = P_{sv}^0 - \Delta P = (250 - 0.75)\text{mmHg} = 249.25\text{mmHg}$

Hence the vapour pressure of 1% urea at 72°C is 249.25mmHg

Example 2

Arrange the following solution in order of increasing in their vapour pressure. Comment on you answer

A: 0.001M $\text{CO}(\text{NH}_2)_2$

B: 0.001M AgCl

C: 0.001M BeCl_2

D: 0.001M AlCl_3

Solution

$$D < C < B < A$$

→
Increase in vapour pressure

Comment:

Vapour pressures of given solution are lower than that of pure water and the lowering varies directly proportional to the number of particle (concentration) of solute formed after ionisation (number of ions per formula unit). The number decrease in order of D, C, B and finally A which does not ionise at all and hence the vapour pressures of solution follow the reverse order.

Example 3

- Compare effect of calcium carbonate and sodium carbonate on vapour pressure of water.
- 1mol of a non-volatile, non-dissociating substance is dissolved in 3mol of solvent. Calculate the ratio of vapour pressure of the solution to that of the pure solvent at the same temperature.

Solution

- Calcium carbonate being insoluble in water does not interact with water molecules so its effect on vapour pressure of water is negligible while sodium carbonate being water soluble interacts with water and therefore decreasing vapour pressure of water.

- Using: $\frac{\Delta P}{P_{sv}^0} = X_{su}$

Where $\Delta P = P_{sv}^o - P_{soln}$

$$\text{And } X_{su} = \frac{n_{su}}{n_{su} + n_{sv}} = \frac{1 \text{ mol}}{(1+3) \text{ mol}} = \frac{1}{4}$$

$$\text{Then } \frac{P_{sv}^o - P_{soln}}{P_{sv}^o} = \frac{1}{4}$$

$$4P_{sv}^o - 4P_{soln} = P_{sv}^o$$

$$\text{From which; } 3P_{sv}^o = 4P_{soln} \text{ or } \frac{3}{4} = \frac{P_{soln}}{P_{sv}^o}$$

Hence the ratio of vapour pressure of the solution to that of the pure solvent is $\frac{3}{4}$.

BOILING POINT ELEVATION AND FREEZING POINT DEPRESSION

Boiling point elevation

Boiling point of a substance is the temperature at which the vapour pressure of the substance is equal to atmospheric pressure.

Always boiling point of solution which contains non-volatile solute is greater than that of the pure solvent due to the lowering in vapour pressure of the solvent in the solution after introduction of the solute.

Experimentally it has been found that the boiling point elevation (increase in boiling point) varies directly proportional to concentration (molality of the solute).

That is: $\Delta T \propto m$

Introducing constant of proportionality, K_b .

$$\text{Then: } \Delta T = K_b m$$

Where: ΔT is the boiling point elevation in $^{\circ}\text{C}$ or K .

m is the molality of the solution in mol/kg

K_b is the boiling point elevation constant (molal elevation constant) in $^{\circ}\text{C kg mol}^{-1}$ or K kg mol^{-1}

The constant is also known as **ebullioscopic constant**

Definition of Ebullioscopic constant (molal elevation constant), K_b

This is the boiling point elevation of the solvent in the solution which is obtained when one mole of non-volatile solute is dissolved in 1kg (1000g) of solvent.

K_b is the property of the solvent, so its value depends on the nature of the solvent (it varies from the solvent to solvent).

It should be noted that:

Sometimes the elevation constant is given per 100g of solvent (K_{100}) in which the constant is 10 times the K_b value i.e. $10K_b$ or $K_b = \frac{K_{100}}{10}$

Freezing point depression

Freezing point of a substance is the temperature at which vapour pressure of solid phase of the substance is equal to the vapour pressure of its liquid phase.

Thus freezing point is the temperature at which liquid and solid phase of the substance are at equilibrium, that is; liquid and solid phase of the substance co-exist.

According to Raoult's law of lowering in vapour pressure, when a non-volatile solute is added to the liquid solvent, its vapour pressure decreases and therefore it would become equal to that of solid solution at lower temperature and hence the freezing point of the liquid decreases.

Like in boiling point elevation, freezing point depression also varies directly proportional to the concentration (molality) of the solute in the solution.

That is: $\Delta T \propto m$

Introducing constant of proportionality, K_f

$$\Delta T = K_f m$$

Where: ΔT is the freezing point depression in $^{\circ}\text{C}$ or K

m is the molality of the solution in mol/kg

K_f is the freezing point depression constant (molal depression constant) in $^{\circ}\text{C kg mol}^{-1}$ or K kg mol^{-1}

The constant is also known as cryoscopic constant.

Definition of cryoscopic constant (molal depression constant), K_f

This is the depression (decrease) in freezing point of the solvent in the solution which is obtained when one mole of non-volatile solute is dissolved in 1kg (1000g) of the solvent. Like K_b , K_f is the property of the solvent.

Also if the constant is given per 100g of the solvent, then $10K_{100} = K_f$ or $K_f = \frac{K_{100}}{10}$ where K_{100} is the depression constant per 100g of the solvent.

The fact that freezing point depression varies directly proportional to the molality agrees with **Blagden's law** which state that: *The depression of the freezing point of dilute solutions is proportional to the amount of the dissolved substance.*

Have you asked yourself this question? ***In the measuring of boiling point elevation or freezing point depression, why we use molality and not molarity?***

This is simply because the measuring of boiling point elevation or freezing point depression involves changing of temperature of the solution. So because molarity changes as the temperature changes; it becomes unsuitable while molality being temperature independent becomes preferable.

Example 4

When 15g of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$ was dissolved in 50g of solvent with relative molecular mass of 180g/mol, the freezing point was depressed by 8°C . Using this data, calculate the freezing point depression constant for the solvent.

Solution

From $\Delta T = K_f m$

$$\text{Where } m = \frac{n_{\text{glucose}}}{m_{\text{sv}} \text{ in Kg}} = \frac{15}{180 \times 0.05} \text{ mol/kg}$$

But $\Delta T = 8^{\circ}\text{C}$

$$\text{Then } 8^{\circ}\text{C} = K_f \times \frac{15}{180 \times 0.05} \text{ mol/Kg}$$

$$\text{or } K_f = 4.8^{\circ}\text{C kg mol}^{-1}$$

Hence the freezing point depression constant is $4.8^{\circ}\text{C kg mol}^{-1}$

Example 5

An organic compound has an empirical formula of CHO_2 . When 1.125g of the compound is dissolved in 125g of water gave a solution freezing at -0.186°C . Calculate the molecular mass of the compound and write its molecular formula ($K_f = 1.86^{\circ}\text{C kg mol}^{-1}$)

Solution

Using: $\Delta T = K_f m$

$$\text{But } m = \frac{n_{\text{su}}}{m_{\text{sv}} \text{ in kg}} = \frac{n_{\text{su}}}{M_{\text{su}} \times M_{\text{sv}} \text{ in kg}}$$

$$\text{Then } \Delta T = \frac{K_f \times m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in Kg}} \text{ where } \Delta T = 0^\circ\text{C} - (-0.186^\circ\text{C}) = 0.186^\circ\text{C}$$

$$\text{From which } M_{\text{su}} = \frac{K_f \times m_{\text{su}}}{\Delta T \times m_{\text{sv}} \text{ in Kg}} = \frac{1.86 \times 1.125}{0.186 \times 0.125} \text{ g/mol} = 90 \text{ g/mol}$$

So molar mass of the organic compound is 90g/mol

Let molecular formula of the compound be $(\text{CHO}_2)_n = \text{C}_n\text{H}_n\text{O}_{2n}$

Then $12n + n + 32n = M_r = 90$; $45n = 90$ or $n = 2$

Hence the molecular formula of the compound is $\text{C}_2\text{H}_2\text{O}_4$

Example 6

Pure ethanol, $\text{C}_2\text{H}_5\text{OH}$ boils at 78.3°C at pressure of 760mmHg, when 2.51g of methol, $\text{C}_{10}\text{H}_9\text{OH}$ is dissolved in 100g of ethanol, the solution boils at 85.9°C at 760mmHg

- Explain why the boiling point of ethanol is raised?
- Calculate the molal boiling point K_b for ethanol

Solution

An introduction of methol which is non-volatile into ethanol lowers the vapour pressure of the latter and hence boiling point of ethanol is increases.

$$\Delta T = K_b m \text{ or } K_b = \frac{\Delta T}{m}$$

$$\text{But } \Delta T = (85.9 - 78.3)^\circ\text{C} = 7.6^\circ\text{C}$$

$$\text{And } m = \frac{m_{\text{methol}}}{M_{\text{methol}} \times m_{\text{ethanol}} \text{ in kg}} = \frac{2.51}{146 \times 0.1} \text{ mol/Kg}$$

$$\text{Then } \Delta T = \frac{7.6 \times 146 \times 0.1}{2.51} ^\circ\text{C mol}^{-1}\text{kg} = 44.2^\circ\text{C kg mol}^{-1}$$

Hence the molal boiling point, K_b is $44.2^\circ\text{C kg mol}^{-1}$

Example 7

Write down the limitation of colligative properties

Study the table below and answer the question that follows:

Solution	Concentration in mol/L	Freezing point ($^\circ\text{C}$)
Cane sugar $\text{C}_{12}\text{H}_{22}\text{O}_{11}$	0.03	- 0.054
Glycerol $\text{C}_3\text{H}_8\text{O}_2$	0.132	- 0.200
Potassium bromide KBr	0.084	- 0.300

Giving reasons comment on the variation of freezing point with respect to concentration of the solution in the above table.

Solution

(a) Limitations of colligative properties are:

- The properties are not observed when the solute is volatile.
- The properties are not observed in concentrated solution.

(b) **Comment:**

Freezing points of given solution decrease from cane sugar, glycerol to potassium bromide, the bromide having lowest freezing point.

Reasons:

Freezing point depressions of given solution increase with an increase in concentration (number of particles) of solute.

- KBr being ionic (strong electrolyte) dissociates (ionises) in the solution according to the equation: $\text{KBr} \rightarrow \text{K}^+ + \text{Br}^-$ thus making concentration of solute (number of particles of solute) almost twice of given concentration. Hence it depresses most the freezing point of water.
- Glycerol and cane sugar being covalent do not dissociate at all in the solution, thus the more concentrated glycerol solution will depress more the freezing point of water.

Example 8

Estimate the freezing point of an antifreeze mixture which is made up by combining one volume of ethylene glycol ($M_w = 62\text{g/mol}$, density = 1.11g/cm^3) with two volumes of water.

Given that: K_f of water = $1.86\text{K kg}^{-1}\text{mol}^{-1}$

Solution

If V is the volume of the glycol in cm^3 . The volume of water will be $2V\text{cm}^3$ (one volume of the glycol was mixed with two volume of water).

Using, $m = \rho V$

Mass of the glycol = $1.11\text{g/cm}^3 \times V\text{cm}^3 = 1.11V\text{g}$

Mass water = $1\text{g/cm}^3 \times 2V\text{cm}^3 = 2V\text{g}$

Number of moles of g the glycol = $\frac{1.11V\text{g}}{62\text{g/mol}} = 0.0179V\text{mol}$

Mass of water (solvent) in kg = $\frac{2V\text{g}}{1000\text{g/kg}} = 0.002V\text{kg}$

Molality = $\frac{\text{number of moles of solute}}{\text{mass of solvent in kg}} = \frac{0.0179V\text{mol}}{0.002V\text{kg}} = 8.95\text{mol/kg}$

Then $\Delta T = K_f m = 1.86\text{K kg}^{-1}\text{mol}^{-1} \times 8.95\text{mol/kg} = 16.647\text{K}$

Thus the freezing point depression is 16.647K (or $^\circ\text{C}$)

But pure water freezes of 0°C

Hence the freezing point of the antifreeze mixture is $0^\circ\text{C} - 16.647^\circ\text{C} = -16.647^\circ\text{C}$

Example 9

A bottle of wine is $11\%\text{C}_2\text{H}_5\text{OH}$ in water; if the bottle is chilled to -3°C , will the wine freeze? K_f of water = 1.86°C/m .

Solution

Mass of $\text{C}_2\text{H}_5\text{OH}$ in 100g of solution is 11g

Thus;

Mass of solute ($\text{C}_2\text{H}_5\text{OH}$) = 11g

Mass of solvent (Water) = $(100 - 11)\text{g} = 89\text{g}$

Freezing point depression, $\Delta T = K_f m = \frac{K_f m_{\text{su}}}{m_{\text{su}} \times m_{\text{sv}} \text{ in kg}}$

$\Delta T = \frac{1.86^\circ\text{C kg mol}^{-1} \times 11\text{g}}{46\text{g mol}^{-1} \times 0.089\text{kg}} = 5^\circ\text{C}$

Freezing point of the solution, $T_f = 0^\circ\text{C} - \Delta T = 0^\circ\text{C} - 5^\circ\text{C} = -5^\circ\text{C}$

Since the freezing point of the solution (-5°C) is less than the bottle temperature (-3°C), the wine will not freeze.

OSMOTIC PRESSURE (π)

If solution and solvent are placed in the same container but are separated by **semi – permeable membrane**; (which allows the passage of solvent particles but not solute particles); it will be observed that the level of the solvent decreases while the solution side will increase. This indicates that the solvent particles are passing through semi permeable membrane by a process called **osmosis**.

The word osmosis is derived from Greek 'osmos' which means **push**.

By definition

Osmosis is the spontaneous flow of solvent through semi-permeable membrane from a solution of low solute concentration to one of higher solute concentration (or from the solvent side which can be said to have zero solute concentration to the solution side).

- It differs from diffusion in the sense that the flow of particles is in one direction only.

Where **semi-permeable membrane** is one which allows only solvent molecules to pass through without allowing the passage of solute molecules. Semi permeable membranes are common in living organisms. The membranes surrounding the plant cells and animal cells are semi – permeable. These membranes are found naturally and hence the term **natural semi – permeable membranes** for them.

- It is also possible to prepare artificial (synthetic) semi permeable membranes like **calcium phosphate** and **copper ferrocyanide**.

Why osmosis occurs?

The region of lower solute concentration has greater vapour pressure exerted by the solution as there is less lowering in the vapour pressure of the solvent in the solution compared to the region of higher solute concentration. This forces (pressurises) the solvent molecules to pass from the region of lower concentration to that of higher concentration until the concentration of the solute and vapour pressures in the two regions balance.

Osmotic pressure is the pressure required to be applied to the side (region) of higher solute concentration (or solution side for solvent-solution system) so as to prevent movement of solvent molecules by osmosis.

The higher the solute concentration (lower solvent concentration), the higher the osmotic pressure is needed and hence more concentrated solution is said to have higher osmotic pressure (provided that the temperature is constant). So it can be said that **during osmosis, solvent molecules moves from the side of lower osmotic pressure to that of higher osmotic pressure until both solutions have an equal osmotic pressure**.

Understanding osmotic pressure in terms of hydrostatic pressure

- As solvent molecules move from the solvent side (or solution side with lower solute concentration) to solution side (or solution side with higher concentration), during osmosis liquid level is decreasing in the solvent side and is increasing in the solution side. As the liquid level in the solution side is increasing, the **hydrostatic pressure** continue to increase too as the osmosis continue (remember; hydrostatic pressure, $P = \rho gh$).
- **Osmotic equilibrium** occurs when osmosis (osmotic flow) forces the liquid in the side of solution with higher solute concentration up to a height that creates a hydrostatic pressure equal to the osmotic pressure of the solution. At this point of osmotic equilibrium (*final state* of the osmosis), solvent molecules pass through the membrane in both directions at equal rates, resulting in zero net osmotic flow between the two sides. (See figure in the next page).

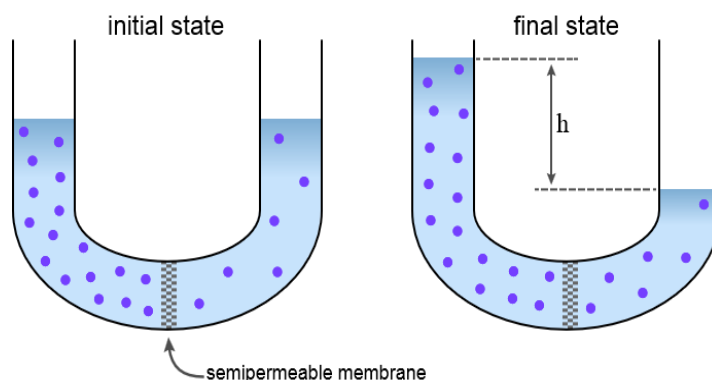


Figure 7.1 Osmosis

The increase in hydrostatic pressure that prevented the osmotic flow (osmosis) in the osmotic equilibrium (final state) is equal to the osmotic pressure. So the osmotic pressure can now be defined as *the hydrostatic pressure required for a solution to achieve osmotic equilibrium with a more dilute solution or pure solvent*.

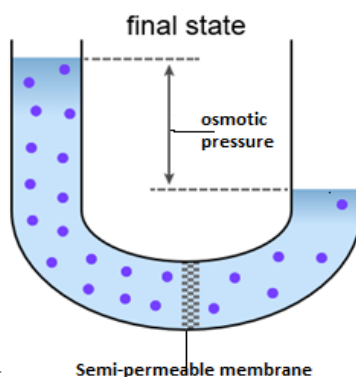


Figure 7.2 Osmotic pressure in terms of hydrostatic pressure

It is interesting to understand that:

Osmosis can be reversed by applying an external pressure that exceeds the osmotic pressure of the solution, thus producing a net flow of solvent from side with higher solute concentration to the side of lower solute concentration. This is osmotic flow is known as **reverse osmosis**. Reverse osmosis is the basis of purification of drinking water through **desalination of sea water**.

So we may conclude that:

In osmosis: Hydrostatic pressure < osmotic pressure

In osmotic equilibrium: Hydrostatic pressure = osmotic pressure

In reverse osmosis: Hydrostatic pressure > osmotic pressure

Osmosis play very important part of our daily life including various biological activities. The use of sugar to preserve jams and, the use of salt to preserve certain meat, is based on osmosis.

- The salt or sugar increases the solute concentration to a level above that present in living organisms. As result, a body of living organisms has lower osmotic pressure than the food (jam or meats).
- So any bacterial cell (which is surrounded by semi – permeable membrane) that wanders into such a medium will have water osmotically drawn out of it, and eventually will die of dehydration.

Some important definition of terms

Hypertonic solution is the solution whose osmotic pressure is greater than that of another solution.

Hypotonic solution is the solution whose osmotic pressure is less than that of another solution

Isotonic solutions are the solutions with the same osmotic pressure.

Thus if A and B are isotonic solutions;

then $\pi_A = \pi_B$

If two isotonic solutions are separated by semi – permeable membrane **no** net flow of solvent molecules through semi – permeable membrane (osmosis) will be observed.

Table 7.1 Differences between osmosis and diffusion

	OSMOSIS		DIFFUSION
1	Definition	1	Definition
2	It applies for liquid only	2	It applies for both liquids and gases
3	It involves movement of molecules from the side of lower concentration to that of higher concentration	3	Molecules move from the side of higher concentration to that of lower concentration
4	There is a role of semi- permeable membrane	4	There is no role of semi- permeable membrane.
5	It can be prevented by applying pressure equals to osmotic pressure to the side of higher solute concentration	5	It cannot be prevented

Similarities between osmosis and diffusion

Osmosis and diffusion are similar in the following ways:

- They both involve the movement of molecules from one region to another and the direction of movement is governed by relative concentration in the two region.
- Their motions are both affected by the temperature.
- Both are useful in molecular mass determination.

Van't Hoff theory of dilute solutions

According to Van't Hoff, properties of gases and dilute solution are very similar. The theory may be stated as: *A solute in a solution behaves exactly like a gas and the osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature occupying the same volume.*

There are number of laws which can be deduced from the theory.

First law:

For dilute solution of a given solute, at constant temperature, the osmotic pressure of the solution is directly proportional to its mass concentration (which means that it is inversely proportional to the volume of solution containing fixed mass of the solute)

That is $\pi \propto C$

And for fixed mass of the solute: $\pi \propto \frac{1}{V}$ or $\pi V = \text{constant}$ and hence $\pi_1 V_1 = \pi_2 V_2$

Hence the first law is equivalent to **Boyle's law**. So the law is also known as **Boyle-Van't Hoff's law** for solution.

Second law:

The osmotic pressure of given concentration of solution is directly proportional to its absolute temperature.

That is $\pi \propto T$ or $\frac{\pi}{T} = \text{constant}$ and hence $\frac{\pi_1}{T_1} = \frac{\pi_2}{T_2}$

This law is equivalent to pressure-temperature law for gases and hence is known as **Van't Hoff's pressure-temperature law** for solution.

Like gas laws, the first and second law may be combined to get single equation as follows:

From the first law: $\pi \propto \frac{1}{V}$ (i)

From the second law; $\pi \propto T$ (ii)

Combining (i) and (ii) gives: $\pi \propto \frac{T}{V}$ Or $\frac{\pi V}{T} = \text{constant}$

And hence $\frac{\pi_1 V_1}{T_1} = \frac{\pi_2 V_2}{T_2}$ (For fixed mass of covalent solute in dilute solution)

The final bolded equation is equivalent to general equation for gases and hence is known as **general equation for solutions**.

When the concentrations are given instead of volume; the above relationship becomes:

$$\frac{\pi_1}{C_1 T_1} = \frac{\pi_2}{C_2 T_2} \text{ as the concentration, } C \propto \frac{1}{V}$$

Also as for gases; it can be shown that: $\pi V = nRT$ or $\pi = CRT$ where $C = \frac{n}{V}$

From which: π is the osmotic pressure of very dilute solution

V is the volume of solution

n is the number of moles of non-volatile covalent solute

R is the universal molar gas constant

T is absolute temperature in Kelvin

C is the molar concentration of the solute

Third law:

From $\pi V = nRT$

Assume who have two solutions, say solution 1 and solution 2.

For solution 1: $\pi_1 V_1 = n_1 R T_1$

For solution 2: $\pi_2 V_2 = n_2 R T_2$

It follows that: $\frac{\pi_1 V_1}{\pi_2 V_2} = \frac{n_1 R T_1}{n_2 R T_2}$

Now if $\pi_1 = \pi_2 = \pi$ and $T_1 = T_2 = T$

Then $\frac{\pi V_1}{\pi V_2} = \frac{n_1 R T}{n_2 R T}$ or $\frac{V_1}{V_2} = \frac{n_1}{n_2}$ ($V \propto n$)

And if $V_1 = V_2 = V$

$$\frac{V}{V} = \frac{n_1}{n_2} \text{ or } n_1 = n_2$$

That is; *osmotic pressure and temperature being the same, equal volumes of solution contains equal number of moles (or molecules) of the solute.*

The result is equivalent to Avogadro's law for gases and hence is known as **Avogadro – Van't Hoff's law** for solution.

Similarities between gases and dilute solutions

The similarities between dilute solution and gases are summarised in the table below

Table 7.2 Similarities between gases and dilute solutions

	GAS		DILUTE SOLUTION
1	$P \propto \frac{1}{V}$ (Boyle's law)	1	$\pi \propto \frac{1}{V}$ (Boyle-Van't Hoff's law)
2	$P \propto T$ (pressure-temperature law)	2	$\pi \propto T$ (Van't Hoff's pressure-temperature law)
3	$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ (general equation for gases)	3	$\frac{\pi_1 V_1}{T_1} = \frac{\pi_2 V_2}{T_2}$ (general equation for solutions)
4	$V \propto n$ (Avogadro's law)	4	$V \propto n$ (Avogadro-Van't Hoff's law)
5	$PV = nRT$	5	$\pi V = nRT$

Example 10

Calculate the molar mass of a solute given that 35g of the solute in 1dm³ of water have an osmotic pressure of $5.15 \times 10^5 \text{ Nm}^{-2}$ at 20°C

Solution

Using $\pi V = nRT$ but $n = \frac{m}{M_r}$

Then $\pi V = \frac{m}{M_r} RT$ or $M_r = \frac{mRT}{\pi V}$

Where: $m = 35\text{g}$, $R = 8.314$, $T = 20^\circ\text{C} = 293\text{K}$

$\pi = 5.15 \times 10^5 \text{ Nm}^{-2}$ and $V = 1\text{dm}^3 = 10^{-3}\text{m}^3$

$M_r = \frac{35 \times 8.314 \times 293}{5.15 \times 10^5 \times 10^{-3}} \text{ g/mol} = 165.56\text{g/mol}$.

Hence molar mass of the solute is 165.56g/mol

Example 11

A polysaccharide has the formula $(\text{C}_{12}\text{H}_{22}\text{O}_{11})_n$. A solution contains 5g/dm³ of the sugar has an osmotic pressure of $7.12 \times 10^2 \text{ Nm}^{-2}$ at 20°C. Find n in the formula.

Solution

Using: $\pi V = \frac{m}{M_r} RT$

From which: $M_r = \frac{mRT}{\pi V}$

Where: $m = 5\text{g}$, $V = 1\text{dm}^3 = 1 \times 10^{-3}\text{m}^3$ (a concentration of 5g/dm^3 means the volume of 1dm^3 contain mass of 5g)

$$R = 8.314, T = 20^\circ\text{C} = 293\text{K and } \pi = 7.12 \times 10^2 \text{Nm}^{-2}$$

$$\text{So: } M_r = \frac{5 \times 8.314 \times 293}{7.12 \times 10^2 \times 10^{-3}} \text{g/mol} = 17107 \text{g/mol}$$

But the molecular formula of the sugar is $(\text{C}_{12}\text{H}_{22}\text{O}_{11})_n$

$$\text{Then } 144n + 22n + 176n = M_r = 17107 \quad \text{Or} \quad 342n = 17107$$

$$n = 50$$

Example 12

Calculate the osmotic pressure of an aqueous solution containing 25gdm^{-3} of a protein of relative molecular mass of 5×10^4 at 27°C .

Solution

$$\text{From } \pi V = nRT$$

$$\pi = \frac{nRT}{V} = \frac{mRT}{M_r V} = \frac{25 \times 8.314 \times 300}{5 \times 10^4 \times 10^{-3}} = 1247.1 \text{Pa}$$

Hence the osmotic pressure of the solution is 1247.1Pa

Example 13

An aqueous solution of cane sugar containing 19.15g of sugar per dm^3 has osmotic pressure of 136300Nm^{-2} at 20°C . Calculate the relative molecular mass of cane sugar

Solution

$$\text{From } \pi V = \frac{m}{M_r} RT$$

$$M_r = \frac{mRT}{\pi V} = \frac{19.15 \times 8.314 \times 293}{136300 \times 10^{-3}} \text{g/mol} = 342 \text{g/mol}$$

Hence the relative molecular mass of cane sugar is 342 .

You should note that:

The relative molecular mass is unit-less but equal in magnitude to molecular mass whose unit is g/mol

EXPERIMENTAL DETERMINATION OF MOLAR MASS OF SOLUTE FROM COLLIGATIVE PROPERTIES

Since all of the colligative properties of solution depend on the concentration of the solute, their measurements can serve as a convenient experimental tool for determining the concentration and thus molar mass of a solute. Due to the fact that, colligative properties are observed when **non – volatile** solute are dissolved in the solvent, the method is appropriate for molar mass determination of **non-volatile substance** in contrary to methods of molar mass determination studied in gas laws which are appropriate for **volatile substances**.

- Once colligative property has been measured, the molar mass of the non – volatile substance (solute) can be determined by one of the following formula (as derived in previous worked examples) depending on type of colligative property which has been really measured.

$$M_{su} = \frac{m_{su} \times M_{sv} \times P_{sv}^0}{m_{sv} \times \Delta P} \quad (\text{From lowering of vapour pressure})$$

$$M_{su} = \frac{K_b \times m_{su}}{\Delta T \times m_{sv} \text{ in Kg}} \quad (\text{From boiling point elevation})$$

$$M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in Kg}} \quad (\text{From freezing point depression})$$

$$M_{su} = \frac{m_{su} RT}{\pi V} \quad (\text{From measured osmotic pressure})$$

There are various methods which can be used to measure colligative properties and hence determination of molar mass of non-volatile solute (from colligative properties it exerts in the solution). Important methods to discuss in this section are:

- Beckmann's method and
- Landsberger's method

Beckmann's method

Beckmann's method can be used to determine molar mass of solute by either measuring boiling point elevation or measuring freezing point depression caused by weighed amount of solute in the solution.

- The process of measuring boiling point elevation so as to determine molar mass of the non-volatile solute is known as **ebullioscopy** (The term ebullioscopy comes from Greek language and means 'boiling measurement').
- The process of measuring freezing point depression so as to determine molar mass of non – volatile solute is known as **cryoscopy** (also comes from Greek and means 'freezing measurement').

To perform ebullioscopy and cryoscopy, Beckmann's method utilizes an apparatus which is known as **Beckmann's apparatus**.

For ebullioscopy:

- The solvent is boiled in the boiling tube (see figure below) which has a platinum wire fused through the bottom and contains a layer of glass beads to promote regular boiling and to prevent superheating of solvent.
- The boiling tube is surrounded by a glass outer jacket in which the same solvent is kept boiling. This prevents radiant heat from affecting the apparatus.
- Both the inner tube and the outer jacket are fitted with condensers.
- The whole apparatus is heated on an asbestos box provided with chimneys for promoting convection currents.
- The box screens off the direct heat of the flame and therefore avoids superheating of the solvent.
- The thermometer is used to note the elevation of boiling point and is of the special type (**Beckmann thermometer**).

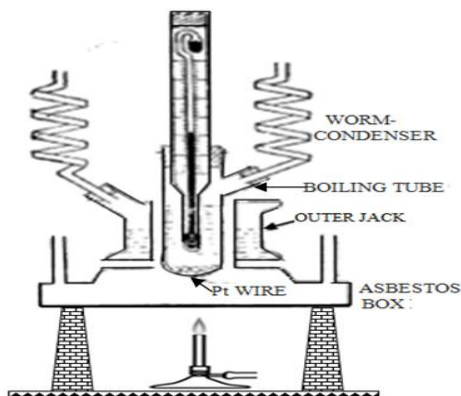


Figure 7.3 Beckmann's boiling point apparatus

The older form of the apparatus described above, which was designed for heating by gas has largely replaced by the apparatus designed for electrical heating. The new type of apparatus permits of results being obtained more rapidly and with greater accuracy.

Procedures for the determination:

- In a determination, weighed quantity (15g up to 20g) of solvent is placed in the boiling tube and heated gently until a steady temperature is reached. This steady temperature is the boiling point of the pure solvent.
- An accurately weighed quantity (0.2g up to 0.5g) of the substance whose molar mass is to be determined is then dropped into the solvent through the side tube and temperature again brought to steady state which indicates the boiling point of the solution.
- The difference between boiling point of the solution and boiling point of pure solvent is the boiling point elevation (ΔT) which can be used to calculate the molar mass of the solute

That is $\Delta T = \text{Boiling point of the solution} - \text{Boiling point of the pure solvent}$

$$\text{And } M_{\text{su}} = \frac{K_b \times m_{\text{su}}}{\Delta T \times m_{\text{sv}} \text{ in kg}}$$

For cryoscopy:

Beckmann's apparatus for determination of freezing point depression consists of:

- The inner **freezing point tube** provided with side tube for introducing the solute and fitted with Beckmann thermometer and platinum stirrer.
- The outer **air-jacket** surrounding the inner tube which ensures a slower and more uniform rate of cooling of the liquid
- A **stout glass or stone cylinder** which contains a suitable cooling mixture and is provided with stirrer.

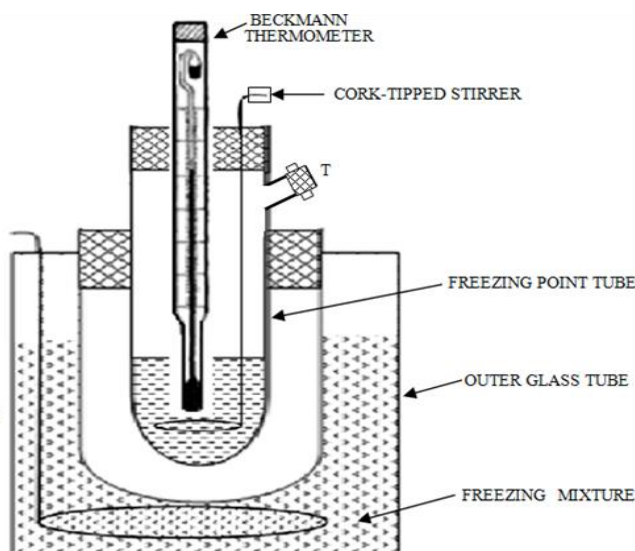


Figure 7.4 Beckmann's freezing point apparatus

Procedures for the determination:

- In an actual determination, weighed quantity (15g – 20g) of solvent is taken in the **inner freezing point tube** and the apparatus set as shown in the diagram so that the bulb of the thermometer is completely immersed in the pure solvent
- Then the **approximate freezing point** of the pure solvent is determined by directly cooling the freezing point tube in the **cooling bath**.
- After freezing the solvent, the frozen solvent is **melted** and then the freezing point tube is placed again in the freezing bath to allow the temperature to fall.
- When it has come down to within about a degree of the **approximate freezing point** determined above, the tube is dried is then cautiously placed in the air jacket.

- Thereafter the temperature is allowed to fall slowly and when it has come again down to about 0.5°C below the freezing point, the tube is stirred vigorously. This will cause the solid to separate and the temperature will rise because the latent heat has been set free.
- The highest temperature reached is noted and the process is repeated to get concordant value of freezing point.
- The freezing point of the pure solvent having been accurately determined, the frozen solvent is then **re-melted** by removing the tube from the bath.
- Then can accurately weighed quantity (0.1g – 0.2g) of the substance whose molar mass is to be determined is introduced in the freezing point tube through the side tube.
- Finally, the freezing point of the solution is determined in the same way as that of the pure solvent.
- The difference between freezing point of the solution and that of the pure solvent is the freezing point depression (ΔT) which can be used to calculate the molar mass of the solute by using the following formula:

$$M_{\text{su}} = \frac{K_f \times m_{\text{su}}}{\Delta T \times m_{\text{sv}} \text{ in kg}}$$

Landsberger's method

This method is the most convenient for the determination of the boiling point elevation in the laboratory and hence molar mass of a non-volatile solute which causes such elevation. In this method, the solution is heated by bubbling through it the vapour of the boiling solvent in an apparatus which is known as **Landsberger's apparatus**.

The Landsberger's apparatus consists of:

- A **boiling flask** which sends vapour of the solvent into the inner tube.
- An **inner boiling tube** which has a bulb with a hole in the side, and is graduated in cm^3 . It is fitted with Beckman thermometer (or an ordinary thermometer graduated to 0.01°C) and a glass tube with bulb blown at the end which has many holes in it. This rose-head ensures uniform distribution of the vapour through the solvent. The bulb reflects back any particles of the solvent which happen to fly about when the boiling becomes brisk.
- An **outer covering tube** which receives hot vapour from the inner tube through the hole. This forms a protecting jacket around the boiling tube, prevents the loss of heat from it due to radiation and, in addition, protects it from draughts of air.

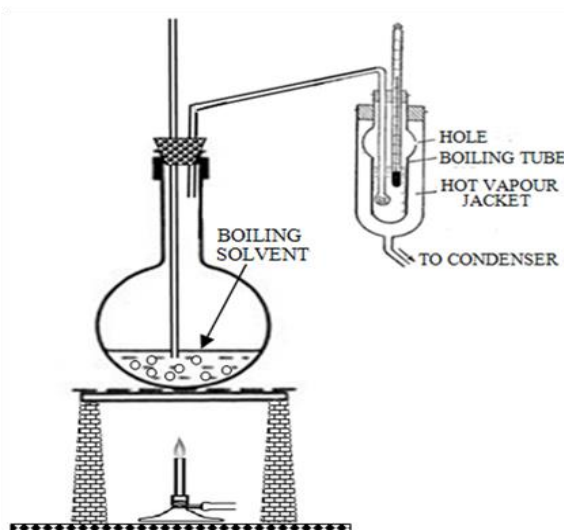


Figure 7.5 Landsberger's boiling point apparatus

Procedure of the determination:

- 5cm³ to 7cm³ of solvent are placed in the inner tube and the vapour of the solvent passed through it.
- At the start, the solvent vapour condenses and more vapour is passed, the liquid becomes warmer and in time boils.
- As soon as the temperature has become constant, the temperature reading is taken. This temperature is the boiling point of the pure solvent.
- Then the supply of solvent vapour is cut off temporarily and a weighed quantity (0.2g-0.5g) of the substance whose molar mass is to be determined is dropped into the solvent in the boiling tube. The boiling point of the solution is then determined as before in the pure solvent.
- Immediately after the temperature is read off, the thermometer and the rose head are carefully raised out of the solution and the volume of the solution is noted.
- As done in the Beckmann's method, after getting boiling point elevation, molar mass of the solute can be calculated from the following formula:

$$M_{\text{su}} = \frac{K_b \times m_{\text{su}}}{\Delta T \times m_{\text{sv}} \text{ in kg}}$$

The reader should know that:

The measurement of molar mass of non – volatile solute through measuring of osmotic pressure (or even lowering in vapour pressure) requires a more advanced apparatus and cannot be carried out as an ordinary laboratory process. However osmotic pressure measurement as the way of determining molar mass of non-volatile solute has the following advantages than relative easier methods based on ebullioscopy and cryoscopy:

1. The osmotic pressure measurements are taken around room temperature.
2. The molarity of the solution is used in measuring osmotic pressure instead of molality. (You should remember that it is easier to measure molarity than molality).
3. Is particularly useful for determination of molar mass of biomolecules (polymers) as they are generally not stable at higher temperatures.

Abnormal results in molar mass measurement from colligative properties

Colligative properties are very useful in determination of molar mass of various compounds (solutes) as seen in the previous section. As in gases, abnormal result in molar mass measurement results from **dissociation** and **association**.

Dissociation

When a non-volatile solute **dissociates (ionises)**, number of the solute particles increases thus making the concentration (molarity, mole fraction or molality) of the solute to become greater than the expected one. So as colligative properties vary directly proportional to concentration of the solute, the value of colligative properties become greater than the expected one.

In all cases (lowering in vapour pressure, boiling point elevation, freezing point depression and osmotic pressure) colligative property varies inversely proportional to the molar mass of the solute and hence unexpectedly greater value of colligative property leads to unexpectedly smaller molar mass of the solute.

It should be understood that:

Dissociation of solute in water occurs for ionic salts (electrolytes) only. It does not occur in covalent compounds like organic compounds.

Association

When a non-volatile solute **associates**, number of moles of solute particles in solution decreases thus making the concentration of the solute smaller than expected one. Since colligative properties vary

directly proportional to concentration of the solute, the value of colligative property is also become smaller than the expected one and hence the measured molar mass of the solute become greater than the expected molar mass (colligative properties varies inversely proportional to molar mass of the solute).

Colligative properties and Vant' Hoff factor

It should be remembered that:

$$\text{Van't Hoff factor, } i = \frac{\text{Observed number of particles}}{\text{Expected number of particles}}$$

Thus when a non-volatile solute is dissolved in solution

$$i = \frac{\text{observed number of moles of the solute}}{\text{Expected number of moles of the solute}}$$

Since colligative properties varies directly proportional to the number of moles of solute, it follows that: $i = \frac{\text{observed colligative property}}{\text{Expected colligative property}}$

$$\text{For lowering in vapour pressure: } i = \frac{\text{Observed lowering in vapour pressure}}{\text{Expected lowering in vapour pressure}}$$

Thus: **Observed lowering in vapour pressure, $\Delta P = i \times \text{expected lowering in vapour pressure}$**

But expected lowering in vapour pressure = $X_{\text{solute}} P_{\text{sv}}^0$

Hence $\Delta P = i X_{\text{solute}} P_{\text{sv}}^0$ (In case there is either dissociation or association)

$$\text{Or } \frac{\Delta P}{P_{\text{sv}}^0} = i X_{\text{solute}}$$

Where ΔP the experimental is (observed) lowering in vapour pressure

$$\text{For boiling point elevation: } i = \frac{\text{Observed boiling point elevation}}{\text{Expected boiling point elevation}}$$

Then: **Observed boiling point elevation, $\Delta T = i \times \text{Expected boiling point elevation}$**

But the expected boiling point elevation = $K_b m$

Hence $\Delta T = i K_b m$

Where ΔT is the observed (experimental) boiling point elevation.

$$\text{For freezing point depression: } i = \frac{\text{Observed freezing point depression}}{\text{Expected freezing point depression}}$$

Then: **Observed freezing point depression, $\Delta T = i \times \text{Expected freezing point depression}$**

But expected freezing point depression = $K_f m$

Hence $\Delta T = i K_f m$

Where ΔT is measured (observed) freezing point depression

$$\text{For osmotic pressure: } i = \frac{\text{observed osmotic pressure}}{\text{Expected osmotic pressure}}$$

So observed osmotic pressure, $\pi = i \times \text{Expected osmotic pressure}$

But the expected osmotic pressure = $\frac{nRT}{V}$

$$\text{Hence } \pi = \frac{i n R T}{V} \text{ or } \pi V = i n R T$$

Where π is the observed osmotic pressure.

For osmotic pressure, the ratio has alternative term which is **osmotic coefficient (g)**.

So the **osmotic coefficient** is defined as *the ratio of observed osmotic pressure to expected osmotic pressure i*

That is, **osmotic coefficient, g** = $\frac{\text{observed } \pi}{\text{expected } \pi}$

It should be noted that:

- If $i > 1$, the solute dissociates (ionises) in the solution
- If $i < 1$, the solute associates in the solution
- If $i = 1$, the solute does not associate or dissociate in the solution, so that; expected colligative property = observed colligative property.

Recall:

$\alpha = \frac{i-1}{N-1}$ Where α is the degree of dissociation.

$\alpha = \frac{i-1}{1/N-1}$ Where α is the degree of association.

Now let us concentrate to the more common scenario (among the two) which is dissociation.

The smallest value of degree of dissociation, α is 0 which is found when there is no dissociation. Substituting $\alpha = 0$ into the above equation gives;

$$0 = \frac{i-1}{N-1} \text{ or } i = 1$$

Hence the lowest limit of Van't Hoff's factor is 1 and is found when there is no dissociation as deduced earlier.

The largest value of α is 1 which is found when there is complete dissociation (this is **theoretical** assumption which assumes that the electrolytic solute is hundred percent ionic with no possibility of ion pairing at all).

Again substituting $1 = \frac{i-1}{N-1}$; $i = N$

Hence the highest limit of Van't Hoff's factor is N (total number of solute particles formed after dissociating one solute particle) and is found when there is complete dissociation of solute in the solution. This is **theoretical value** of Van't Hoff's factor. Practically, the value will be less than N and hence its **actual value** lies between 1 and N ($1 < i < N$).

The reader should understand that:

- Strong attraction between cation and anion (as explained earlier in the introduction) is the main reason for not achieving the theoretical value of Van't Hoff's factor. This makes difficult to break the ionic bond and leads to ion pairing as well and hence the actual value of Van't Hoff's factor becomes smaller than the theoretical one. However strong ionic compounds (strong electrolytes) may be assumed to have the theoretical value ($i = N$) because they tend to ionise almost completely in the solution.
- The Van't Hoff's factor is also (apart from nature of solute) affected by concentration of solution. In the concentrated solution, there is less water (compared) and therefore the Van't Hoff's factor deviates more from theoretical value due to the following reasons:
 - Less water means that there is not enough water to enable breaking of all ionic bonds.
 - Less water means that even after forming some ions, those ions (cations and anions) are very close to each other making ion pairing much easier.
- Practically, Van't Hoff's factor may be increased to the theoretical value by **diluting the solution to infinite** whereby there are so much water that will enable breaking all ionic bonds and there is no possibility of ion pairing because the ions are now very far apart.

Example 14

An aqueous solution is 0.8402 molal in Na_2SO_4 . It has a freezing point of -4.218°C .

- Determine the effective number of particles arising from each Na_2SO_4 formula unit in this solution.
- What is the theoretical value of Van't Hoff's factor of the sulphate?
- In comparison to the theoretical Van't Hoff factor (stated in b), and that determined in (a); what behaviour of the sodium sulphate in solution accounts for the difference?

Solution

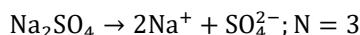
$$(a) \Delta T = 0^\circ\text{C} - (-4.218^\circ\text{C}) = 4.218^\circ\text{C}$$

Using $\Delta T = iK_f m$;

$$\text{From which; } i = \frac{\Delta T}{K_f m} = \frac{4.218}{1.86 \times 0.8402} = 2.7$$

Hence the effective number of particles per formula unit of Na_2SO_4 is 2.7.

- Theoretical value of Van't Hoff's factor assumes that the compound is hundred percent ionic with no ion pairing at all and therefore ionises completely in the solution as per equation;



Hence theoretical value of Van't Hoff's factor is 3.

- Since sodium possess some degree of polarization, it is partially covalent and therefore not all sodium-sulphate bonds (attractions) are broken during the dissolution. Also in aqueous solution, ion pairing between some of Na^+ and some of SO_4^{2-} occurs decreasing number of ions (solute particles) even further making the experimental Van't Hoff's factor obtained in (a) to be smaller than the theoretical one obtained in (b).

Example 15

Calculate the osmotic pressure (in torr) of 5.82L of an aqueous 0.148M solution at 25°C if the solute concerned is totally ionized into three ions.

Solution

Since the solute is totally ionized into three ions; $i = 3$

$$\begin{aligned} \text{From } \pi V &= inRT \text{ or } \pi = \frac{inRT}{V} = iCRT \\ &= 3 \times 0.148 \times 0.082 \times 298 = 10.85\text{atm} \end{aligned}$$

But $1\text{atm} = 760\text{torr}$

Hence the osmotic pressure of the solution is $10.85 \times 760\text{torr}$ or 8246torr .

Example 16

A solution containing 5.4g of strontium chloride, SrCl_2 in 170g of water freezes at -0.982°C at 101300Nm^{-2} pressure. Calculate the apparent degree of dissociation of the salt ($K = 1.86^\circ\text{C}$ per 1000g of water). Given that: Atomic mass of $\text{Sr} = 88, \text{Cl} = 35.5$

Solution

$$\text{Observed freezing point depression} = 0^\circ\text{C} - (-0.982^\circ\text{C}) = 0.982^\circ\text{C}$$

If SrCl_2 was undissociated:

Molar mass of SrCl_2 would be $88+71 = 159\text{g/mol}$

$$\text{Expected freezing point depression} = K_f m = \frac{k_f \times m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in Kg}}$$

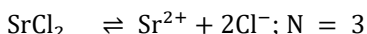
Substituting given values.

Expected freezing point depression

$$= \frac{1.86 \times 5.4}{159 \times 0.17} ^\circ\text{C} = 0.3716^\circ\text{C}$$

$$\text{Using: } i = \frac{\text{observed freezing point depression}}{\text{Expected freezing point depression}} = \frac{0.982}{0.3716} = 2.64$$

One mole of SrCl_2 dissociates to give three moles of ions according to the following equation.



$$\text{Degree of dissociation is given by: } \alpha = \frac{i-1}{N-1} = \frac{2.64-1}{3-1} = 0.82 \text{ or } 82\%$$

Hence the apparent degree of dissociation of the salt is 82%

Example 17

By dissolving 8.5g of common salt in 125g of water at a certain temperature, the vapour pressure was depressed from 2666Nm^{-2} to 2567Nm^{-2} . Calculate the degree of dissociation of common salt at this dilution and temperature.

Solution

Common salt is NaCl whose molar mass is 58.5g/mol

$$n_{\text{NaCl}} = \frac{m_{\text{NaCl}}}{M_{\text{NaCl}}} = \frac{8.5}{58.5} \text{ moles} = 0.1453 \text{ moles}$$

$$n_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} = \frac{125}{18} \text{ moles} = 6.9444 \text{ moles}$$

$$X_{\text{NaCl}} = \frac{n_{\text{NaCl}}}{n_{\text{NaCl}} + n_{\text{H}_2\text{O}}} = \frac{0.1453}{(0.1453 + 6.9444)} = 0.02$$

$$\text{Expected lowering in vapour pressure} = X_{\text{solute}} P_{\text{sv}}^0 = X_{\text{NaCl}} P_{\text{H}_2\text{O}}^0$$

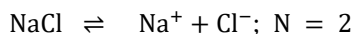
$$= 0.02 \times 2666\text{Nm}^{-2} = 53.32\text{Nm}^{-2}$$

$$\text{But observed lowering in vapour pressure} = (2666 - 2567)\text{Nm}^{-2} = 99\text{Nm}^{-2}$$

Using:

$$i = \frac{\text{Observed lowering in the vapour pressure}}{\text{Expected lowering in the vapour pressure}} = \frac{99}{53.32} = 1.86$$

One mole of NaCl dissociates to produce two moles of ions according to the following equation:



Degree of dissociation is given by:

$$\alpha = \frac{i-1}{N-1} = \frac{1.86-1}{2-1} = 0.86 \text{ or } 86\%$$

Hence degree of dissociation of the common salt is approximately 86%

Example 18

0.75g of ethanoic acid, CH_3COOH , when dissolved in 125g of benzene, depresses the freezing point of benzene by 0.255°C . What is the molecular state of ethanoic acid in benzene solution?

($K = 5^\circ\text{C}$ per 1000g of benzene)

Solution

To understand the molecular state of ethanoic acid in benzene, it is supposed to determine the observed (measured) molecular mass of ethanoic acid which is compared by the expected one.

Expected molecular mass of CH_3COOH is 60g/mol

$$\text{Using } \Delta T = K_f m = \frac{K_f \times m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}$$

$$M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}} = \frac{5 \times 0.75}{0.255 \times 0.125} \text{ g/mol} = 118 \text{ g/mol}$$

Thus the observed molar mass of benzene is 118g/mol.

Since the observed molar mass is almost twice the expected one, two molecules of ethanoic acid associates in the solution to form dimer. Hence molecular state of ethanoic acid in benzene solution is dimer as illustrated below.



Dimerization of ethanoic acid in the benzene solution

Example 19

A 0.01M solution of methanoic acid had an osmotic pressure of 28350 Nm^{-2} at 25°C . Calculate the degree ionisation of methanoic acid at this dilution and temperature.

Solution

Expected osmotic pressure = $\frac{nRT}{V}$ but $\frac{n}{V} = [\quad]$

Then expected osmotic pressure = $[\quad] RT$

But $[\quad] = 0.01 \text{ mol/dm}^3 = \frac{0.01}{10^{-3}} \text{ mol/m}^3 = 10 \text{ mol/m}^3$

So expected osmotic pressure = $10 \times 8.314 \times 298 \text{ Nm}^{-2} = 24775.72 \text{ Nm}^{-2}$

But observed osmotic pressure = 28350 Nm^{-2}

$$i = \frac{\text{observed osmotic pressure}}{\text{Expected osmotic pressure}} = \frac{28350}{24775.72} = 1.144$$

One mole of methanoic acid ionises (dissociates) to produce two moles of ions according to the following equation.



Then $\alpha = \frac{i-1}{N-1} = \frac{1.144-1}{2-1} = 0.144$ or 14.4%

Hence degree of ionisation of HCOOH is 14.4%

MISCELLANEOUS WORKED EXAMPLES ON COLLIGATIVE PROPERTIES

Example 20

A 5.00g sample of a compound is dissolved in enough water to form 100.0 mL of solution. This solution has an osmotic pressure of 25torr at 25°C . If it is assumed that each molecule of the solute dissociates into two particles (in this solvent), what is the molar mass of this solute?

Solution

Since 1 molecule of the solute dissociates into two particles; $i = 2$

Using $\pi V = i n R T$ but $n = \frac{m}{M_r}$

Then $\pi V = i \frac{m}{M_r} R T$ or $M_r = \frac{i m R T}{\pi V}$

Where: $m = 5\text{g}$, $R = 0.082$, $T = 25^\circ\text{C} = 298\text{K}$

$\pi = 25 \text{ torr} = \frac{25}{760} \text{ atm}$ and $V = 100 \text{ mL} = 0.1 \text{ dm}^3$

$$M_r = \frac{2 \times 5 \times 0.082 \times 298}{\frac{25}{760} \times 0.1} \text{ g/mol} = 74285 \text{ g/mol}$$

Hence molar mass of the solute is 74285g/mol.

Example 21

2g of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) dissolved in 25g of benzene shows a depression in freezing point equal to 1.62K. Molal depression constant for benzene is 4.9Kkgmol^{-1} . What is the percentage association of acid if it forms dimer in solution?

Solution

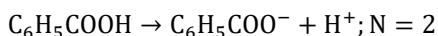
Using: $\Delta T = iK_f m$

$$\text{But } m = \frac{n_{\text{su}}}{m_{\text{sv}} \text{ in kg}} = \frac{m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}$$

$$\text{Then } \Delta T = \frac{i \times K_f \times m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}$$

$$\text{From which } i = \frac{\Delta T \times M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}{K_f \times m_{\text{su}}} = \frac{1.62 \times 122 \times 0.025}{4.9 \times 2} = 0.5042$$

Benzoic acid ionises according to the following equation:



$$\text{Then } \alpha = \frac{\frac{i-1}{N-1}}{\frac{1}{2}-1} = \frac{0.5042-1}{\frac{1}{2}-1} = 0.9916 \text{ or } 99.16\%$$

Hence degree of association of the acid is 99.16%

Example 22

The vapour pressure of water is 12.3kPa at 300K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.

Solution

Number of moles of solute in 1kg of water is 1mol (1 molal solution)

$$\text{And number of moles of water} = \frac{1000\text{g}}{18\text{gmol}^{-1}} = 55.5556\text{mol}$$

$$M_r = \frac{1\text{mol}}{(1 + 55.5556)\text{mol}} = 0.01768$$

$$\text{Using } \Delta P = X_{\text{su}} P_{\text{sv}}^0 = 0.01768 \times 12.3\text{kPa} = 0.22\text{kPa}$$

$$\text{Then } P_{\text{soln}}^0 = P_{\text{sv}}^0 - \Delta P = (12.3 - 0.22)\text{kPa} = 12.08\text{kPa}$$

Hence the vapour pressure of the solution is 12.08kPa

Example 23

A 5% solution (by mass) of cane sugar ($M_r = 342\text{g/mol}$) in water has freezing point of 271K. What will be the freezing point of 5% glucose ($M_r = 192\text{g/mol}$) in water if freezing point of pure water is 273.15K?

Solution

$$\Delta T = (273.15 - 271)\text{K} = 2.15\text{K}$$

$$m_{\text{su}} = 5\text{g}, m_{\text{sv}} = (100 - 5)\text{g} = 95\text{g} = 0.095\text{kg}$$

$$\text{Using } \Delta T = K_f m = K_f \times \frac{m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}$$

$$\text{From which } K_f = \frac{\Delta T \times M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}{m_{\text{su}}}$$

$$\text{Then } \frac{\Delta T_s \times M_s \times m_{sv} \text{ in kg}}{m_s} = \frac{\Delta T_g \times M_g \times m_{sv} \text{ in kg}}{m_g}$$

$$\text{Substituting } \frac{2.15\text{K} \times 342\text{g mol}^{-1} \times 0.095\text{kg}}{5\text{g}} = \frac{\Delta T_g \times 192\text{g/mol} \times 0.095\text{kg}}{5\text{g}}$$

From which; $\Delta T_g = 3.83\text{K}$

Hence the freezing point will be $(273.15 - 3.83)\text{K} = 269.32\text{K}$

Example 24

The boiling point of an aqueous solution is 101.21°C . What is the freezing point? ($K_f = 1.86^\circ\text{C kg mol}^{-1}$, $K_b = 0.52^\circ\text{C kg mol}^{-1}$)

Solution

$$\text{Using } \Delta T = K_b m \text{ or } m = \frac{\Delta T}{K_b}$$

But boiling point of pure water is 100°C .

And thus $\Delta T = (101.21 - 100)^\circ\text{C} = 1.21^\circ\text{C}$

$$\text{Then } m = \frac{1.21^\circ\text{C}}{0.52^\circ\text{C kg mol}^{-1}} = 2.33\text{mol/kg}$$

$$\text{Then using } \Delta T = K_f m = 1.86^\circ\text{C kg mol}^{-1} \times 2.33\text{mol/kg} = 4.33^\circ\text{C}$$

But freezing point of pure water is 0°C .

$$\text{Thus freezing point of the solution} = 0^\circ\text{C} - 4.33^\circ\text{C} = -4.33^\circ\text{C}$$

Hence the freezing point is -4.33°C .

Example 25

At 286K , the osmotic pressure of a glucose (Molar mass: 180g/mol) solution is 9.97atm . What is the freezing point of the solution (given the density of the solution is 1.12g/mL and $K_f = 1.86^\circ\text{C kg mol}^{-1}$)?

Solution

$$\text{Using } \pi V = nRT \text{ or } \pi = \frac{nRT}{V} = CRT$$

$$\text{From which } C = \frac{\pi}{RT} = \frac{9.97}{0.082 \times 286} \text{mol/L} = 0.4251\text{mol/L}$$

$$\text{Using } m = \rho V;$$

$$\text{Mass of the solution in 1L (1000mL)} = 1.12\text{g/mL} \times 1000\text{mL} = 1120\text{g}$$

$$\text{Using } m = nM_r;$$

Mass of the solute (glucose) in 1L of the solution

$$= 0.4251\text{mol} \times 180\text{g/mol} = 76.518\text{g}$$

Thus mass of solvent (water) in 1L of the solution

$$= (1120 - 76.518)\text{g} = 1043.482\text{g} = 1.043482\text{kg}$$

$$\text{Then molality of the solution} = \frac{0.4251\text{mol}}{1.043482\text{kg}} = 0.4074\text{mol/kg}$$

It follows that; $\Delta T = K_f m$

$$= 1.86^\circ\text{C kg mol}^{-1} \times 0.4074\text{mol/kg} = 0.76^\circ\text{C}$$

But freezing point of pure water is 0°C

$$\text{Hence freezing point of the solution} = 0^\circ\text{C} - 0.76^\circ\text{C} = -0.76^\circ\text{C}$$

Example 26

Cyclohexanol, $C_6H_{11}OH$, is sometimes used as the solvent in molar mass determination. If 0.235g of benzoic acid $C_7H_6O_2$, dissolved in 12.45g of cyclohexanol, lowered the freezing point of pure cyclohexanol by 6.55 °C.

- Calculate molality of benzoic acid.
- What is the molal freezing point constant (K_f) of the solvent?
- What will be the K_f value if the molality found in (a) above is doubled?

Solution

$$(a) \text{ Molality} = \frac{n_{su}}{m_{sv} \text{ in kg}} = \frac{m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$$

$$= \frac{0.235g}{122g/mol \times 0.01245kg} = 0.1547mol/kg$$

Molality of benzoic acid is 0.1547mol/kg

- Using $\Delta T = K_f m$;

$$\text{From which } K_f = \frac{\Delta T}{m} = \frac{6.55^\circ C}{0.1547mol/kg} = 42.34^\circ Ckg/mol$$

The molal freezing point constant is 42.34°Ckg/mol.

- The K_f value will not change and will remain to be 42.34°Ckg/mol (K_f value does not depend on the concentration of solute, it depends on the nature of the solvent).

Example 27

0.6mL of acetic acid, having density 1.06g/mL, is dissolved in 1litre of water. The depression in freezing point observed for this strength of acid was 0.0205°C. With reason state whether the acid undergoes dissociation or association in water and hence calculate the corresponding degree of dissociation or association. ($K_f = 1.86^\circ C/m$)

Solution

Using $m = \rho V$;

$$\text{Mass of the acid} = 1.06g/mL \times 0.6mL = 0.636g$$

$$\text{And mass of water} = 1g/mL \times 1000mL = 1000g = 1kg$$

$$\text{Using } \Delta T = K_f m = K_f \times \frac{m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$$

$$\text{From which; } M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}} = \frac{1.86 \times 0.636}{0.0205 \times 1} g/mol = 57.7g/mol$$

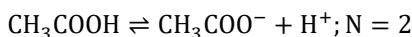
Thus the observed molar mass of the acid is 57.7g/mol

But the expected molar mass of the acid if would be no dissociation is 60g/mol

Since the observed molar mass is smaller than the expected one, the acid undergoes dissociation in water.

$$\text{Van't Hoff's factor, } i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{60}{57.7} = 1.04$$

Acetic acid ionises according to the following equation:



$$\text{Using } \alpha = \frac{i-1}{N-1} = \frac{1.04-1}{2-1} = 0.4 = 4\%$$

Hence the degree of dissociation is 4%.

Example 28

A solution containing 30g of non-volatile solute exactly in 90g of water has a vapour pressure of 2.8kPa at 298K. Further, 18g of water is then added to the solution and the new vapour pressure becomes 2.9kPa at 298 K. Calculate:

- Molar mass of the solute.
- Vapour pressure of water at 298K.
- Why vapour pressure increased after further addition of 18g of water?

Solution

Using; $M_{su} = \frac{m_{su} \times M_{sv} \times P_{sv}^o}{m_{sv} \times \Delta P}$ where $\Delta P = P_{sv}^o - P_{soln} = P_{sv}^o - 2.8$

Before further addition of 18g of water.

$$M_{su} = \frac{30 \times 18 \times P_{sv}^o}{90 \times (P_{sv}^o - 2.8)} \dots \dots \dots (i)$$

After further addition of 18g of water.

$$M_{su} = \frac{30 \times 18 \times P_{sv}^o}{108 \times (P_{sv}^o - 2.9)} \dots \dots \dots (ii)$$

Equating (i) and (ii) gives;

$$\frac{30 \times 18 \times P_{sv}^o}{90 \times (P_{sv}^o - 2.8)} = \frac{30 \times 18 \times P_{sv}^o}{108 \times (P_{sv}^o - 2.9)}$$

From which $P_{sv}^o = 3.4\text{kPa}$

Substituting $P_{sv}^o = 3.4\text{kPa}$ in (i) gives;

$$M_{su} = \frac{30 \times 18 \times 3.4}{90 \times (3.4 - 2.8)} \text{ g/mol} = 34\text{g/mol}$$

Hence:

- Molar mass of the solute is 34g/mol and
- The vapour pressure of water is 3.4kPa
- Further addition of water which is solvent decreases solute concentration and thus leading to less lowering in vapour pressure and hence higher vapour pressure for the solution.

Example 29

- Silver chloride is a non-volatile material, but does not dissolve in water. What effect will it have on the boiling point of water?
- Calculate the osmotic pressure of solution obtained by mixing 100cm³ of 0.25M solution of urea and 100cm³ of solution of 0.1M solution of cane sugar at 293K.

Solution

- Negligible effect; because it does not dissolve in water and therefore cannot interact with water molecules and hence no elevation in boiling point of water will be observed.

$$(b) \text{ Using } M_3 = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2} = \frac{100 \times 0.25 + 100 \times 0.1}{100 + 100} = 0.175\text{M}$$

Thus molarity of the solution containing solutes mixture is 0.175M

$$\text{Using } \pi = [] RT = 0.175 \times 0.082 \times 298\text{atm} = 4.3\text{atm}$$

The osmotic pressure is 4.3atm.

Example 30

A 1.60g sample of a mixture of naphthalene (C₁₀H₈) and anthracene (C₁₄H₁₀) is dissolved in 20.0g benzene (C₆H₆). The freezing point of the solution is found to be 2.81°C. What is the composition as mass percent of the sample mixture? (The freezing point of benzene is 5.51°C and K_f is 5.12 °Ckg/mol).

Solution

$$\Delta T = 5.51^{\circ}\text{C} - 2.81^{\circ}\text{C} = 2.7^{\circ}\text{C}$$

$$\Delta T = K_f m = K_f \times \frac{n_{\text{su}}}{m_{\text{sv}} \text{ in kg}}$$

$$\text{From which; } n_{\text{su}} = \frac{\Delta T \times m_{\text{sv}} \text{ in kg}}{K_f} = \frac{2.7 \times 0.02}{5.12} = 0.01 \text{ mol}$$

Let mass of naphthalene be n

Then mass of anthracene will be $1.6 - n$

Then using $n = \frac{m}{M_r}$;

$$\text{Number of moles of naphthalene} = \frac{n}{128}$$

$$\text{Number of moles of anthracene} = \frac{1.6 - n}{178}$$

$$\text{It follows that: } n_{\text{su}} = 0.01 = \frac{n}{128} + \frac{1.6 - n}{178}; 23.04 = 50n$$

$$\text{From which } n = 0.4608 \text{ and } 1.6 - n = 1.6 - 0.4608 = 1.1392$$

$$\% \text{naphthalene} = \frac{0.4608 \text{ g}}{1.6 \text{ g}} \times 100\% = 28.8\%$$

$$\% \text{anthracene} = \frac{1.1392 \text{ g}}{1.6 \text{ g}} \times 100\% = 71.2\%$$

Hence the composition is 28.8% naphthalene and 71.2% anthracene by mass.

DIGGING DEEPER EXERCISE 7

EXERCISE 7A: BINDER QUESTIONS

Question 1

A salt solution sits in an open beaker. Assuming constant temperature and pressure; would you expect the vapour pressure of the solution to decrease, to increase or to remain the same over time? Explain.

Question 2

The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.

Question 3

Osmotic pressure and freezing point depression have the same origin. Explain.

Question 4

What are isotonic solutions? Explain.

Question 5

Why 0.1molar HCl shows greater depression in freezing point than 0.1molar acetic acid?

Question 6

Why electrolytes have abnormally high values of colligative properties?

Question 7

Equimolar solutions of sucrose and sodium chloride in water are not isotonic. Explain giving reasons.

Question 8

Arrange the following aqueous solutions in order of decreasing freezing points:

- 0.10m KNO_3
- 0.10m BaCl_2
- 0.10m $\text{C}_2\text{H}_4(\text{OH})_2$
- 0.10m Na_3PO_4

Question 9

Why benzoic acid dissolved in benzene shows a lesser value of osmotic pressure than expected one while when dissolved in water it shows greater value than the expected one?

Question 10

What is the relationship between the Van't Hoff factor for a compound and its lattice energy? Explain.

Question 11

List down two factors to which colligative properties depend.

Question 12

Calculate the mass of ascorbic acid (Vitamin C, $\text{C}_6\text{H}_8\text{O}_6$) to be dissolved in 75g of acetic acid to lower its melting point by 1.5°C . $K_f = 3.9\text{Kkgmol}^{-1}$

Question 13

The vapour pressure of pure benzene at certain temperature is 640mmHg. A non-volatile solid weighing 2.175g is added to 39g of benzene. The vapour pressure of the solution is 600mmHg. What is the molecular mass of the solid substance?

Question 14

Pure 2-methyl-2-propanol has a freezing point of 25.50°C , however it absorbs water (as an impurity) on exposure to humid air. If the freezing point of a 100.0g sample of 2-methyl-2-propanol is 24.59°C , how many grams of water are present in the sample? K_f (2-methyl-2-propanol) = 4.68°C/m .

Question 15

An antifreeze solution is prepared from 222.6g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) and 200g of water.

- Calculate the molality of the solution.
- If the density of the solution is 1.072g/mL, then what shall be the molarity of the solution?
- At what temperature will the solution freeze? ($K_f = 1.86^\circ\text{C}/\text{m}$)

EXERCISE 7B: REAL QUESTIONS**Question 16**

Explain why a raw mango shrivels when placed in concentrated salt solution.

Question 17

Explain why wilted flowers revive when placed in fresh water.

Question 18

Explain why addition of salt or sugar can protect food against bacteria actions and therefore helps as the method of food preservation.

Question 19

To get the hard boiled eggs, why common salt is added to water before boiling the eggs?

Question 20

NaCl is less expensive than either CaCl_2 or MgCl_2 . However in salting of roads in cold-weather climates, CaCl_2 and MgCl_2 are used most frequently.

- What is the main aim of salting the road?
- Why CaCl_2 and MgCl_2 are more preferred?

Question 21

Explain how colligative properties are important in making antifreeze?

Question 22

Many people get thirsty after eating foods such as ice cream or potato chips that have a high sugar or salt content, respectively. Suggest an explanation for this phenomenon.

Question 23

You take a bottle of a soft drink out of your refrigerator. The contents are liquid and stay liquid even when you shake them. Thirstily, you remove the cap, and the liquid freezes solid! Offer a possible explanation of this observation.

Question 24

If you were stranded on a desert island, why would drinking seawater lead to an increased rate of dehydration, eventually causing you to die of thirst?

Question 25

Your friend, **Kipute** was given an assignment on topic of colligative properties. However, she is not sure about her response to some of questions. Below are responses, **Kipute** doubted about their accuracy.

- Isotonic solutions at given temperature have the same boiling point elevation and freezing point depression.
- Two different solutions with the same effective molality in the solution exhibit the same boiling point elevation.
- Colligative properties do not depend on the nature of solvent.

If **Kipute** came to you and seek for your help; then guide your friend by telling her whether each statement is correct or not and provide for her clear explanation to support your guidance.

EXERCISE 7C: HOT QUESTIONS**Question 26**

Calculate the mass of a non-volatile solute (molar mass 40g/mol) which should be dissolved in 114g of octane to reduce its vapour pressure to 80%

Question 27

A 5% solution (by mass) of cane sugar in water has freezing point of 271K. Calculate the freezing point of 5% glucose in water if the freezing point of pure water is 273.15K.

Given that:

Molar mass of glucose = 180g/mol

Molar mass of cane sugar = 342g/mol

Question 28

Two elements A and B form compound having formula AB_2 and AB_4 . When dissolved in 20g of benzene (C_6H_6), 1g of AB_2 lowers the freezing point by 2.3K whereas 1g of AB_4 lowers it by 1.3K. The molal depression constant for benzene is 5.1Kkg/mol. Calculate atomic masses of A and B.

Question 29

Calculate the osmotic pressure of a solution 0.1m of sucrose (Mwt = 342g/mol) at 20°C

Question 30

At what temperature will salt solution boil if 20g salt (NaCl) is added to 1kg of water?

Question 31

Determine the amount of $CaCl_2$ ($i = 2.47$) dissolved in 2.5L of water such its osmotic pressure is 0.75 atm at 27°C

Question 32

Determine the osmotic pressure of a solution prepared by dissolving 25mg of K_2SO_4 in 2L of water at 25°C, assuming that is completely dissociated

Question 33

An aqueous solution of nitrous acid (HNO_2) freezes at $-0.198^\circ C$. If the solution was prepared by adding 0.1 mole of the acid to 1000g of water, what percentage of the HNO_2 is dissociated in the solution? ($K_f = 1.86$)

Question 34

An aqueous solution of a non-volatile and non-electrolyte substance boils at $100.5^\circ C$. Calculate osmotic pressure of this at 27°C K_b (For water is 0.5)

Question 35

Given that the vapour above an aqueous solution contains 18.3mg water per litre at $25.0^\circ C$, what is the concentration of the solute within the solution in mole fraction? Vapour pressure of pure water at $25.0^\circ C$ is 23.8mmHg. Assume ideal behaviour.

Chapter 8

DISTRIBUTION LAW

INTRODUCTION

Distribution law or **partition law** gives generalisation which governs the **distribution** or **partition** of solute between immiscible solvents. The law explains what happens when a non – volatile solute is introduced to the container containing immiscible mixture and the solute is capable of dissolving in both liquids (solvents). Distribution law was discovered by Nernst and therefore is also known as **Nernst's distribution law**.

It states that: *When a non – volatile solute is introduced into the container containing two immiscible solvents mixture, the solute tends to distribute itself (irrespective to its amount) in such a way that there is a fixed ratio of concentration of the solute in the two solvents, provided that the molecular state of the solute remains the same in the two solvents and the temperature is kept constant.*

The fixed ratio obtained according to the **partition law** is known as **partition coefficient (K_d)** or **distribution coefficient** or **distribution ratio**.

Definition of partition coefficient (K_d)

This is the temperature dependent constant which is obtained as the ratio of concentration of the non-volatile solute in the two immiscible solvents mixture when the solute is allowed to distribute itself in the mixture.

That is;
$$K_d = \frac{\text{Concentration of the solute in the first solvent}}{\text{Concentration of the solute in the second solvent}} \dots \dots \dots (i)$$

$$K_d = \frac{\text{Concentration of the solute in the upper layer}}{\text{Concentration of the solute in the lower layer}} \dots \dots \dots (ii)$$

Qualitatively, the partition coefficient gives relative solubility of the solute in the given solvents. So from equation (i), if K_d is large then the solute is more soluble in the first solvent and vice versa. For example, if K_d is 5, it means that the solute is 5 times more soluble in the first solvent than in the second solvent.

That is;

$$\frac{\text{concentration of solute in first solvent}}{\text{concentration of solute in second solvent}} = \frac{\text{solubility of solute in first solvent}}{\text{solubility of solute in second solvent}} = K_d$$

Hence knowing the value of partition coefficient (K_d) and the solubility of solute in one of the solvents, the solubility of the solute in the second solvent can be calculated.

You should be aware of this fact:

Although basically the law requires the use of molar concentration (remember, it state just 'concentration' which in turn must means molar concentration as pointed earlier on methods of representing concentration), mass concentration can also be used as shown below.

$$K_d = \frac{[\text{solute}] \text{ in the first solvent}}{[\text{solute}] \text{ in the second solvent}}$$

$$\text{But } [\text{solute}] = \frac{\text{mass concentration of solute}}{\text{molar mass of the solute}}$$

It follows that:

$$\begin{aligned} K_d &= \frac{\frac{\text{mass concentration of solute in the first solvent}}{\text{molar mass of the solute}}}{\frac{\text{mass concentration of solute in the second solvent}}{\text{molar mass of the solute}}} \\ &= \frac{\text{mass concentration of solute in the first solvent}}{\text{mass concentration of solute in the second solvent}} \end{aligned}$$

Hence: $K_d = \frac{\text{mass concentration of solute in the first solvent}}{\text{mass concentration of solute in the second solvent}}$

So, the possibility of using mass concentration instead of molar concentration is due to the cancellation of the molar mass when molar concentration is written in terms of mass concentration.

DERIVATION OF DISTRIBUTION LAW

If we take two immiscible solvents, say A and B in a beaker, they form separate layers. When a solute X which is soluble in both solvents is added, it gets **distributed** or **partitioned** between them. Molecules of X pass from solvent A to B and from solvent B to solvent A. Finally, a dynamic equilibrium is set up. At equilibrium, the rate at which molecules of X pass from one solvent to the other is balanced. This explanation is the basis of derivation of the Nernst's partition law as shown below.

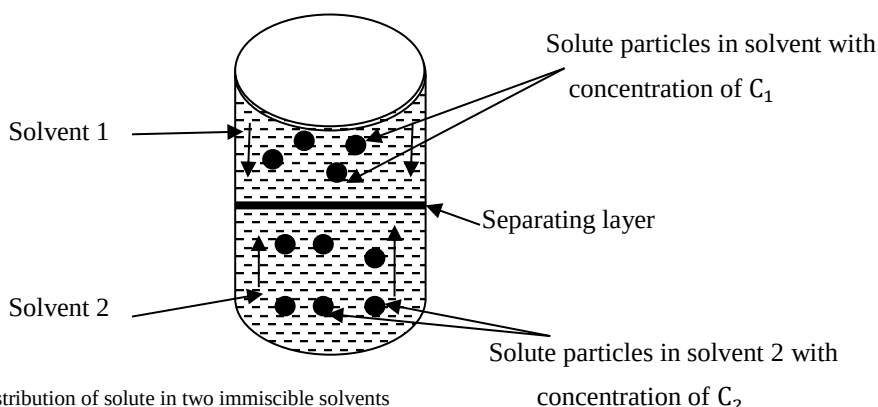


Figure 8.1 Distribution of solute in two immiscible solvents

The rate of diffusion of solute particles from one solvent to another is directly proportional to the concentration of the solute in the solvent.

So if;

R_1 is the rate of diffusion of the solute from the solvent 1 to solvent 2

R_2 is the rate of diffusion of the solute from the solvent 2 to solvent 1

The $R_1 \propto C_1$ or $R_1 = K_1 C_1 \dots \dots \dots$ (i) (K_1 is the constant for proportionality)

And $R_2 \propto C_2$ or $R_2 = K_2 C_2 \dots \dots \dots$ (ii) (K_2 is the constant for proportionality)

After certain time of diffusion, the equilibrium will be established where; $R_1 = R_2$

Thus at equilibrium: $K_1 C_1 = K_2 C_2$ or $\frac{K_2}{K_1} = \frac{C_1}{C_2}$

But $\frac{K_2}{K_1}$ gives another constant which is known as the **partition coefficient, K_d**

Hence $K_d = \frac{\text{Concentration of solute in the solvent 1}}{\text{Concentration of solute in the solvent 2}}$

Where K represents the constant and the subscript 'd' stands for **distribution** and hence K_d is also known as **distribution constant**.

SOLVENT EXTRACTION

One of the common applications of distribution law is in the **solvent extraction**

Principle of solvent extraction

Solvent extraction is the method of removing (extracting) a solute from a certain solvent by introducing the second solvent (**extractive solvent**) which is immiscible to the first one and then allowing the solute to distribute itself in the two solvents. The layer of extractive solvent is then removed with significant amount of the solute and on successive extractions which are done by introducing fresh extractive solvent again and again, the solute is finally completely removed from the first solvent (or very small amount remain in the first solvent).

Taking solvent extraction in consideration, the partition (distribution) coefficient may be written as follows:

$$K_d = \frac{\text{Concentration of the solute in the extractive solvent}}{\text{Concentration of the solute in the residue solution}} \dots \dots \dots (iii)$$

Conditions for efficient solvent extraction

For the solvent extraction to be more efficient the following conditions should be fulfilled:

- 1) The solute must be more soluble in extractive solvent than in the first solvent.

This implies that, K_d should be large ($K_d > 1$) if the portion coefficient is found according to the equation (iii).

Be careful:

If the extractive solvent appears in the lower layer, then the partition coefficient obtained by equation (ii) and (iii) are reciprocal to each other. Thus if K_d appears to be small (less than one), this suggests the partition coefficient is obtained by using equation (ii) and extractive solvent is in the lower layer.

- 2) The volume of extractive solvent should be divided into small portions (partitions) rather than using the whole volume at once.

Here, the greater number of portions of volume of extractive solvent, the greater amount of the solute will be extracted.

LIMITING CONDITIONS FOR DISTRIBUTION LAW

Below are conditions for the distribution law to be applicable.

- 1) **Constant temperature:** Partition coefficient is temperature dependent. So the temperature must be kept constant while doing experiment involving the distribution law.
- 2) **Same molecular state:** The molecular state of the solute must be the same in the two solvents. The law does not hold if there is **dissociation** or **association** or any other **chemical reaction** in one of the solvents.
- 3) **Equilibrium concentration:** The concentration of the solute must be noted after equilibrium has been established.
- 4) **Dilute solution:** The concentration of the solute in the two solvents must be low. The law does not hold when the concentration is high.
- 5) **Non miscibility of solvents:** The two solvents must be immiscible or only slightly soluble in each other.

Modification of distribution law in change of molecular state of solute

It has been pointed that, distribution law is true if and only if the molecular state in the two solvents remain the same. In case there is either dissociation or association in one of the solvent, the law does not hold.

That is, if there is either dissociation or association,

$$\frac{\text{concentration solute in the first solvent}}{\text{concentration of solute in the second solvent}} \neq \text{constant}$$

We are going to look the required modification for each case (of dissociation and association) separately.

Case 1: If the solute undergoes association

Suppose the solute is present as simple molecule X in solvent A while n molecules of X associate to form X_n in solvent B.

Assuming that a few simple molecules of X are also present in the solvent B (X is in equilibrium with X_n) as shown in the figure below.

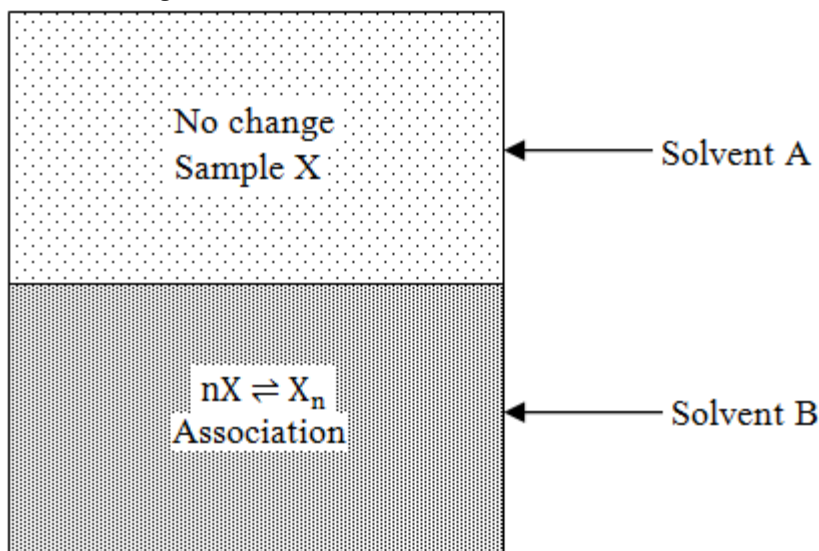


Figure 8.2 Distribution of solute in immiscible solvents with association of the solute in one of the solvents

Now let C_1 be $[X]$ in solvent A

C_2 be $[X_n]$ in solvent B

C_3 be $[X]$ in solvent B

Considering the equilibrium between X in solvent A and X in solvent B, we get:

$$\frac{C_1}{C_3} = K_d \dots\dots\dots (i)$$

Also considering the equilibrium: $nX \rightleftharpoons X_n$

$$K_c = \frac{[X_n]}{[X]^n} = \frac{C_2}{(C_3)^n}$$

$$\text{Or } (C_3)^n = \frac{C_2}{K_c}$$

From which, $C_3 = \sqrt[n]{\frac{C_2}{K_c}} \dots\dots\dots(ii)$

Substituting (ii) in (i) gives: $\frac{C_1}{\sqrt[n]{K_c}} = K_d$

$$\text{Or } \frac{C_1 \times \sqrt[n]{K_c}}{\sqrt[n]{C_2}} = K_d \text{ or } \frac{C_1}{\sqrt[n]{C_2}} = \frac{K_d}{\sqrt[n]{K_c}}$$

But $\frac{K_d}{\sqrt[n]{K_c}}$ gives another constant, say K

$$\text{Thus } \frac{C_1}{\sqrt[n]{C_2}} = K$$

Hence when a solute associate as X_n in second solvent while it remains unchanged as a simple molecule in the first solvent, the distribution equation is modified as:

$$K = \frac{C_1}{\sqrt[n]{C_2}}$$

Since the solute exists largely as associated molecules, the total concentration of X determined experimentally in solvent B is taken as the concentration of the associated molecules X_n .

Case 2: If the solute undergoes dissociation

Suppose the solute is present as normal molecule X in solvent A and it dissociated into Y and Z in solvent B.

Also assuming that a few normal molecules of undissociated X are also present in the solvent B as shown in the figure below.

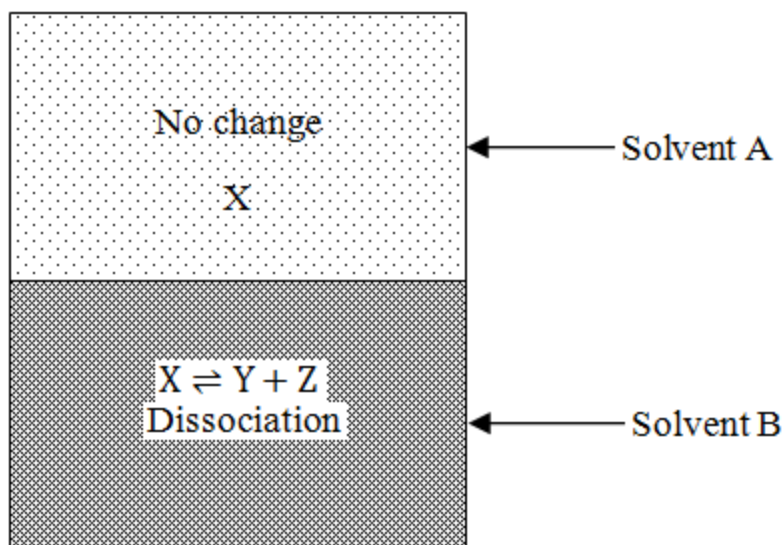


Figure 8.3 Distribution of solute in immiscible solvents with dissociation of the solute in one of the solvents

Now let C_1 be $[X]$ in solvent A

And C_2 be total $[X]$ in solvent B before the dissociation

If α is the degree of dissociation of X in solvent B; then:



At equilibrium $1 - \alpha \quad \alpha \quad \alpha$

But fraction of X which remain undissociated in X, $1 - \alpha$

$$= \frac{\text{concentration of X which is undissociated}}{\text{original concentration of X before dissociation, } C_2}$$

Thus concentration of X which is undissociated in B = $(1 - \alpha)C_2$

Then applying distribution law; $K_d = \frac{[\text{Normal X}] \text{ in A}}{[\text{Normal X}] \text{ in B}} = \frac{C_1}{C_2(1 - \alpha)}$

Hence the modified distribution equation when a solute dissociate in the second solvent while remains undissociated in the first solvent is;

$K_d = \frac{C_1}{C_2(1 - \alpha)}$ where α is the degree of dissociation of the solute in the second solvent.

Have you noticed this.....?

From the formula;

$$K_d = \frac{C_1}{C_2(1 - \alpha)}$$

You will find that, if $\alpha = 1$ (the solute is completely dissociated in the second solvent), $1 - \alpha$ becomes $1 - 1 = 0$ and therefore over equation becomes $K_d = \frac{C_1}{0} = \infty$. Hence the partition coefficient is undefined when the solute is completely dissociated in one of the two solvents.

WORKED EXAMPLES ON DISTRIBUTION LAW

Example 1

Z is allowed to reach an equilibrium distribution between the liquid ethoxyethane and water. The ether layer is 50cm^3 in volume and contains 4g of Z. The aqueous layer is 250cm^3 in volume and contains 1g of Z. What is the partition coefficient of Z between ethoxyethane and water?

Solution

$$K_d = \frac{\text{Concentration of the solute in ethoxyethane (first solvent)}}{\text{Concentration of the solute in the water (second solvent)}}$$

Then $K_d = \frac{4\text{g}/50\text{cm}^3}{1\text{g}/250\text{cm}^3} = 20$

So the partition coefficient of Z between ethoxyethane and water is 20.

Example 2

An organic acid is allowed to reach an equilibrium distribution in a separating funnel containing 50cm^3 of ethoxyethane and 500cm^3 of water. On titration, 25cm^3 of ethoxyethane layer required 22.5cm^3 of 1mol dm^{-3} sodium hydroxide solution while 25cm^3 of the aqueous layer required 9cm^3 of 0.1mol dm^{-3} sodium hydroxide. Calculate the partition coefficient for the acid between ethoxyethane and water.

Solution

Equation for the neutralisation reaction: $\text{RCOOH} + \text{NaOH} \rightarrow \text{RCOONa} + \text{H}_2\text{O}$

From which $n_a = 1$, $n_b = 1$

Using $\frac{M_a V_a}{M_b V_b} = \frac{n_a}{n_b}$ But $n_a = n_b$

Then $M_a V_a = M_b V_b$ Or $M_a = \frac{M_b V_b}{V_a}$

For organic (ethoxyethane) layer:

$V_a = 25\text{cm}^3$, $M_b = 1\text{M}$ and $V_b = 22.5\text{cm}^3$

$$\text{Then } M_a = \frac{1 \times 22.5}{25} M = 0.9M$$

For aqueous layer:

$$V_a = 25\text{cm}^3, M_b = 0.1M \text{ and } V_b = 9\text{cm}^3$$

$$\text{Then } M_a = \frac{0.1 \times 9}{25} M = 0.036$$

$$K_d = \frac{[\text{Acid}] \text{ in organic layer}}{[\text{Acid}] \text{ in aqueous layer}} = \frac{0.9}{0.036} = 25$$

Hence the partition coefficient for the acid between ethoxyethane and water is 25.

Example 3

The following figures relate to iodine in tetrachloromethane (carbon tetrachloride) and water when the solutions are in equilibrium at a certain temperature.

Grams of Iodine per dm³

In CCl ₄	17.50	15.80	13.20	6.50
In H ₂ O	0.200	0.180	0.150	0.075

- Calculate the distribution constant of iodine between these two solvents.
- What is the effect of shaking 1 dm³ of water containing 0.3g of iodine with 10 cm³ of tetrachloromethane?

Solution

Concentration of I ₂ in CCl ₄ /gdm ⁻³	17.500	15.800	13.200	6.500
Concentration of I ₂ in H ₂ O/gdm ⁻³	0.200	0.180	0.150	0.075
$K = \frac{\text{Concentration of I}_2 \text{ in CCl}_4}{\text{Concentration of I}_2 \text{ in H}_2\text{O}}$	87.500	87.778	88.000	86.667

$$K_d = \frac{87.500+87.778+88.000+86.667}{4} = 87.486$$

- Hence the partition coefficient of Iodine between carbon tetrachloride and water is 87.486.
- Let mass of iodine extracted in CCl₄ be x.

Then mass of iodine left in water will be 0.3 – x

$$\text{So } 87.486 = \frac{\frac{x}{10}}{0.3 - \frac{x}{1000}} = \frac{100x}{0.3 - x}; \quad x = 0.14\text{g} \quad \text{And } 0.3 - x = 0.16\text{g}$$

So iodine will distribute itself in the two solvents, such that 0.14g will be found in organic (CCl₄) layer and 0.16g will be left in the water (aqueous) layer.

Example 4

X is 12 times more soluble in trichloromethane than in water. What mass of X will be extracted from 1 dm³ of an aqueous solution containing 25g by shaking with 100 cm³ of trichloromethane?

Solution

The extractive solvent is trichloromethane (CHCl₃)

Let mass of x extracted in grams be y

Then mass of x which remains in the residue solution will be $25 - y$

Using:

$$K_d = \frac{\text{Concentration of X in CHCl}_3}{\text{Concentration of X in H}_2\text{O}}$$

But $K_d = 12$ (X is 12 times more soluble in CHCl_3 than in H_2O)

$$\text{Then } 12 = \frac{y/100}{25-y/1000} = \frac{10y}{25-y}$$

$$22y = 300, y = 13.6$$

Hence 13.6 of X will be extracted

Example 5

If iodine is shaken with 100mL of water and 100mL of an organic solvent, the concentration of iodine in the water layer is 0.004M and in the organic solvent is 0.01M.

- Calculate the partition coefficient for iodine between the organic solvent and water.
- The aqueous layer is separated and shaken with 50mL of the pure organic solvent. What will be the molar concentration of iodine in the organic solvent at equilibrium?

Solution

$$K_d = \frac{[\text{Iodine}] \text{ in organic solvent}}{[\text{Iodine}] \text{ in water}} = \frac{0.01\text{M}}{0.004\text{M}} = 2.5$$

The partition coefficient for iodine between the organic solvent and water is 2.5.

Total number of moles of iodine in water layer before shaking with fresh organic solvent = $\frac{100}{1000} \times 0.004\text{mol} = 0.0004\text{mol}$

If number of moles of iodine that went to organic layer is 'a',

Then number of moles of iodine that remained in water layer will be $0.0004 - a$

$$\text{Thus } 2.5 = \frac{\frac{a}{50}}{\frac{0.0004-a}{100}}; a = 0.00022$$

$$\text{Then } [\text{Iodine}] \text{ in organic solvent} = \frac{0.00022\text{mol}}{50 \times 10^{-3}\text{L}} = 0.0044\text{M}$$

The molar concentration of iodine in the organic solvent is 0.0044M

Example 6

The distribution coefficient of A between water and ethoxyethane is 90 in favour of ethoxyethane. An aqueous solution with a volume of 500 cm^3 contains 5g of A. What mass of A will be extracted by:

- 100 cm^3 of ethoxyethane
- Two successive portions of 50 cm^3 of ethoxyethane
- What can you conclude from the result obtained in (i) and (ii) above?

Solution

The phrase, "in favour of ethoxyethane" means that A is more soluble in the ethoxyethane;

$$\text{That is } K_d = \frac{\text{Concentration of A in ethoxyethane}}{\text{Concentration of A in water}} = 90$$

- Let mass of A extracted in grams be x

$$\text{Then: } 90 = \frac{x/100}{5-x/500} = \frac{5x}{5-x}$$

$$95x = 450, x = 4.74\text{g}$$

Mass of A extracted by 100cm^3 of ethoxyethane is 4.74g.

(ii) Let mass of A extracted in the first extraction be m_1

$$\text{Then } 90 = \frac{m_1/50}{5-m_1/500} = \frac{10m_1}{5-m_1}$$

$$100m_1 = 450, m_1 = 4.5\text{g}$$

$$\text{Mass of A remained after the first extraction} = 5 - m_1 = (5 - 4.5)\text{g} = 0.5\text{g}$$

Let mass of A extracted in the second extraction be m_2

$$\text{Then } 90 = \frac{m_2/50}{0.5-m_2/500} = \frac{10m_2}{0.5-m_2}$$

$$100m_2 = 45, m_2 = 0.45$$

$$\text{Total mass extracted} = m_1 + m_2 = (4.5 + 0.45)\text{g} = 4.95\text{g}$$

Hence mass of A extracted by two successive portions of 50cm^3 of ethoxyethane is 4.95g.

(iii) The greater amount of A is extracted when the volume of extracted solvent is divided into small portions rather than using the whole volume at once.

Alternative solution for (ii)

The easier method of dealing with problems which involve more than one extraction is by using the following general formula for mass of solute left unextracted:

$$W_r = W_o \left(\frac{V_b}{V_b + K_d V_a} \right)^n$$

Where: W_r is the mass of solute which remain in residue solution after n extractions.

W_o is the original mass of the solute before extraction

V_b is the volume of residue solution

V_a is the volume of an extraction solvent used in each extraction (experiment)

n is the number extractions.

K_d is the partition coefficient obtained **according to the equation (iii)**

And in this question:

$$W_o = 5\text{g}, V_b = 500\text{cm}^3, V_a = 50\text{cm}^3, K_d = 90 \text{ and } n = 2$$

$$\text{Then } W_r = 5 \left(\frac{500}{500 + (50 \times 90)} \right)^2 = 0.05\text{g}$$

$$\text{Mass of A extracted after two extractions} = W_o - W_r = (5 - 0.05)\text{g} = 4.95\text{g}$$

Hence mass of A extracted by two successive portions of 50cm^3 of ethoxyethane is 4.95g

The reader should understand that:

When the formula in the alternative solution is used, the extractive solvent must appear on numerator in the formula for finding K_d (equation (iii) in **page 180** must be used). **If the extractive solvent is the lower layer and the given K_d is found according to equation (ii), the 'required' K_d is the reciprocal of the given K_d .** You may have better understanding of this fact if you understand the derivation of the formula as shown in the next page:

If:

W_o is the total mass of the solute in the solution at the beginning of the solvent extraction,

V_a is the volume of extractive solvent used in each extraction,

V_b is the volume of the residue solution,

W_r is the mass remained after all extractions.

Then with the formula: $K_d = \frac{\text{Concentration of solute in the extractive solvent}}{\text{Concentration of solute in the residue solution}}$

The W_r after 'n' extractions can be found as follows;

For first extraction:

$$K_d = \frac{W_o - W_1}{\frac{V_a}{\frac{W_1}{V_b}}}$$

Where W_1 is the mass of solute remained in the residue solution after first extraction.

Then making W_1 the subject of the above formula as follows;

$$K_d = \frac{V_b(W_o - W_1)}{V_a W_1} \text{ or } V_a W_1 K_d = V_b W_o - V_b W_1$$

From which or $V_a W_1 K_d + V_b W_1 = V_b W_o$ or $W_1 (V_a K_d + V_b) = V_b W_o$

$$\text{Thus } W_1 = \frac{V_b W_o}{V_a K_d + V_b}$$

For second extraction

W_o of the second extraction, is W_1 of the first extraction and if W_2 is the mass of the solute remained in the residue solution after the second extraction;

The formula $W_1 = \frac{V_b W_o}{V_a K_d + V_b}$ in the second extraction becomes;

$$W_2 = \frac{V_b W_1}{V_a K_d + V_b}$$

$$\text{But } W_1 = \frac{V_b W_o}{V_a K_d + V_b};$$

$$\text{Then } W_2 = \left(\frac{V_b}{V_a K_d + V_b} \right) \left(\frac{V_b W_o}{V_a K_d + V_b} \right) = W_o \left(\frac{V_b}{V_a K_d + V_b} \right)^2$$

For third extraction;

Here W_o of the third extraction is W_2 of the second extraction

And W_3 will represent mass of the solute remained in the residue solution after the third extraction

$$\begin{aligned} \text{Then } W_3 &= \frac{V_b W_2}{V_a K_d + V_b} = \left(\frac{V_b}{V_a K_d + V_b} \right) W_o \left(\frac{V_b}{V_a K_d + V_b} \right)^2 \\ &= W_o \left(\frac{V_b}{V_a K_d + V_b} \right)^3 \end{aligned}$$

$$\text{Thus } W_3 = W_o \left(\frac{V_b}{V_a K_d + V_b} \right)^3$$

For nth extraction;

$$\text{According to the trend drawn above; } W_n = W_o \left(\frac{V_b}{V_a K_d + V_b} \right)^n = W_r$$

Example 7

The **Moguli** oil company is disturbed by the presence of impurity **M** in its four-star petroleum. One dm^3 of petrol contains 5g of **M**. In the effort to reduce the concentration of **M** in the petroleum, **Moguli** has discovered the secret of extracting **M** from the petrol by using solvent **S**. The partition coefficient of **M** between petrol and **S** is 0.01

- What are the conditions necessary for the partition of the solute between the given solvents to remain constant?
- Calculate the total mass of **M** removed from 1 dm^3 of petrol using one portion of 100 cm^3 of solvent **S**. In other case use two 50 cm^3 portions of solvent, **S**.

Solution

(a)

(i) The state of solute must remain the same in both solvents. Thus there must be no chemical reaction, association or dissociation of solute in either of the solvent.

(ii) The temperature must be constant.

$$(b) W_r = W_o \left(\frac{V_b}{V_b + K_d V_a} \right)^n \dots\dots\dots (1)$$

The partition coefficient of **M** between petrol and **S** = $\frac{\text{Concentration of M in petrol}}{\text{Concentration of M in S}} = 0.01$

But the extractive solvent is **S**, and the equation (1) requires **S** on numerator in K_d expression.

$$\text{So the required } K_d = \frac{\text{Concentration of M in S}}{\text{Concentration of M in petrol}} = \frac{1}{0.01} = 100$$

So the useful K_d is 100.

First case: By using one portion of 100 cm^3

$$W_o = 5\text{g}, V_b = 1000 \text{ cm}^3, V_a = 100 \text{ cm}^3, K_d = 100, n = 1$$

$$W_r = 5 \left(\frac{1000}{1000 + (100 \times 100)} \right)^1 = 0.45\text{g}$$

$$\text{Mass of M removed} = W_o - W_r = (5 - 0.45)\text{g} = 4.55\text{g}$$

Second case: By using two 50 cm^3 portions of **S**

$$W_o = 5\text{g}, V_b = 1000 \text{ cm}^3, V_a = 100 \text{ cm}^3, K_d = 100, n = 2$$

$$W_r = 5 \left(\frac{1000}{1000 + (100 \times 50)} \right)^2 = 0.14\text{g}$$

$$\text{Total mass of M removed} = W_o - W_r = (5 - 0.14)\text{g} = 4.86\text{g}$$

Alternative solution:

$$\text{Given that: } K_d = \frac{\text{Concentration of M in petrol}}{\text{Concentration of M in S}} = 0.01$$

1st case:

By using one portion of 100 cm^3 of **S**

Let mass of **M** extracted by extractive solvent **S** be y

Then mass of **M** which remain in petroleum will be $5 - y$

$$\text{Then } 0.01 = \frac{5-y}{100} = \frac{5-y}{100} \text{ or } y = 4.55\text{g}$$

Hence mass of **M** removed is 4.55g

2nd case:

By using two 50cm³ portions of **S**

Let mass of **M** extracted in the first extraction be m_1

$$\text{Then } 0.01 = \frac{5-m_1/1000}{m_1/50} = \frac{5-m_1}{20m_1}$$

From which $m_1 = 4.17\text{g}$

Mass of **M** remained after first extraction = $5 - m_1 = (5 - 4.17)\text{g} = 0.83\text{g}$

Let mass of **M** extracted in the second extraction be m_2

$$\text{Then } 0.01 = \frac{0.83-m_2/1000}{m_2/50} = \frac{0.83-m_2}{20m_2} \quad \text{or} \quad m_2 = 0.69\text{g}$$

Total mass of **M** extracted = $m_1 + m_2 = (4.17 + 0.69)\text{g} = 4.86\text{g}$

Example 8

If 10g of acid is dissolved in the mixture of 100cm³ of water and 100cm³ of ether. Calculate:

- The amount of acid extracted by 100cm³ of ether in one extraction only.
- The amount of acid extracted by using four consecutive extractions of 25cm³ in each extraction.

$$\text{Given that: } \frac{[\text{Acid}] \text{ in water}}{[\text{Acid}] \text{ in ether}} = 0.2$$

Solution

$$W_r = W_o \left(\frac{V_b}{V_b + K_d V_a} \right)^n \dots\dots\dots (1)$$

$$\text{The partition coefficient of acid between water and ether} = \frac{\text{Concentration of acid in water}}{\text{Concentration of acid in ether}} = 0.2$$

But the extractive solvent is ether, and the equation (1) requires the extractive solvent on numerator in K_d expression.

$$\text{So the required } K_d = \frac{\text{Concentration of acid in ether}}{\text{Concentration of acid in water}} = \frac{1}{0.2} = 5$$

So the useful K_d is 5.

First case: By using one portion of 100cm³

$$W_o = 10\text{g}, V_b = 100\text{cm}^3, V_a = 100\text{cm}^3, K_d = 5, n = 1$$

$$W_r = 10 \left(\frac{100}{100 + (5 \times 100)} \right)^1 = 1.7\text{g}$$

$$\text{Mass of acid removed} = W_o - W_r = (10 - 1.7)\text{g} = 8.3\text{g}$$

- The amount extracted by one extraction only is 8.3g

Second case: By using two 50 cm³ portions of ether

$$W_o = 10\text{g}, V_b = 100\text{cm}^3, V_a = 25\text{cm}^3, K_d = 5, n = 4$$

$$W_r = 10 \left(\frac{100}{100 + (5 \times 25)} \right)^4 = 0.4\text{g}$$

$$\text{Total mass of acid removed} = W_o - W_r = (10 - 0.4)\text{g} = 9.6\text{g}$$

- The amount extracted by four extractions is 9.6g

Example 9

The following data have been obtained on the distribution of phenol between water and chloroform.

C_1	0.094	0.163	0.254	0.436
C_2	0.254	0.761	1.850	5.430

Where C_1 is the molar concentration in the aqueous layer and C_2 is the molar concentration in the chloroform layer; what conclusion do you draw from these results regarding the molecular condition of phenol in the chloroform solution?

Solution

C_1	0.094	0.163	0.254	0.436
C_2	0.254	0.761	1.850	5.430
$\frac{C_1}{C_2}$	0.370	0.214	0.137	0.080
$\frac{C_1}{\sqrt{C_2}}$	0.187	0.187	0.187	0.187

Thus $\frac{C_1}{\sqrt{C_2}} = \text{constant}$, suggesting that two molecules of phenol associate in the chloroform solution to form a dimer.

Hence phenol exists as dimer in the chloroform solution.

Example 10

A crude sample of lead containing 2% of silver by mass; what mass of silver would be left in 1000kg of the lead if it was thoroughly agitated with 50kg of zinc at 800°C and the zinc removed? (At 800°C the solubility of silver in a given mass of zinc is 300 times its solubility in an equal mass of lead).

Solution

It is given that: $K_d = \frac{\text{Mass percentage of silver in zinc}}{\text{Mass percentage of silver in lead}} = 300$

Mass of silver in 1000kg of impure lead = $\frac{2}{100} \times 1000\text{kg} = 20\text{kg}$

Let mass of silver extracted by 50kg of zinc be $x\text{kg}$

Then mass of silver left in lead will be $(20 - x)\text{kg}$

It follows that: $300 = \frac{x/50}{(20-x)/1000} = \frac{20x}{20-x}$, $x = 18.75\text{kg}$

Mass of silver extracted by zinc = 18.75kg

Thus mass of silver left in lead = $(20 - 18.75)\text{kg} = 1.25\text{kg}$

Hence mass of silver left in lead after the extraction is 1.25kg

It is worth to understand this:

The above example illustrates very important industrial application of distribution law which is known as **desilverization of lead** or **Parke's Process** whereby silver is extracted from lead.

APPLICATIONS OF DISTRIBUTION LAW

There are many applications of distribution law in the laboratory as well as in industry. Applications which we have seen so far are:

1. Solvent extraction
2. Determination of solubility
3. Determination of association
4. Determination of dissociation
5. Desilverization of lead or Parke's process

Other applications include deduction of formula of complex ion, partition chromatography, confirmatory test of bromide and iodide ions and determination of equilibrium constant.

DIGGING DEEPER EXERCISE 8

EXERCISE 8A: BINDER QUESTIONS

Question 1

Write down three factors which determine the value of partition coefficient?

Question 2

List any three limitations of Nernst's distribution law.

Question 3

- (i) What is the solvent extraction?
- (ii) Explain two conditions for solvent for solvent extraction to be more successful.

Question 4

The distribution coefficient of iodine between water and carbon disulphide is 0.0017. One litre of aqueous solution containing one gram of iodine is shaken with 100mL of carbon disulphide till the equilibrium is reached. Calculate the amount of iodine extracted by carbon disulphide.

Question 5

The distribution coefficient of an alkaloid between chloroform and water is 20 in favour of chloroform. Calculate the mass of the alkaloid remaining in aqueous solution when 100mL containing 1gram has been shaken with:

- (a) 100ml chloroform
- (b) Two successive 50mL portions

Question 6

12g of an organic substance A is present in 100g of its aqueous solution. How much of it would be left behind after extracting the solution with two successive applications of 50mL each of ether? The distribution coefficient of A between water and ether is 2 in favour of ether.

EXERCISE 8B: REAL QUESTIONS

Question 7

"Partition law helps to study different aspects of chemistry." List down at least three applications that will defend the quotation.

Question 8

Briefly explain how Nernst's distribution law is useful in daily life.

Question 9

Kipute was doing an experiment for determining partition coefficient of butanedioic acid between water and ether. After doing calculation from obtained experimental data, she found the partition coefficient to be 0.03. Explain why the final result was incorrect.

Question 10

Your friend, **Kipute**, was given the following problem.

X is 15 times more soluble in trichloromethane than in water. What mass of X will be extracted from 0.5 dm³ of an aqueous solution containing 25g by shaking with 100 cm³ of trichloromethane?

After solving, she found the answer to be 18.75g of X. How could help your friend to check the work without re-working the problem?

Question 11

In doing experiments to determine partition coefficient, **Mr. Akilikubwa**, normally shake the mixture in the separating funnel for three minutes and allow the mixture to settle and form separating layer for about three minutes too. On another day, **Mr. Akilikubwa** was doing an experiment to determine partition coefficient of iodine between carbon disulphide and water;

That is $K_d = \frac{\text{Concentration of iodine in carbon disulphide}}{\text{Concentration of iodine in water}}$

In contradiction to what is usually doing, **Mr. Akilikubwa** shook the mixture for five minutes and he did it more vigorously; alternating hand whenever he felt tired.

- In terms of intermolecular forces, explain why the shaking was different.
- What is your expectation on the amount of time required for the liquid mixture to form the separating layer? Explain.
- What is your prediction on the amount of the partition coefficient? Explain.

EXERCISE 8C: HOT QUESTIONS

Question 12

The extraction of an organic substance from an aqueous solution by a solvent is probably the most important application of distribution law. The process is carried by shaking the aqueous solution with an organic solvent like ether, in a separating funnel.

- What term is given to represent the process explained above?
- What role does ether play in this process?
- What features do ether possess that make it to fit that role (in (ii) above)?
- Give at least other three substances which may substitute ether.

Question 13

Mr. Akilikubwa reported the following results for the distribution of acetic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) between water and carbon tetrachloride (CCl_4).

[Acid] in CCl_4	0.292	0.725	1.41
[Acid] in H_2O	4.87	7.98	10.7

Assuming that acetic acid has its normal molecular weight in water, calculate its molar mass in CCl_4 .

Question 14

At 25°C , an aqueous solution of iodine containing 0.0516 gL^{-1} is in equilibrium with a carbon tetrachloride (CCl_4) solution containing 4.412 gL^{-1} . The solubility of iodine in water at 25°C is 0.34 gL^{-1} . Find the solubility of iodine in carbon tetrachloride.

Question 15

Ammonia was extracted using silane and water. The concentration of ammonia was noted by means of titration, with the silane layer requiring 22.3 mL of 0.01 M HCl and the water layer requiring 13.6 mL of 0.2 M HCl for complete neutralisation. Find K_d for ammonia between silane and water.

Question 16

18 g of compound **X** distribute themselves between water and equal volume of an immiscible solvent **Y** so that 2 g of **X** are in water. Calculate to the nearest integer, the percentages **X** left in 1000 cm^3 of water containing 1 g of **X** are extracted by one litre of **Y**.

Question 17

An aqueous solution of succinic acid at 15°C , containing 0.07 g in 10 mL is in equilibrium with an ether solution which has 0.013 g in 10 mL . The acid has its normal molecular weight in both of the solvents. What is the mass concentration of the ether solution which is in equilibrium with an aqueous solution containing 0.024 g in 10 mL ?

Question 18

An aqueous solution contains 10 g of solute per litre. When 1 litre of the solution is treated with 100 mL of ether; 6 g of the solute are extracted. How much more of the solute would be extracted from the aqueous solution by further 100 mL ether? Assume that the molecular state of the solute is the same in ether and water.

Question 19

An organic acid is distributed between 500mL each of a solvent A and water. In water it is dissociated. The amount of the acid in an aqueous layer was 6g and in solvent A, it was 0.72g. If the distribution coefficient of the acid between the solvent A and water is 0.16, calculate the degree of dissociation, assuming the acid has normal molecular weight in A.

Question 20

100cm³ of a 0.15mol dm⁻³ solution of aqueous methylamine was shaken with 75cm³ of an organic solvent at 25°C and left in the separating funnel to allow an equilibrium to be established. Only 50cm³ of the aqueous layer was run off and titrated against 0.225mol dm⁻³ dilute hydrochloric acid with an end point of 14.1cm³ of HCl.

- (i) Calculate the partition coefficient of methylamine between water and the organic solvent.
- (ii) In which solvent does methylamine more soluble?

EXAMINATION QUESTIONS FOR PART TWO

Question 1

- (a) Can azeotropes be separated into pure components by fractional distillation? Explain.
- (b) A solution has a 1:3 ratio of cyclopentane to cyclohexane. The vapour pressures of the pure compounds at 25°C are 331mmHg for cyclopentane and 113mmHg for cyclohexane. What is the mole fraction of cyclopentane in the vapour above the solution?

Question 2

- (a) State whether the following statements are true or false. In each case give reason(s) to support your answer.
- Azeotropes are compounds and not mixtures.
 - Raoult's law of ideal solutions is applicable both to the liquid and vapour phase compositions.
- (b)
- Is the aqueous methanol solution ideal or non-ideal solution? Explain.
 - What is the molality of an aqueous methanol solution whose mole fraction is 0.2?

Question 3

- (a) What does Konowaloff's rule say?
- (b) Two liquids X and Y on mixing form an ideal solution. The vapour pressure of the solution containing 3mol of X and 1mol of Y is 550mmHg. But when 4 mol of X and 1mol of Y are mixed, the vapour pressure of solution thus formed is 560 mm Hg. What will be the vapour pressure of pure X and pure Y at this temperature?

Question 4

- (a) Explain why we cannot prepare absolute alcohol by fractional distillation.
- (b) A solution containing hexane and pentane has a pressure of 252torr. Hexane has a pressure at 151torr and pentane has a pressure of 425torr. What is the mole fraction of pentane?

Question 5

- (a) What is zeotrope?
- (b) 100g of liquid A (molar mass 140g/mol) was dissolved in 1000g of liquid B (molar mass 180g/mol). The vapour pressure of pure liquid B was found to be 500torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475torr

Question 6

- (a) What type of deviation is shown by a mixture of ethanol and acetone? Give reason.
- (b) The vapour pressure of pure liquids A and B are 450 and 700mmHg respectively, at 350K.
- Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg.
 - Find the composition of the vapour phase.

Question 7

- (a) Explain why addition of 1mol of NaCl to 1L of water, increases the boiling point of water, while addition of 1mol of methyl alcohol to 1L of water decreases its boiling point.
- (b) The vapour pressure of benzene is 1.1atm whilst the vapour pressure of toluene is 0.7atm. What is the % by mass of benzene in the vapour phase if the total pressure is 0.83atm?

Question 8

- (a)
- What general name is given to constant boiling binary mixture which show deviation from Raoult's law and whose components cannot be separated by fractional distillation.
 - How many types of such mixture are there? Name them with an example in each case.
- (b) Pentane and hexane form an ideal solution. The vapour pressures of pentane and hexane are 511 and 150 torr, respectively. A solution is prepared by mixing 25mL pentane (density, 0.63g/mL) with 45mL hexane (density, 0.66g/mL).
- What is the vapour pressure of the resulting solution?
 - What is the composition by mole fraction of pentane in the vapour that is in equilibrium with this solution?

Question 9

- (a) List down five conditions of which the compound to be separated by steam distillation must fulfil.
- (b) When compound Q with a relative molecular mass of 120 is steam distilled, the mixture boils at 98°C. The vapour pressure of water is 94300Pa at this temperature. If the atmospheric pressure is 100900Pa, calculate the composition by mass of the distillate?

Question 10

- (a) Differentiate between zeotropic mixture and azeotropic mixture.
- (b) What is the composition of a methanol–propanol solution that has a vapour pressure of 174torr at 40°C? At 40°C, the vapour pressures of pure methanol and pure propanol are 303 and 44.6 torr, respectively. State any assumption(s) made in your calculations.

Question 11

- (a) Why very dilute solutions are regarded as ideal solutions irrespective to the nature of the solute and solvent?
- (b) Liquid A has vapour pressure x, liquid B has vapour pressure y. What is the mole fraction of the vapour above the solution if the liquid mixture is 80% A?

Question 12

- (a)
 - (i) What does the term 'ideal solution' stands for?
 - (ii) What type of liquids form ideal solutions?
- (b) A mixture of benzene (Vapour Pressure 1.1atm) and toluene (Vapour Pressure 0.7atm) is prepared. The mole fraction of benzene in the vapour phase is 0.65. Assuming ideal behaviour, calculate the mole fraction of toluene in the liquid phase.

Question 13

- (a)
 - (i) What does the term azeotrope represent?
 - (ii) What type of azeotrope is formed by positive deviation from Raoult's law? Give an example.
- (b) Acetone and methanol form an ideal solution. At 25°C, the vapour pressures of pure acetone and pure methanol are 0.342atm and 0.188atm respectively. Calculate the mole fraction of acetone in a solution that boils at 25°C and 0.248atm.

Question 14

- (a) A solution of chloroform and acetone is an example of maximum boiling azeotrope. Explain why?
- (b) The vapour pressure of methyl alcohol at 298 K is 96 torr. Its mole fraction in a solution with ethyl alcohol is 0.305, what is its vapour pressure if it obeys Raoult's law.

Question 15

- (a) Solution can be classified in several categories based on number of factors. One factor which is commonly considered in classifying solution is the physical state.
 - (i) How many types of solutions are formed?
 - (ii) Write briefly about each type with an example.
 - (iii) Give an example of solid solution in which the solute is a gas.
- (b) A solution is prepared by mixing 0.0300mol dichloroethane and 0.0500mol of dibromoethane at 25°C. Assuming the solution is ideal, calculate the composition of the vapour (in terms of mole fractions) at 25°C. (At 25°C. the vapour pressures of pure dichloroethane and pure dibromoethane are 133 and 11.4 torr, respectively).

Question 16

- (a) Explain why the boiling point of immiscible solution is less than either of the component.
- (b) Two liquids A and B forms ideal solution at 300K. The vapour pressure of a solution containing 1mol of A and 2mol of B at 300K is 2×10^5 Pa. When one more mole of B is added to the solution, the vapour pressure of the solution is 2.1×10^5 Pa.
 - (i) Without doing any calculation state whether B is more volatile or less volatile than A. Give reason.
 - (ii) Calculate vapour pressure of A and B in the pure state.

Question 17

- (a) What does Raoult's law say about?
- (b) Heptane and octane form an ideal solution. At 40°C, the vapour pressure of pure heptane is 0.522atm, and the vapour pressure of pure octane is 0.238atm. A solution is made of 5.32g heptane and 8.80g octane. Calculate the mole fraction of octane in the vapour at the above temperature.

Question 18

- (a) Liquid immiscible with water can be efficiently separated from their mixture with water through steam distillation. State any two conditions necessary for steam distillation to be efficient.
- (b) An organic acid liquid distills in steam. The partial pressure of the two liquids, i.e. an organic acid and water at the boiling point are 5.3kPa and 95kPa respectively. If the distillate contains the organic to water mass ratio of 0.48, calculate the molar mass of the organic acid.

Question 19

- (a)
- (i) What is the main message of Raoult's law?
- (ii) With reference to Raoult's law, distinguish positive deviation from negative deviation.
- (b) The vapour pressure of ethanol at 20°C is 43.6mmHg while that of benzene at the same temperature is 75.2mmHg. The mole fraction of benzene is 0.09 for a mixture of benzene and ethanol at 20°C. Calculate the:
- (i) Total vapour pressure of the mixture
- (ii) Mole fraction of benzene in vapour phase

Question 20

- (a) Explain how an increase in temperature, increases vapour pressure of a liquid.
- (b) Nitrobenzene ($C_6H_5NO_2$) and water form a mixture of immiscible liquids which boils at 99°C. Calculate the percentage by mass of nitrobenzene in the distillate when the mixture is distilled at 1.013×10^5 Pa given that the vapour pressure of water at 99°C is 9.749×10^4 Pa.

Question 21

- (a) Briefly explain the principle of solvent extraction.
- (b)
- (i) 50g of acid are dissolved in 1L of water. The distribution coefficient, K_d , of acid between ether and water is 3.

$$\text{That is } K_d = \frac{\text{concentration of acid in ether}}{\text{concentration of acid in water}} = 3$$

A volume of 1000cm³ of ether is available for the use in the extraction process. Two experiments were performed to extract acid from water. In the first experiment, 1000cm³ of ether was used once in single extraction. In the second experiment, two extractions were performed, each using 500cm³ of ether. Compare the amounts of acid left in the aqueous solution in each case and recommend the best method to extract the acid from water.

- (ii) The distribution coefficient given in (i) above is not strictly correct. What is the main reason of this?

Question 22

- (a) Compare and contrast fractional distillation from steam distillation.
- (b) Steam is passed through a flask containing about 20g of chlorobenzene (C_6H_5Cl). The mixture is found to boil at 91°C at 760mmHg. The vapour of water at 91°C is 540mmHg. Calculate:
- (i) Mole composition of the distillate
- (ii) The mass composition of the distillate
- (iii) Total volume of the distillate obtained when 90% of chlorobenzene has been steam distilled. (Density of chlorobenzene is 1.1g/cm³).

Question 23

- (a)
- Identify whether the mixture of nitric acid and water shows positive or negative deviation from Raoult's law.
 - What interaction between nitric acid and water leads to this type of deviation?
- (b) Given the following result for the distribution of phenol between water and chloroform
- | | | | |
|--|--------|--------|---------|
| Concentration of phenol in water (g/dm ³) | 8.836 | 15.322 | 23.876 |
| Concentration of phenol in chloroform (g/dm ³) | 23.876 | 71.534 | 173.900 |
- Use the above result to deduce whether phenol exists in normal state or dimerises in chloroform
 - Describe clearly the reason for the state of phenol in chloroform deduced in (i) above.

Question 24

- (a) Show how the equation of partition law of solute 'x' dissolved in two immiscible solvents **A** and **B** will be represented when solute 'x':
- Associate in solvent **A** and remain normal in solvent **B**
 - Dissociate in solvent **A** and associate in solvent **B**
 - Dissociate in solvent **B** and remain normal in solvent **A**
- (b) Iodine was shaken with equal volumes of tetra chloromethane and water.
- (i) Calculate the mean distribution constant of iodine between these two solvents from the result:

	I	II	III
25cm ³ CCl ₄ layer required cm ³ 0.1M thiosulphate	27.7	21.2	14.0
25 cm ³ H ₂ O layer required cm ³ 0.01M thiosulphate	3.15	2.40	1.6

- (ii) What mass of iodine would dissolve in the water if 5g of iodine were taken with 1dm³ of tetrachloromethane and 2 dm³ of water?

Question 25

- (a) Under what main condition does solution formed upon mixing two liquids **A** and **B** behave as ideal solution?
- (b) 1.00g of iodine was shaken with 50cm³ of tetrachloromethane and 50cm³ of water. 25cm³ of aqueous layer required 4.5cm³ of 0.01M sodium thiosulphate solution. Calculate the distribution constant of iodine between these solvents.

Question 26

Liquid **A** and **B** form an ideal solution when mixed together. If the boiling point of pure **A** is higher than the boiling point of pure **B** at 1 atmospheric pressure. Sketch:

- A vapour- composition curve for the solution of liquid **A** and **B**
- A temperature –composition curve for the solution of liquids **A** and **B**
- Explain what will happen when an equimolar solution of mixture **A** and **B** is distilled at atmospheric pressure of 1atm.

Question 27

The vapour pressures of several solutions of water-propanol (CH₃CH₂CH₂OH) were determined at various compositions, with the following data collected at 45°C:

X _{H₂O}	Vapour pressure mmHg
0	74.0
0.15	77.3
0.37	80.2
0.54	81.6
0.69	80.6
0.83	78.2
1.00	71.9

Based on the above data, answer the following questions:

- (a) Are solution of water and propanol ideal? Explain.
- (b) Predict the sign of enthalpy of solution, ΔH_{soln} , for water-propanol solutions.
- (c) Are the interactive forces between propanol and water molecules weaker than, stronger than, or equal to the interactive forces between the pure substances? Explain.
- (d) Which of the solutions in the data would have the lowest normal boiling point? What special name is given for this solution?

Question 28

A solution is made by mixing 50.0 g acetone (CH_3COCH_3) and 50.0 g methanol (CH_3OH). At 25°C the vapour pressures of pure acetone and pure methanol are 271torr and 143torr respectively. Assume ideal solution and gas behaviour:

- (a) What is the vapour pressure of this solution at 25°C ?
- (b) What is the composition of the vapour expressed as a mole fraction?
- (c) The actual vapour pressure of this solution is 161torr. Explain any discrepancies.

Question 29

- (a) A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.
 - (i) What is the initial effect of the change on vapour pressure?
 - (ii) How do rates of evaporation and condensation change initially?
 - (iii) What happens when equilibrium is restored finally and what will be the final vapour pressure?
- (b) The vapour pressure of pure liquid A and B are 450mmHg and 700mmHg respectively at 350K. If the total vapour pressure is 600mmHg; calculate the following:
 - (i) Composition of liquid mixture.
 - (ii) Composition of the vapour phase.

Question 30

- (a)
 - (i) What statement of Raoult's law of volatile liquids?
 - (ii) Give any three examples of ideal solutions.
 - (iii) Give two main assumptions for Raoult's law to be valid?
- (b) During nuclear fuel reprocessing, solvent extraction with an organic solvent is used to recover uranium salts from aqueous solution. If the partition coefficient of a uranium salt between the organic solvent and acidified water has a value of 50, calculate the ratio of the total number of moles of uranium in the organic solvent layer to that in water layer after 500dm^3 of an aqueous solution of uranium salt has been extracted with 200dm^3 of organic solvent.

Question 31

- (a) Alcohol dissolves in water to give a solution that boils at a lower temperature than pure water while table salt dissolves in water to give a solution that boils at a higher temperature than pure water. Explain this fact in terms of vapour pressure.
- (b) If a solute, **X**, is shaken with two immiscible solvents, **Y** and **Z**, at constant temperature, it is found that:

$$\frac{(\text{Concentration of X in Y})}{(\text{Concentration of X in Z})} = \text{a constant}$$

- (i) What name is given to the constant.
- (ii) For **X** = phenylamine, **Y** = water and **Z** = ethoxyethane the value of the constant is 0.20. Calculate the mass of phenylamine extracted into the ethoxyethane layer when 100cm^3 of water containing 20g of phenylamine per dm^3 is treated with 100cm^3 of ethoxyethane.
- (iii) How could the efficiency of extraction of phenyl amine have been improved using the same total volume of ethoxyethane?

Question 32

- (a) What is wrong with each of the following statements:
 - (i) When polar liquids are mixed together, the resulting mixture is always ideal solution.
 - (ii) Boiling point of any solution containing two volatile liquids always lies between boiling points of the pure liquids.

- (iii) Solution containing alcohol and water is appropriately separated into its pure components by simple fractional distillation.
- (b) When 500cm^3 of an aqueous solution containing 4g of a solute G per litre was shaken with 100cm^3 of pentan-1-ol, 1.5g of the solute G was extracted. Assuming the molecular state of the solute remained the same in both solvents, calculate:
- Partition coefficient of the solute G between pentan-1-ol and water.
 - Mass of the solute G which remained in the aqueous solution after a further shaking with 100cm^3 of pentan-1-ol.

Question 33

Ethyl benzoate is liquid with a boiling point of 213°C . It is virtually insoluble in water

- (a) The vapour pressures of water and ethyl benzoate at 50°C are

Ethylbenzoate	0.2kPa
Water	12.25kPa

- What would be the total vapour pressure of an equimolar mixture of the two liquids at 50°C ?
 - What would be the effect on the total vapour pressure if you increased the proportion of water so that there were 3 moles of water to 1 mole of ethylbenzoate?
- (b) The vapour pressures of water and ethyl benzoate at 99°C are:
- Ethyl benzoate 2.34kPa
 Water 97.76kPa
- What can you say about the boiling point of the mixture at atmosphere pressure (101.325kPa)?

Question 34

- (a) Give at least two examples of each of the following:
- Ideal solution
 - Non-ideal solution with negative deviation
 - Non-ideal solution with positive deviation
 - Solid solution
- (b) A solution consists of 3.88g benzene, C_6H_6 , and 2.45g toluene, $\text{C}_6\text{H}_5\text{CH}_3$. The vapour pressure of pure benzene at 20°C is 75mmHg and that of toluene at 20°C is 22mmHg. Calculate the mole fraction of benzene in the vapour. (Molar mass of benzene = 78.0 g/mol and toluene = 92.0 g/mol).

Question 35

- (a) Give at least three advantages of steam distillation.
- (b) Liquids A and B form an ideal solution. The vapour pressure of pure A is 0.700atm at the normal boiling point of a solution prepared from 0.250 mole of B and 0.650 mole of A. What is the vapour pressure of pure B at this temperature?

Question 36

- (a) Raoult's law only really works for ideal solutions. An ideal solution is defined as one which obeys Raoult's law. How do the following affect how ideal a solution is?
- The concentration of the solution.
 - The forces between the particles in the solution.
- (b) The vapour pressure of water at 95°C is 635mmHg. A water insoluble organic liquid X, of relative molecular mass 160, steam distills at 95°C under atmospheric pressure of 760mmHg. Calculate the mass of the distillate during the collection of 40g of X.

Question 37

- (a) Explain clearly what is wrong with each of the following statements:
- Ideal solution is the solution which obeys Raoult's law.
 - Non-ideal solution with positive deviation are warm to touch.
- (b) Chlorobenzene which is soluble in water, steam distills at 91°C under atmospheric pressure of 101300Pa. A sample of the steam distillate contains 23.7g of chlorobenzene for every 10g of water. Calculate the vapour pressure of water and chlorobenzene at 91°C .

Question 38

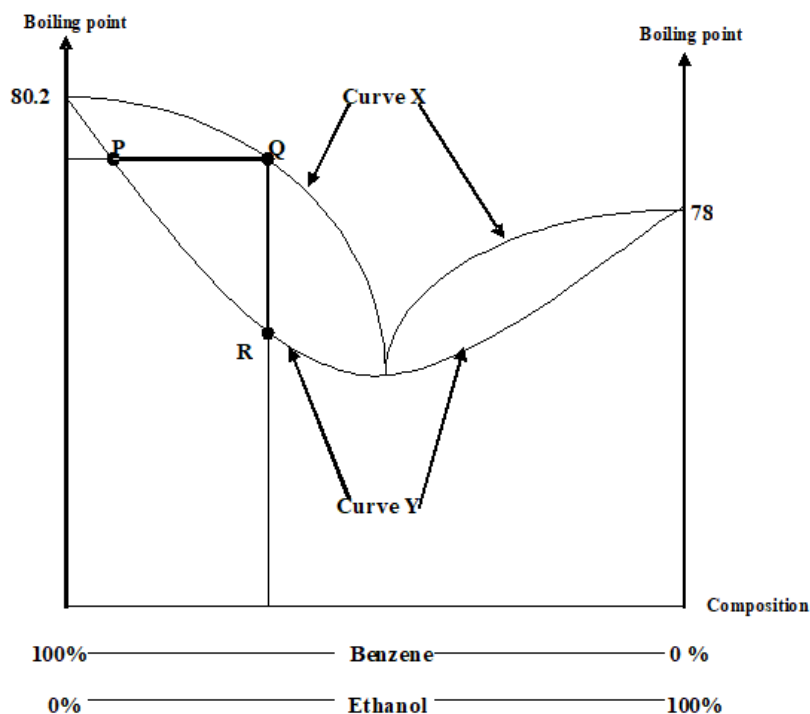
- (a) Vapour pressure is an important physical property of substance. Knowing vapour pressure of substance at **given** temperature help us to know volatility of the substance.
- How is vapour pressure related to intermolecular forces?
 - Why in measurement of vapour pressure, temperature must be '**given**'?
 - Explain how vapour pressure is related to volatility.
- (b) Chloroform and methanol form an ideal solution. The solution boils at 22 °C and 0.255atm. At 22°C, the vapour pressure of pure methanol is 0.192atm and the vapour pressure of pure chloroform is 0.311atm. What is the mole fraction of chloroform in the solution?

Question 39

- (a) On your own words, give the meaning the following terms:
- Saturated vapour pressure
 - Azeotropic point
 - Ideal solution
- (b) Ethanol and water form an azeotropic mixture which boils at 78.1°C with 95.6% ethanol. The boiling point of pure ethanol and water are 78.4°C and 100°C respectively.
- Draw a temperature-mole fraction phase diagram of ethanol-water solution.
 - What happens when a solution of less than 50% ethanol is boiled?
 - How pure ethanol may be obtained from the azeotropic mixture?

Question 40

The diagram below illustrates the boiling point-composition relationship for benzene – ethanol system.



- What do the curves **X** and **Y** represent?
- What is the relation between **P**, **Q** and **R**
- From the above boiling point-composition diagram, sketch labelled diagram to illustrate the vapour pressure-composition relationships for the benzene –ethanol system.

Question 41

- (a) Addition of non-volatile solute lowers the freezing point and elevates the boiling point of a solvent. Explain giving reason(s).
- (b) What is the approximate osmotic pressure of a 0.118m solution of LiCl at 10.0 °C? The freezing point of this solution is -0.415 °C. State any assumption made to reach to your answer. ($K_f = 1.86^\circ\text{C kg mol}^{-1}$).

Question 42

- (a) Explain why a carrot that has become limp because of water loss into the atmosphere becomes firm once again when placed into the water.
- (b) 18g of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, is dissolved in 1kg of water in a saucepan. At what temperature will water boil at 1atm? K_b for water is $0.52^\circ\text{C kg mol}^{-1}$.

Question 43

- (a) Quote in words and derive Raoult's law for lowering of vapour pressure.
- (b) An aqueous solution of KI has a freezing point of -1.95 °C and an osmotic pressure of 25.0atm at 25.0 °C. Assuming that the KI completely dissociates in water, what is the density of the solution? ($K_f = 1.86^\circ\text{C kg mol}^{-1}$)

Question 44

- (a)
- (i) Differentiate between osmosis and osmotic pressure.
- (ii) Is the osmotic pressure of a solution a colligative property? Explain.
- (b) How many grams of sucrose (molar mass 342g/mol) should be added to 500.0 grams of water so that the difference in freezing point and boiling point is 105.0°C ($K_f = 1.86^\circ\text{C kg mol}^{-1}$, $K_b = 0.52^\circ\text{C kg mol}^{-1}$)

Question 45

- (a) Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing:
- (i) 1.2% sodium chloride solution?
- (ii) 0.4% sodium chloride solution?
- (b) A compound contains 42.9%C, 2.4%H, 16.6%N, and 38.1%O by mass. The addition of 3.16g of this compound to 75.0mL of cyclohexane ($d = 0.779 \text{ g/mL}$) gives a solution with a freezing point of 0.0°C. The normal freezing point of cyclohexane is 6.5°C and its freezing point depression constant is 20.2°C/m. What is the molecular formula of the solute?

Question 46

- (a) **Concentration** of solution can be expressed in different methods. The choice of the convenient method in different circumstances depends on number of factors. **Molarity** and **molality** are broadly used as among methods of representing concentration with the former being more often used than the latter.
- (i) Differentiate **molality** from **molarity**.
- (ii) Why molarity is more famous than molality?
- (iii) In determination boiling point elevation and freezing point depression molality (**not** molarity) is used while in determination osmotic pressure molarity (**not** molality). Give an explanation to support the choice.
- (b) An 18.2% by mass aqueous solution of an electrolyte is prepared (molar mass = 162.2 g/mol). If the vapour pressure of the solution is 23.51torr, into how many ions does the electrolyte dissociate? The vapour pressure of water at this temperature is 26.02 torr.

Question 47

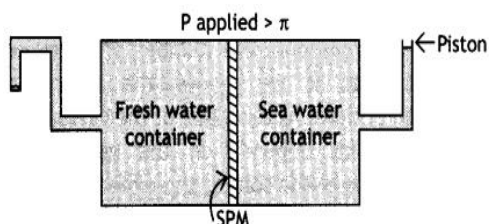
- (a) Show that for very dilute solutions, molality $\cong$ molarity.
- (b) A solid mixture contains MgCl_2 and NaCl . When 0.5g of this mixture is dissolved in enough water to form 1.0L of solution, the osmotic pressure at 25.0°C is observed to be 0.399atm. What is the mass percent of MgCl_2 in the solid?

Question 48

- (a) Consider a 4% starch solution and a 10% starch solution separated by a semipermeable membrane, which starch solution will decrease in volume as osmosis occurs? Give reason to support your choice.
- (b) What is the normal boiling point of a 2.70M solution of KBr that has a density of 1.80 g/mL?

Question 49

- (a) Given below is the sketch of a plant for carrying out a process.



- Name and define the process occurring in the above plant.
 - To which container does the net flow of solvent take place?
 - What does SPM stand for?
 - Name one SPM which can be used in this plant.
 - Give the main practical use of the plant.
- (b) A solution containing 8.6g per litre of urea ($M_w = 60\text{g/mol}$) was found to be isotonic with a 5% solution of an organic non-volatile solute. Calculate the molar mass of the latter.

Question 50

- Why the boiling point 0.1M BaCl_2 solution is more than 0.1M NaCl solution?
- Calculate the mass of a non-volatile solute (molar mass 40g/mol) which should be dissolved in 114g octane to reduce its vapour pressure to 80%.

Question 51

- Which would have the lower vapour pressure—an aqueous solution that is 0.12 M in glucose or one that is 0.12 M in CaCl_2 ? Why?
- Calculate the vapour pressure lowering caused by addition of 50g of sucrose (molecular mass = 342) to 500g of water if the vapour pressure of pure water at 25°C is 23.8mmHg.

Question 52

- Magnesium chloride is dissolved in water to make the solution in which its concentration is 0.1M.
 - What is the theoretical value of Van't Hoff's factor of MgCl_2 in aqueous solution?
 - Explain why the value mentioned in (i) above cannot be realized in practice.
 - Explain what can be done to make the experimental value of Van't Hoff's factor of $\text{MgCl}_2(\text{aq})$ to approach the theoretical value.
- What mass of non-volatile solute (urea) needs to be dissolved in 100g of water in order to decrease the vapour pressure of water by 5%. What will be molality of solution? (molecular weight of urea is 60g/mol).

Question 53

- The vapour pressure of water at 25°C was observed to be 3167Pa. Explain briefly what will happen to this vapour pressure if 4g of sugar are dissolved into the water at the same temperature.
- The osmotic pressure of solution containing 0.2g of the monobasic acid **B** per litre was 94.6mmHg at 15°C while a solution of 4g of **B** in 100g of benzene depressed freezing point of that solvent by 2.13°C . If an aqueous solution of **B** containing 0.5g required 10.9cm³ of 1M sodium hydroxide for neutralisation. What conclusion can you make about the state of **B** in water and benzene? (K_f of benzene is $49^\circ\text{C per 100g}$)

Question 54

- Assuming the price per kilogram is the same:
 - Which is a better salt to use for deicing wintry roads— NaCl or MgCl_2 ? Why?
 - Would magnesium chloride be an effective deicer at a temperature of -8°C ?
- A solution of calcium nitrate contains 15g of anhydrous salt in 1000g of water freezes at -0.435°C . Calculate the degree of dissociation of the salt.

Given that: Freezing point constant for water, $K_f = 1.86^\circ\text{C kg mol}^{-1}$

Question 55

- (a) List the following solutions in order of increasing melting point:

0.1m sugar, 0.1mNaCl, 0.08m CaCl₂, 0.04mNa₂CO₃

- (b) The freezing point of pure benzene was found to be 5.481°C. A solution of 0.321g hydrocarbon naphthalene (C₁₀H₈) in 25g of this benzene began to freeze at 4.91°C. A solution of 0.305g of benzoic acid in 25g of the same solvent began to freeze at 5.226°C
- (i) Calculate the molar freezing point depression constant for 1000g of benzene (K_f)
- (ii) Calculate the relative molecular mass of benzoic acid in benzene solution.

Question 56

- (a) A solution is prepared by dissolving 1.5g of a compound in 25mL of water at 25°C. The boiling point of the solution is 100.45°C. What is the molar mass of the compound if it is non- volatile and non-electrolyte. (Density of water at 25°C is 0.997g/mL and K_b = 0.52)
- (b) Independent conductivity measurements indicate that the compound is ionic with general formula AB₂ or A₂B. What is the molar mass of the compound if the compound behaves ideally. Explain the difference between the actual formula and that calculated from the boiling elevation experiment
- (c) Calculate the Vant Hoff's factor, i for this solution.

Question 57

- (a) With reason, predict whether Van't Hoff factor is less than one, greater than one or equal to one in the following:
- (i) CH₃COOH dissolved in water.
- (ii) CH₃COOH dissolved in benzene.
- (iii) CO(NH₂)₂ dissolved in water.
- (b) How many grams of urea ((NH₂)₂CO) must be added to 450g of water to give a solution with a vapour of 2.5mmHg less than that of pure water at 30°C (The vapour pressure of water at 30°C is 31.8mmHg)

Question 58

- (a) Out of 1 M glucose and 2 M glucose, which one has a higher boiling point and why?
- (b) What happens when the external pressure applied becomes more than the osmotic pressure of solution?
- (c) A solution is prepared from 2.0g of a non- volatile solute and 90.10g of water at 60°C, the vapour pressure of the solution is 0.194 atm. According to Raoult's law, what is the approximate molecular mass of the solute (The vapour pressure of pure water at 60°C is 0.196atm)

Question 59

- (a) *Measurement of osmotic pressure is more widely used for determining molar masses of macromolecules than the elevation in boiling point or depression in freezing point of their solutions.* Give two reasons to support this fact.
- (b) Calculate the boiling point of solution prepared by dissolving 2.4g of biphenyl (C₁₂H₁₀) in 75.00g of benzene (C₆H₆). (The boiling point of benzene is 80.1°C and boiling point constant is 2.53°Ckg/mol).

Question 60

- (a) Why does sodium chloride solution freeze at a lower temperature than water?
- (b) The osmotic pressure of aqueous solution containing 10g of BaCl₂ per litres was found to be 3.2atm at 15°C. Calculate the apparent degree of dissociation of BaCl₂ in water.

Question 61

- (a) Among the following solutions, which one is hypertonic? Explain.
- A: 0.1M aqueous calcium chloride
- B: 0.1M aqueous glucose
- C: 0.1M aqueous ammonium phosphate
- D: 0.1M benzoic acid solution in benzene
- (b) A cooling system of a marine car contains 6dm³ of water. What mass of ethylene glycol (C₂H₆O₂) must be added to the water to produce a solution which will depress the freezing point of water by 13°C (K_f of water = 1.86°Ckg mol⁻¹)

Question 62

- (a) Why adding salt to the ice makes the ice to melt?
- (b) Calculate the concentration in gdm^{-3} of a glucose solution which has an osmotic pressure of 2.32 atmospheres at 12°C . (Glucose is $\text{C}_6\text{H}_{12}\text{O}_6$)

Question 63

- (a) Why osmosis does not take place in two isotonic solutions separated by a semi-permeable membrane?
- (b) The vapour pressure of benzene at 20°C is 10000Nm^{-2} , what would be the effect on this vapour pressure of dissolving 4.1g of naphthalene (C_{10}H_8) in 60g of benzene, at the same temperature?

Question 64

- (a) The Van't Hoff factor for a concentrated solution of NaCl is much less than 2, while that for a dilute solution is only slightly less than 2. Explain.
- (b) The vapour pressure of solution of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, in water has a vapour pressure of 2311Nm^{-2} at 20°C . Pure water at this temperature has a vapour pressure of 2333Nm^{-2} , what is the concentration of sucrose solution in gdm^{-3} .

Question 65

- (a) The addition of lead (II) ions to a solution of magnesium chloride leads to an increase in the vapour pressure of the solution. Explain.
- (b) Calculate the relative molecular mass of a compound, a 2% aqueous solution of which boils at 99.877°C when the boiling point of pure is 99.700°C ($K = 0.52^\circ\text{C}$ per 1000g of water).

Question 66

- (a) List down four uses of freezing point depression.
- (b) Calculate the relative molecular mass of benzoic acid on the basis of the following experimental results:
Mass of ethanol 16.150g.

Boiling Point/ $^\circ\text{C}$	Mass of benzoic acid dissolved/g
78.100	-
78.230	0.2400
78.360	0.4727
78.505	0.7470

$K = 1.07^\circ\text{C}$ per 1000g of ethanol

Question 67

- (a) Between 0.1M BaCl_2 and 0.1M CaCl_2 which one has larger Van't Hoff's factor? Explain.
- (b) A solution of 0.36g of sulphur in 24g of carbon disulphide boils at 0.14°C above the boiling point of the pure solvent at the same pressure. What is the molecular formula of sulphur in this solvent? (K_b of carbon disulphide = 2.35°Ckg/mol)

Question 68

- (a) As a solution freezes, the freezing temperature continues to decrease. Why is this so?
- (b) A motor car radiator has a capacity of 4dm^3 . What is the least mass of glycerol, $\text{C}_3\text{H}_8\text{O}_3$, which will convert the water it contains when full into a non-freezing mixture, if it is to encounter temperatures as low as -6°C ? Given that K_f of water = 1.86°Ckg/mol . (Assume the laws which hold for dilute solutions are valid for concentrated ones and that the solution has a density of 1kgdm^{-3})

Question 69

- (a) A solute in a solution behaves exactly like a gas and the osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature occupying the same volume.
- (i) Which theory is this statement based?
- (ii) The theory stated in (i) above is useful in deducing number of laws. State them.

- (b) A certain solution of urea has an osmotic pressure of 100000Nm^{-2} at 15°C . What will be its osmotic pressure at 0°C .

Question 70

- (a) Van't Hoff's factor may help us to determine degree of dissociation or association of non-volatile solute in the solution. Briefly explain the relationship between Van't Hoff's factor and concentration of the solution.
- (b) An aqueous solution of certain compound, containing 7.00g of the compound in 100cm^3 of solution, and an osmotic pressure of 9.3atmospheres at 18°C . What mass of this compound in 250cm^3 of solution would give an osmotic pressure of 10 atmospheres at 10°C .

Question 71

- (a) The Van't Hoff factor for a 0.05molal FeCl_3 solution is much smaller than 4, while that for the same concentration of NaCl is only slightly less than 2. Explain.
- (b) An aqueous solution of 1.00g of very weak acid in 1dm^3 of solution has an osmotic pressure of 288mmHg at 12°C . Calculate the relative molecular mass of the acid. At what temperature would you expect this solution to freeze? ($K = 1.86^{\circ}\text{Ckg/mol}$).

Question 72

- (a) What do the following laws say?
- Van't Hoff's law of osmotic pressure
 - Blagden's law
- (b) A solution of urea, CON_2H_4 , containing 1.754g/dm^3 , is isotonic at the same temperature with a solution of 10.00g of certain sugar in 1 dm^3 of aqueous solution. Calculate the relative molecular of the sugar.

Question 73

- (a) Colligative properties are very useful for experimental determination of molar masses of non-volatile solute.
- Mention three colligative properties apart from osmotic pressure.
 - State two methods which employ colligative properties in the molar mass determination.
 - In the determination of molar mass, is it better to use diluted or concentrated solution? Explain.
 - In the experiment of determining molar mass; it is better to employ osmotic pressure measurement than other ways like ebullioscopy and cryoscopy. Give one reason to oppose and two reasons to support this statement.
- (b) Two solutions, **A** and **B** of glucose have the same osmotic pressure of 324100Nm^{-2} at 0°C and 20°C respectively. Calculate how many more grams of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, are present per dm^3 of solution **A** than of solution **B**.

Question 74

- (a) Give a reason for each of the following:
- Meat can be classified as fresh (not frozen) even though it is stored at -1°C . Why wouldn't meat freeze at this temperature?
 - One mole of sodium chloride depresses the freezing point of 1kg of water almost twice as much as one mole of glycerine.
- (b) Illustrate the analogy between gases and dilute solutions by calculating the molar gas constant, R , in $\text{atmdm}^3\text{K}^{-1}$ from the following data comparing it with R for perfect gas. Cane sugar solution at 15°C . Cane sugar $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

Concentration / gdm^{-3}	Osmotic pressure/ mmHg
10	535
20	1016
40	2082
60	3075

Question 75

- (a) Arrange the following aqueous solution in order of increasing freezing point:
 $0.01\text{M C}_2\text{H}_5\text{OH}$, $0.01\text{M Ba}_3(\text{PO}_4)_2$, $0.01\text{M Na}_2\text{SO}_4$, 0.01M KCl , $0.01\text{M Li}_3\text{PO}_4$
Provide clear reason(s) for arrangement.
- (b) A molar solution of weak, monobasic acid has a freezing point of -1.93°C at atmospheric pressure, 101300m^{-2} . What is the degree of ionisation of the acid and the osmotic pressure at 12°C of this molar solution? ($K = 1.86^\circ\text{C kg/mol}$ and assume that the molar volume of a gas is 22.4dm^3 at s.t.p and that the ionisation of the acid unchanged by the temperature rise to 12°C)

Question 76

- (a) What is the meaning of the following:
(i) Cryoscopy
(ii) Ebullioscopy
- (b) A certain calcium chloride solution has the same freezing point as a solution containing 3.00g of sodium chloride in 1000g of water. Calculate the mass of anhydrous calcium chloride per 100g of water in the given solution, assuming that, at these dilutions, both salts are entirely dissociated.

Question 77

- (a) What do you understand by the following:
(i) Colligative properties
(ii) Freezing point
(iii) Non-volatile solute
(iv) Boiling point
- (b) What mass of glycerol ($\text{C}_2\text{H}_6\text{O}_2$) would be necessary to produce the same anti-freezing effect in a dm^3 of water as 20g of sodium chloride? Assume the sodium chloride is 97% dissociated.

Question 78

- (a) Briefly explain with reason(s) whether the osmotic pressure method would be satisfactory for determining relative molecular mass of ethanoic acid in a concentrated solution of the acid in a suitable solvent.
- (b) 0.47g of a non- electrolyte, of relative molecular mass 58, in 90g of water had a freezing point of -0.167°C . A solution of zinc chloride containing 2.90g of the anhydrous salt in 1000g of water had a freezing point of -0.111°C . Calculate the apparent degree of dissociation of zinc chloride in this solution, using the above data alone.

Question 79

- (a) What are colligative properties?
- (b) 0.75g of ethanoic acid, CH_3COOH , when dissolved in 125g of benzene, depresses the freezing point of benzene by 0.255°C . What is the molecular state of ethanoic acid in benzene solution? ($K = 5^\circ\text{C per 1000g of benzene}$)

Question 80

- (a)
(i) What is boiling point of liquid?
(ii) How boiling point is affected by external pressure?
- (b) Assuming potassium iodide to be completely dissociated under the given conditions, at what temperature would you expect a solution containing 1.66g of potassium iodide in 100g of water, to freeze? (K_f of water = 1.8°C kg/mol)

Question 81

- (a) Give the meaning of the following terms:
(i) Colligative properties
(ii) Ebullioscopic constant
(iii) Osmotic pressure
- (b) A 100mL aqueous sodium chloride solution is 13.5% NaCl by mass and has a density of 1.12g/mL . What would you add (solute or solvent) and what mass of it to make the boiling point of the solution 104.4°C ?

Use Van't Hoff's factor for NaCl as 1.8 and $K_b = 0.512^\circ\text{C kg mol}^{-1}$.
(Show your work clearly including manipulation of units).

Question 82

- (a)
- Is molarity or molality dependent on temperature? Explain your answer.
 - Why is molality and not molarity used in mathematical equations describing the amount of freezing point depression and boiling point elevation?
- (b) A solution is prepared from 90g of water and 10.6g of a non-volatile, non-dissociating solute. The vapour pressure of the solution at 60°C is found to be $1.891 \times 10^4 \text{ Nm}^{-2}$. Calculate the approximate molecular mass of the solute given that, the vapour pressure of water at 60°C is $1.992 \times 10^4 \text{ Nm}^{-2}$. Show your work clearly including manipulation of units.

Question 83

- (a)
- Why is the observed freezing point for electrolyte commonly less than the calculated value?
 - Is the discrepancy in (i) above, greater for concentrated or diluted solution? Explain.
- (b) The freezing point of t-butanol is 25.50°C and K_f is 9.1°C/molal. Usually t-butanol absorbs water on exposure to air. If the freezing point of a 10.0g sample of t-butanol is 24.59°C, how many grams of water are present in the sample?

Question 84

- (a) Define the following two terms: osmotic pressure and reverse osmosis.
- (b) Calculate the osmotic pressure at 25°C of a suspension containing 60g/L of solid particles each particle having a mass of 10^{-9} g .

Question 85

- (a) Briefly explain the following in terms of vapour pressure:
- Boiling point of water rise due to addition of table salt.
 - Freezing point of a solution is lower than that of a pure solvent.
- (b) The freezing point depression of a 0.05molal solution of calcium nitrate in water was found to be 0.265°C. Calculate the degree of dissociation of the solute. (K_f for water = $1.86^\circ \text{Cm}^{-1}$)

Question 86

- (a) Calculate the freezing point of a solution of 22.5g of cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) in 450g of water.
- (b) If a solution of potassium chloride in water had a freezing point of -0.048°C , compare this value to the one obtained in (a) above and state from which solution will the ice first separate.
(Use K_f for water = $1.86^\circ \text{Ckgmol}^{-1}$)

Question 87

- (a) Calculate the boiling point and freezing point of a solution that is 3.725mCaCl₂ in ethanol from the following data:

Solvent	Normal freezing point (°C)	Normal boiling point (°C)	$K_f (^\circ \text{Ckgmol}^{-1})$	$K_b (^\circ \text{Ckgmol}^{-1})$
Ethanol	-117.3	78.5	1.99	1.22

- (b) Do you expect the magnitude of practical values to be greater than or smaller than or the same as one calculated in (a) above? Explain.

Question 88

An aqueous solution is 1.0%NaCl by mass and has density of 1.071 gcm^{-3} at 25°C. The observed osmotic pressure of this solution is 7.83atm at 25°C.

- (a) What fraction of the mole of NaCl in this solution exists as ion pair?
- (b) Calculate the freezing point of this solution.
Use K_f for water = $1.86^\circ \text{Ckgmol}^{-1}$

Question 89

5.00g of an organic solid was dissolved in 100.0g of benzene. The boiling temperature of this solution was 82.3°C. The organic compound is 46.7% nitrogen, 6.67% hydrogen, 26.7% oxygen, and the remainder is carbon. Given that: the boiling temperature of pure benzene is 80.2°C; K_b for benzene = 2.53°C/m.

- Determine empirical formula of the organic solid.
- Determine molecular formula of the organic solid.

Question 90

- Colligative properties are very useful in determination of molar mass of non-volatile solutes.
 - What is the non-volatile solute?
 - Explain why osmotic pressure is more preferred in the determination of molar mass of substance with large molar mass like protein than freezing point depression or boiling point elevation?
- A solution is prepared by mixing 50.0g glucose ($C_6H_{12}O_6$) with 600.0g water. What is the vapour pressure of this solution at 25°C? (At 25°C the vapour pressure of pure water is 23.8torr)

Question 91

Consider the following solutions:

0.010m Na_3PO_4 in water

0.020m $CaBr_2$ in water

0.020mKCl in water

0.020MHF in water

- Complete the following table for the above solutions:

Solution	Van't Hoff factor,i	Effective molality of solute,m
0.010m Na_3PO_4		
0.020m $CaBr_2$		
0.020mKCl		
0.020MHF		

- Which solution(s) would have the same boiling point as 0.040m $C_6H_{12}O_6$ in water?
- Which solution(s) would have the lowest freezing point?
- Which solution(s) would have highest vapour pressure 30°C?
- Which solution(s) would have nearly the same osmotic pressure as 0.020m $C_6H_{12}O_6$ in water?

Question 92

- Explain what is mostly likely to happen when cucumber is placed in a concentrated salt solution.
- A 10.40g mixture of table sugar ($C_{12}H_{22}O_{11}$) and table salt (NaCl) is dissolved in 150g of water, the freezing point is found to be -2.24°C. Calculate the percent by mass of sugar in the original mixture. Use K_f for water = 1.86°Ckgmol⁻¹

Question 93

Ethylene glycol, $CH_2(OH)CH_2(OH)$, is a common automobile antifreeze.

- Calculate the freezing point of a solution containing 651g of ethylene glycol in 2505 g of water.
- Would you keep the substance in your car radiator during the summer? Give reason to support your answer. K_f = 1.86°C/m and K_b = 0.52°C/m.

Question 94

- Does seawater boil at the same temperature as distilled water? If not, which has the higher boiling point? Explain your answer.
- The vapour pressure of water is 12.3kPa at 300K. Calculate the vapour pressure of 1molal solution of a non-volatile solute in it.

Question 95

Elemental analysis of an unknown pure substance indicated that the percent composition by mass is as follows:

Element	Percentage by mass
Carbon	49.02
Hydrogen	2.743
chlorine	48.23

A solution that is prepared by dissolving 3.15g of substance in 25g of benzene, C_6H_6 , has freezing point of $1.12^\circ C$. (The normal freezing point of benzene is $5.50^\circ C$ and the molal freezing point depression constant, K_f for benzene is $5.12^\circ C/molal$)

- Determine the empirical formula of the unknown substance.
- Using the data gathered from the freezing point depression method, calculate the molar mass and hence molecular formula of the unknown substance.
- Calculate the mole fraction of benzene in the solution described above.
- The vapour pressure of pure benzene at $35^\circ C$ is 150mmHg. Calculate the vapour pressure of benzene over the solution described above at $35^\circ C$.

Question 96

- The boiling point of diethyl ether is $34.6^\circ C$. Would this compounds be considered non-volatile? Give reason.
- A 5% solution of cane sugar (Mwt = 342g/mol) is isotonic with 1% solution of a substance X. Calculate the molecular weight of X.

Question 97

- Boiling point elevation is directly proportional to the molal concentration of the solute. Is it also directly proportional to the molar concentration of the solution? Why or why not?
- Vapour pressure of CCl_4 at $25^\circ C$ is 143mmHg. 0.5g of a non-volatile solute (Mwt = 65) is dissolved in 100mL of CCl_4 . Find the vapour pressure of the solution. (Density of CCl_4 = $1.58g/cm^3$)

Question 98

- Colligative properties are very special physical property of the solution. They are very special in different perspective; from their origin to their useful application.
 - List down three things which make colligative properties special.
 - Mention at least four properties of solution which are **not** regarded as colligative properties.
- 0.004M solution of Na_2SO_4 is isotonic with 0.01M solution of glucose at the same temperature. What is the apparent degree of dissociation of Na_2SO_4 ?

Question 99

- Two beakers of equal volume are placed in a room. Beaker A contains pure water and beaker B contains salt water. After a day of evaporation, which has more liquid in it and why?
- When placed in a concentrated salt solution, certain yeasts are able to produce high internal concentrations of glycerol to counteract the osmotic pressure of the surrounding medium. Suppose that the yeast cells are placed in an aqueous solution containing 4.0% NaCl by mass; the solution density is 1.02 g/mL at $25^\circ C$.
 - Calculate the osmotic pressure of a 4.0% aqueous NaCl solution at $25^\circ C$.
 - If the normal osmotic pressure inside a yeast cell is 7.3atm, corresponding to a total concentration of dissolved particles of 0.30M, what concentration of glycerol must the cells synthesize to exactly balance the external osmotic pressure at $25^\circ C$?

Question 100

- When two aqueous solutions with identical concentrations are separated by a semipermeable membrane, no net movement of water occurs. What happens when a solute that cannot penetrate the membrane is added to one of the solutions? Why?
- The melting point depression of biphenyl (melting point = $69.0^\circ C$) can be used to determine the molecular mass of organic compounds. A mixture of 100.0g of biphenyl and 2.67g of naphthalene ($C_{10}H_8$) has a melting point of $68.50^\circ C$. If a mixture of 1.00g of an unknown compound with 100.0g of biphenyl has a melting point of $68.86^\circ C$, what is the molar mass of the unknown compound?

PART THREE

CHEMICAL KINETICS

Chapter 9

INTRODUCTION TO CHEMICAL KINETICS

Not all possible reactions are detectable. Many reactions are very slow at room temperature and some reactions may take even many years to be observable. Reactions like conversion of diamond to graphite or hydrogen and oxygen (to give water) are all possible at normal conditions but are not detectable because they are so slow that no reasonable change can be observed.

In real life, the reactions must occur at fairly high rate to be useful. If we want to produce ammonia for producing fertilizer for example, we cannot just mix nitrogen and hydrogen at room temperature and pressure and waiting for them to react; we will wait for years and years and nothing significant will be obtained! To get the ammonia, we must understand and apply factors governing the rate of reaction between nitrogen and hydrogen, and this is what chemical kinetics is all about!

Chemical kinetics is the branch of physical chemistry which is concerned about the study of determination of rates of chemical reactions and factors affecting it. The study of chemical kinetics deals with the qualitative and quantitative study of:

- The rates of reactions
- The factors affecting rate of reactions and
- The mechanism of reactions

RATE OF REACTION

Rate of reaction is the quantity of reactant consumed or the quantity of a product formed in unit time. It is the change of concentration of reactants or products per unit time in the course of a chemical reaction.

$$\text{Rate of the reaction} = \frac{\text{Change in concentration}}{\text{Time taken}}$$

The rate of reaction is expressed in unit of (concentration)(time)⁻¹ like: Ms⁻¹ (or moldm⁻³s⁻¹), Mmin⁻¹ (or moldm⁻³min⁻¹) etc.

- For gases, it can be expressed in terms of partial pressure like atm s⁻¹ or atm min⁻¹.

As the reaction proceeds, the concentration of products increases while that of reactants decreases. Thus the change of concentration of products is positive while that of reactants is negative.

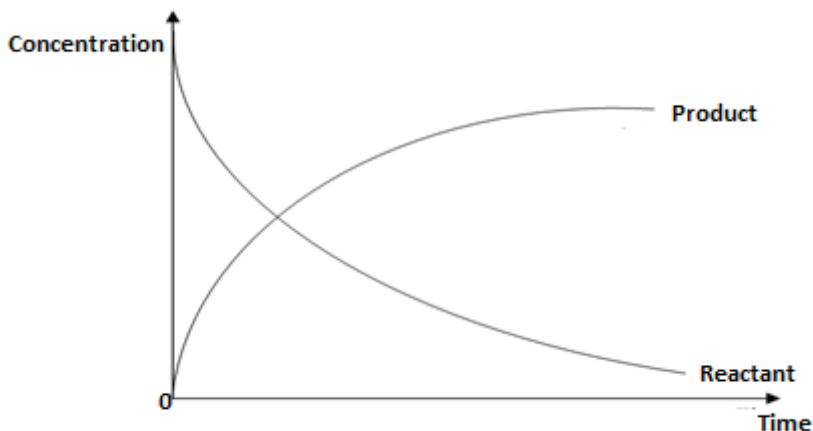


Figure 9.1 Variation of concentration of products and reactants in the reaction

- Reaction rate is the amount of reaction which occurs in unit time and therefore, if we wish to measure the rate of a chemical reaction we must choose some property of the reaction which will indicate how far the reaction has changed, and observe the way in which the magnitude of that property varies with time.

- It is advantageous to choose a property of the reaction which can be observed without disturbing the reaction itself. Thus, in a reaction where a colourless substance is changing to a coloured one, the rate at which the intensity of the colour increases would give the rate of reaction. In a similar way, for a reaction in which a gas is liberated from solution it may be, it may be possible to collect that gas and measure the way which the volume of gas increasing with time.

Reaction rate as an average rate

When the reaction rate is represented as the change in concentration divided by change in time, the result is known as **average rate** of the reaction.

$$\text{That is: Average rate} = \frac{\text{change in concentration}}{\text{time taken}} = \frac{C_{t_2} - C_{t_1}}{t_2 - t_1} = \frac{\Delta C}{\Delta t}$$

Where C_{t_1} and C_{t_2} are molar concentration at time t_1 and t_2 respectively.

Reaction rate as an instantaneous rate

As the reaction proceeds, concentration of reactants decreases and whence the rate of reaction decreases.

- Thus the rate of reaction is maximum at $t = 0$ (at the beginning of the chemical reaction) and continues to decrease as the time for the reaction increases until the reaction is complete where the rate is zero.
- So the graph of concentration against time for the common reaction whose rate of reaction decreases with decrease in concentration of reactants will look as follows;

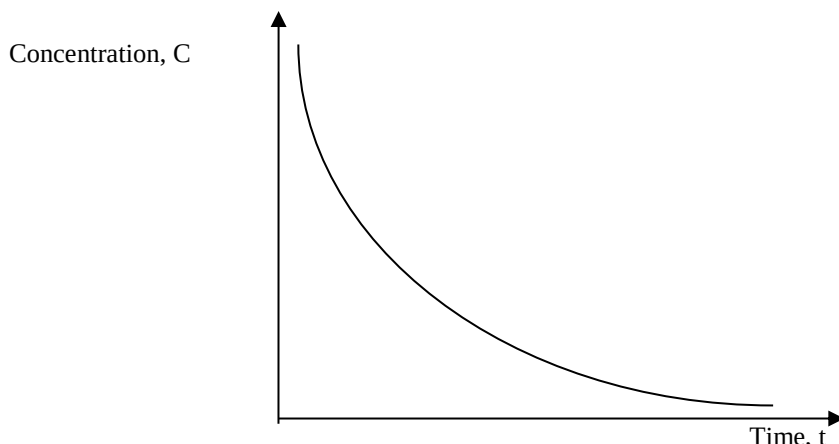


Figure 9.2 Variation of reactants concentration versus time of the reaction

Things to note from the graph:

- Slope of the curve $\left(\frac{\Delta C}{\Delta t}\right)$ represents the rate of reaction.
- When t approaches zero (at the beginning of the reaction) the curve is very steep (the curve has large slope) indicating high rate of the reaction when concentration of the reactant is still large.
- As the reaction proceed (t increases) the curve becomes less steep (the slope becomes small) indicating low rate of the reaction as the concentration of the reactant decreases. When the reaction is about to reach completion, (where the concentration of the reactant approaches zero) the curve is almost horizontal meaning the slope and hence the rate of reaction approaches zero.
- Like any curve, the slope of the above curve is not constant. It varies as t varies. This means that the rate of reaction also varies as t varies. This provides very important conclusion that:
 - We can only find rate of reaction at particular **instant** time hence the term **instantaneous rate of reaction**.

The average rate of reaction defined earlier is just an estimation of the rate of reaction over given time interval. It is the mean of several instantaneous rates of reaction taken over period of time.

- When the change in time ($t_2 - t_1$) approaches zero (that is $t_1 \approx t_2$), the average rate of reaction provides good approximation to the instantaneous rate of the reaction.

Thus; **instantaneous rate of reaction** = $\frac{\Delta C}{\Delta t}$ as $\Delta t \rightarrow 0$

- This is formally shortened as $\frac{dC}{dt}$ (derivative of C with respect to t).
That is $\frac{dC}{dt}$ stands for $\frac{\Delta C}{\Delta t}$ as $\Delta t \rightarrow 0$

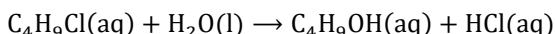
Thus in the formal mathematical language; **instantaneous rate of reaction** = $\frac{dC}{dt}$

Because reactions slow down over time, instantaneous rate of reaction is the better way of expressing the rate of reaction. In chemistry we are usually interested in the instantaneous reaction rate at the very beginning of the reaction. So whenever we talk about just rate of reaction (without any extra information), the implication will be the instantaneous rate of reaction at the very beginning of the reaction.

- The instantaneous rate of reaction is also known as **reaction velocity** (or **reaction speed**).

Reaction rates and stoichiometry

Consider the following reaction:



In this reaction the mole ratio of all species is 1:1. For any one mole of C_4H_9Cl (or H_2O) which disappear, there is one mole of C_4H_9OH or (or HCl) which is formed.

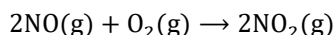
- Thus, the rate of disappearance of C_4H_9Cl is the same as the rate of appearance of C_4H_9OH

Hence in this case:

$$\text{Rate} = \frac{-d[C_4H_9Cl]}{dt} = \frac{-d[H_2O]}{dt} = \frac{d[C_4H_9OH]}{dt} = \frac{d[HCl]}{dt}$$

(Note: the negative sign appears in species of reactants side because their concentrations are decreasing during the reaction)

Now consider another reaction:



Hence we **cannot** say that $\frac{-d[O_2]}{dt} = \frac{-d[NO]}{dt}$ or $\frac{-d[O_2]}{dt} = \frac{d[NO_2]}{dt}$

Because from the reaction stoichiometry, it is clearly seen that for every **one** mole of O_2 which react, there must be also **two** moles of NO which reacts at the same time. Or for any **one** mole of O_2 which disappears, there are must be **two** moles of NO_2 which are produced at the same time.

- This means that the rate of disappearance of NO must be twice that of O_2

That is: $\frac{-d[NO]}{dt} = \frac{-2d[O_2]}{dt}$ or $\frac{-1}{2} \frac{d[NO]}{dt} = \frac{-d[O_2]}{dt} \dots \dots \dots$ (i)

- And the rate of appearance of NO_2 must be twice the rate of disappearance of O_2

That is: $\frac{d[NO_2]}{dt} = \frac{-2d[O_2]}{dt}$ or $\frac{1}{2} \frac{d[NO_2]}{dt} = \frac{-d[O_2]}{dt} \dots \dots \dots$ (ii)

Combining (i) and (ii) gives appropriate equation of rate in terms of rate of individual species appearing in the reaction which is;

Rate = $\frac{-1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}$ (Have you noticed how stoichiometric coefficient appears in this equation?)

Generally, for the reaction: $aA + bB \rightarrow cC + dD$

The reaction rate can be written in a number of different but equivalent ways as follows:

$$R = \frac{-1}{a} \frac{d[A]}{dt} = \frac{-1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

Example 1

- (a) How the rate at which ozone disappears is related to the rate at which oxygen appears in the reaction: $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$?
 (b) If the rate of which O_2 appears is $6.0 \times 10^{-5} \text{M/s}$ at particular instant, at what rate is O_3 disappearing at the same time?

Solution

(a) $\frac{-1}{2} \frac{d[\text{O}_3]}{dt} = \frac{1}{3} \frac{d[\text{O}_2]}{dt}$

(b) Given that $\frac{d[\text{O}_2]}{dt} = 6.0 \times 10^{-5} \text{M/s}$

Then substituting $\frac{-1}{2} \frac{d[\text{O}_3]}{dt} = \frac{1}{3} \times 6.0 \times 10^{-5} \text{M/s}$

Or $\frac{-d[\text{O}_3]}{dt} = \frac{2}{3} \times 6.0 \times 10^{-5} \text{M/s} = 4 \times 10^{-5} \text{M/s}$

Hence the rate of disappearing O_3 is $4 \times 10^{-5} \text{M/s}$

Example 2

Consider the reaction: $2\text{H}_3\text{PO}_4 \rightarrow \text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$

Using the information in the following table, calculate

- (a) The average rate of formation of P_2O_5 between 10.0s and 40.0s
 (b) The average rate of decomposition of H_3PO_4 between 10s and 40s

Time (s)	0	10.0	20.0	30.0	40.0	50.0
$[\text{P}_2\text{O}_5]/\text{M}$	0	1.5×10^{-3}	4.5×10^{-3}	6.3×10^{-3}	7.5×10^{-3}	8.1×10^{-3}

Solution

Using;

Average rate of formation of product = $\frac{\text{Change in concentration over certain time interval}}{\text{the time interval}}$

Thus the average of formation of $\text{P}_2\text{O}_5 = \frac{\Delta[\text{P}_2\text{O}_5]}{\Delta t} = \frac{[\text{P}_2\text{O}_5]_{t=40} - [\text{P}_2\text{O}_5]_{t=10}}{\Delta t} = \frac{(7.5 \times 10^{-3} - 1.5 \times 10^{-3})}{(40 - 10)\text{s}}$
 $= 2 \times 10^{-4} \text{Ms}^{-1}$

- (a) Hence the average rate of formation of P_2O_5 is $2 \times 10^{-4} \text{Ms}^{-1}$

Average rate of decomposition of H_3PO_4 is related to the average rate of formation of P_2O_5 by following $\frac{-1}{2} \frac{\Delta[\text{H}_3\text{PO}_4]}{\Delta t} = \frac{\Delta[\text{P}_2\text{O}_5]}{\Delta t}$

Where the negative sign(-) indicate that the concentration of H_3PO_4 is decreasing in the reaction

Thus $-\frac{\Delta[\text{H}_3\text{PO}_4]}{\Delta t} = \frac{2\Delta[\text{P}_2\text{O}_5]}{\Delta t} = 2 \times 2 \times 10^{-4} \text{Ms}^{-1} = 4 \times 10^{-4} \text{Ms}^{-1}$

- (b) Hence the rate of decomposition of H_3PO_4 is $4 \times 10^{-4} \text{Ms}^{-1}$

Example 3

Consider the following reaction: $\text{Fe(s)} + 2\text{AgNO}_3(\text{aq}) \rightarrow 2\text{Ag(s)} + \text{Fe(NO}_3)_2(\text{aq})$

In an experiment, an iron nail placed into a solution of AgNO_3 and the following data is collected:

Time (hour)	Mass (g) of Fe
0.0h	2.95g
2.0h	1.87g
4.0h	0.98g

Calculate the overall rate of this reaction in grams of Ag produced per hour. (Atomic masses: Fe = 55.8, Ag = 107.9).

Solution

Mass of iron reacted in 4h = $(2.95 - 0.98)\text{g} = 1.97\text{g}$

Using $n = \frac{m}{M_r}$

Number of moles of iron reacted in 4h = $\frac{1.97\text{g}}{55.8\text{g/mol}} = 0.0353\text{mol}$

Rate of Fe = $\frac{0.0353\text{mol}}{4\text{h}} = 8.825 \times 10^{-3}\text{mol/h}$

Rate of Fe and Ag are related by the following equation:

Rate of Ag = $2 \times 8.825 \times 10^{-3}\text{mol/h} = 0.01765\text{mol/h}$

Using $m = nM_r$;

Rate of Ag in g/h = $0.01765\text{mol/h} \times 107.9\text{g/mol} = 1.9\text{g/h}$

Hence the overall rate of production of silver is 1.9g/h

Collision theory and rate of reaction

Collision theory attempts to explain the results of kinetic experiments in terms of the individual atoms and molecules that are undergoing chemical reactions.

- Specifically, collision theory explains the temperature dependence of reaction rates, as well as some aspects of the behaviour of catalyst. Generally, most of factors affecting reaction rate can be explained by the collision theory.

Collision theory recognises that, for a reaction to take place, at least three conditions must be met:

First condition: A collision between reacting particles must take place

- For a chemical reaction to take place the molecules must collide. Even if the reaction involves the decomposition of single molecule, that molecule must have collided with something to give it the energy necessary to decompose.
- *The number of collisions between particles per second* is known as **collision frequency**.
- So it is reasonable to expect that the reaction rate will depend on collision frequency; the greater the number of collision per second (collision frequency), the faster the rate of reaction. The increase in collision frequency explains why **stirring** increase the rate reaction.

Second condition: The colliding particles must be properly oriented in such a way that a reaction takes place.

- Not every collision will result into reaction. Only collisions of properly oriented molecules may result into reaction.
- For example, if hypothetical molecules, A_2 and B_2 react according to the equation, $A_2 + B_2 \rightarrow 2AB$, then according to the **first condition**; for the reaction to take place A_2 and B_2 (**not** A_2 and A_2 or B_2 and B_2) must collide. The second condition say that not every collision between A_2 and B_2 results into collision unless the two molecules are properly oriented.

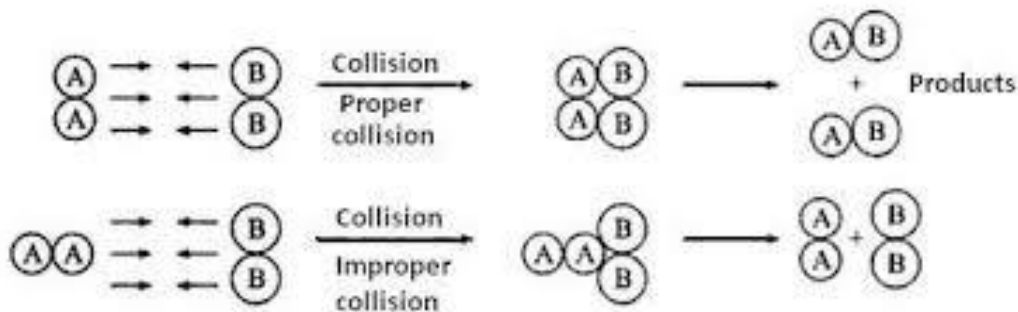


Figure 9.3 Proper and improper collisions

Third condition: The collision must be sufficiently energetic for it to result in a chemical reaction.

- The reaction may not occur even after collision between properly oriented reacting molecules. For the reaction to take place, the **collision energy** of the molecules must be large enough to overcome **activation energy** (E_a).
- This means that collision must occur with **enough energy** to overcome the electron-electron repulsion of the valence shell electrons of the reacting species and must have enough energy to transform translational energy into vibration energy in order to penetrate into each other so that electrons can rearrange and form new bonds. Such collisions are termed to be **effective collisions**.
- If the collision energy is above the activation energy, the **activated complex** (*the unstable intermediate which is formed when the two molecules collide*) disintegrates into products and therefore the reaction occurs but if the energy is below the activation energy the activated complex disintegrates into reactants and therefore the reaction does not occur.

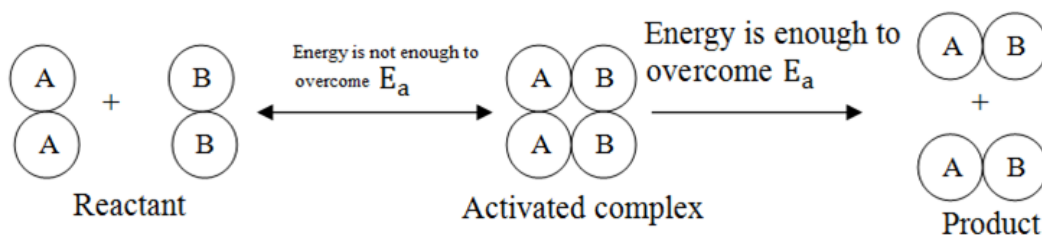


Figure 9.4 Formation of activated complex

- Lower activation energy means more collisions will result into reaction and hence greater the reaction rate.

Definition of terms:

Collision energy is the combined energy of colliding particles.

So in terms of collision energy, **activation energy** may be defined as *the minimum collision energy required for a collision to be successful*.

Activated complex is the unstable chemical specie that results upon successful collision (collision between reacting particles with activation energy) that momentarily exists with partially formed and broken bonds. It is the intermediate product which is formed when reactants have just attained activation energy

Activated complex is also known as transition state, why?

This is because the activated complex is the maximum energy value between two energy states (reactant energy and product energy). The transition state is higher energy than the product so it moves from that 'transition' state to the product.

- In one sentence the activated complex **transit** from the reactant to the product and hence the term transition state. (See figure below).

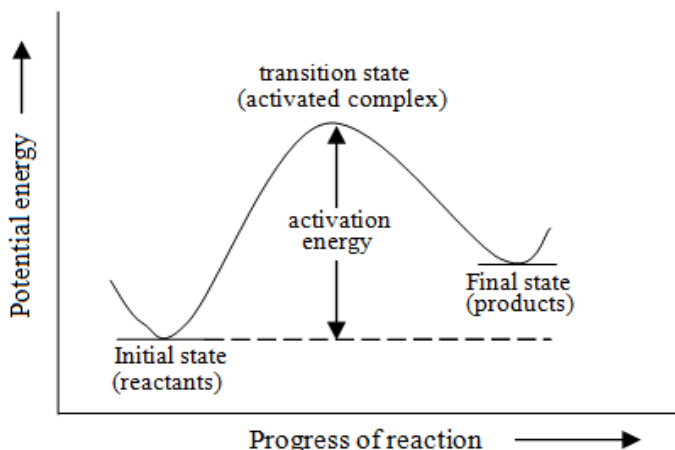


Figure 9.5 Energy profile diagram to show formation of activated complex

Activation energy and reaction rate

At room temperature, reactant particles have some potential energy. This potential energy is usually less than the **threshold energy** which is the minimum energy required for reactants to change into products. However, if energy is supplied in the form of heat, light etc., the reactant molecules absorb this energy so that their potential energy becomes equal to or greater than the threshold value. Hence, they start to change into products. In other words, the reactants need to be **activated** so as to change into products and hence the energy needed to do such activation is known as **activation energy**.

By definition:

Activation energy is the minimum amount of energy required to activate atoms or molecules to a state in which they can undergo a chemical reaction.

If reactant particles possess energy equal to or greater than the activation energy, they can cross the 'energy barrier' and the reaction occur.

- Conversely, if the reactant particles do not possess the activation energy required for a reaction, this reaction will not occur.

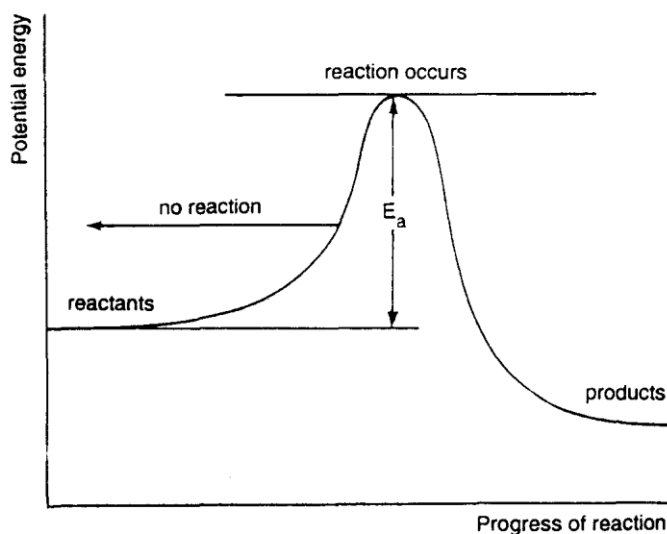


Figure 9.6 Potential energy diagram for a reaction

Some molecules will get energy equal to or greater than activation energy during collision and are called **activated molecules**.

- The collisions taking place between activated molecules are called **activated collisions** (or **effective collisions** or **fruitful collisions**).
- The products are formed only during the activated collisions.

Activated molecules constitute a small fraction of total molecules. Therefore, the effective (activated) collisions constitute a small fraction of total collisions and hence all the chemical reactions do not occur as fast as one could expect if all collision would be effective.

- If activation energy for the reaction is low, means that greater number of reactant particles may have that energy and hence the reaction rate will be high and vice-versa.

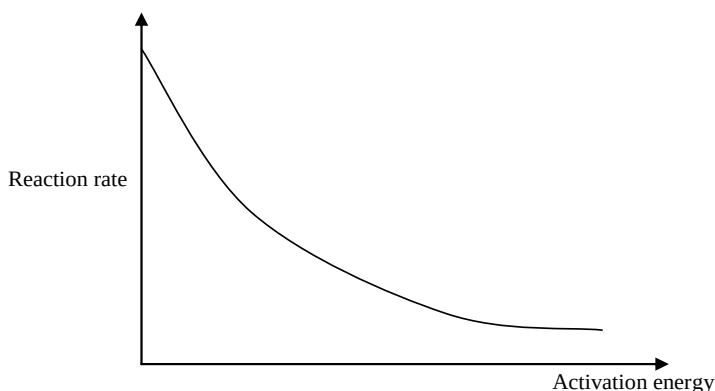


Figure 9.7 Graph to show relation between activation energy and reaction rate

The activation energy depends on the nature of chemical bonds, which are breaking during the reaction. Stronger the bond, greater the activation energy. However, it does not depend on the enthalpy of reaction.

- **The reaction may be highly exothermic, which in turn means that it is thermodynamically favoured but still can be very slow if the activation energy is very high.** A good example of this is **the rusting of iron** which is very slow exothermic reaction. In other words, rusting of iron is **thermodynamically favoured** (it is exothermic) but it is **kinetically unfavoured** (it is slow) due to high activation energy for the rusting process.
- **Or the reaction may be highly exothermic, (thermodynamically favoured), but still need to be initiated by applying suitable conditions** due to presence of the activation energy. A clear example of this is burning of wood. The wood burning is highly exothermic but wood cannot burn itself. It starts burning only after igniting it.

The facts that:

- Exothermic reactions may be slow and
- Exothermic reactions may not start if there are no suitable initiating conditions, are evidences of presence of activation energy for reactions.

Threshold energy versus activation energy

Although the two terms are commonly used interchangeably, there is a subtle difference between the two.

- **Threshold energy** is the minimum amount of energy required by colliding reactant particles to yield products.

Now because at standard conditions (or any other conditions), reactants are already having some **average energy** (*The potential energy possessed by normal reactant particles under standard conditions*) which is lower than the threshold energy; there is some energy which must be subjected to the reactant particles so as to attain the threshold energy. This energy is known as **activation energy**. So the activation energy is difference between threshold energy and average energy.

That is; **Activation energy = threshold energy – average energy**

However, the two terms are very close related; high threshold energy implies that high activation energy is required for the reaction to take place. Or if the reactants have gained enough activation, automatically implies that the reactants have attained threshold energy and hence they can be used interchangeably despite the difference in their actual meaning.

Factors affecting rate of reaction

The rate of a chemical reaction is affected by several factors including:

• Concentration of reactants	• Nature of reactants
• Pressure	• Surface area
• Temperature	• Intensity of light
• Catalyst	• Nature of solvent

Concentration

Rate of a reaction is directly proportional to the concentration of reactants.

Explanation

The frequency of collisions and hence the effective collisions between reactant particles increases with increase in concentration. Therefore, according to the collision theory, the rate of a reaction should increase with increase in the concentration since the rate is directly proportional to the collision frequency.

Pressure

The partial pressure is another way of expressing concentration of gases.

- The partial pressure of the gas can be increased in two ways.

1) By increasing amount of a particular gas

When mass and therefore number of moles of particular gas in the given volume of reacting mixture is increased at constant temperature, partial pressure (concentration) of the gas ($P = \frac{nRT}{V}$) increases. This increases the frequency of collision of reacting particles and hence the rate of reaction is increased too.

2) By increasing total pressure of the system

When total pressure of the system is increased, the partial pressure of each gas ($P_{\text{gas}} = X_{\text{gas}}P_{\text{total}}$) in the given amount of reactant mixture increases and whence collision frequency increases too leading to higher reaction rate.

Another way of explaining this is that: the increase in the total pressure of the system (compression) decreases volume (which automatically increases concentration) of the gases, making them more compact and hence greater collision frequency which in turn means faster reaction rate.

You should keep in mind that:

- Since the partial pressure of gases do not change by adding total pressure through addition of inert gas or any other gas which has no reaction with the present reaction mixture, rate of reaction is not affected when noble gases or non – reacting gases are added to the reaction mixture.
- Since liquid and solid are incompressible, changing in total pressure of the system has no effect on the rate of chemical reactions with liquid and solid reactants.

Temperature

Generally, the rate of chemical reaction increases with rise in temperature due to the following reasons:

- Rise in temperature increases average kinetic energy of colliding particles and therefore makes the collisions more energetic which in turn increase numbers of reacting particles which attains activation energy.
- Rise in temperature, increases the frequency of collision of reacting particles by increasing speed of the particles.
- In other words, increase in temperature increases the rate of reaction by increasing collision energy and collision frequency. However, the second factor of increasing collision frequency as result of temperature increase is the minor factor compared to the first factor.

Generally, the rate of normal chemical reactions (with positive activation energy) doubles for every increase in temperature of 10°C (or 10K).

- *The ratio of rate constants of reaction of two different temperatures which differ by 10°C is called **temperature coefficient**.*

However, it is not always true that the rate of a reaction increases with increase in **temperature**.

- Certain reactions like biological reaction which are catalysed by enzyme may be slowed down with increase in temperature since the enzyme (biological catalyst) may lose their activity at high temperature.

Catalyst

Catalyst increases the rate of reaction by giving alternative mechanism (route) of the reaction which has lower activation energy.

- Lower activation energy, means more colliding particle will have that energy and hence greater rate of reaction.

Catalyst are not consumed during the course of the reaction (at the end of the reaction, both identity and amount of the catalyst is conserved).

Nature of reactants

This can further be sub-divided into:

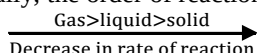
- Physical state of reactants and
- Chemical identity of reactants

The physical state:

Solids will react much more slowly than liquid (or aqueous solutions) and gases for example;

$K_2SO_4(s) + Ba(NO_3)_2(s) \rightarrow$ No reaction while the reaction is very fast in aqueous solution.

Generally, the order of reaction rate of the three common states of matter is as follows:

**The chemical identity:**

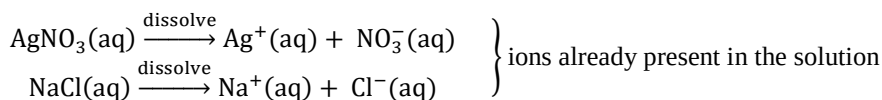
Rate of a reaction depends on the nature of bonding in the reactants.

Usually the ionic compounds (consist of ions) react faster than covalent compounds (consist of molecules).

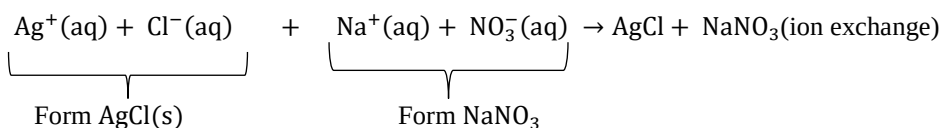
Explanation

The reaction between ionic compounds in water occurs very fast they involve only exchange of ions, which were already separated in aqueous solutions during their dissolution. For example: AgCl is precipitated out immediately when $AgNO_3$ solution is added to NaCl.

That is:



Then:



Whereas, the reaction between covalent compounds take place slowly because they require energy for the breaking the existing covalent bonds. For example, the esterification of ethanoic (acetic) acid occurs slowly since the breaking of covalent bonds present in the reactants requires energy.

Also the more bonds between reacting atoms in a molecule, the slower the reaction rate because more energy is required to break bonds in the molecule. In other words, these reactants with more bonds to break are said to have higher activation energy and hence slower rate of reaction.

Surface area

The rate of a reaction increases with increase in the surface area of solid reactant. The greater surface area exposed, the greater chance of collisions between reacting particles, hence, the reaction should proceed at a much faster rate due to the increase of the collision frequency.

- The surface area of a solid can be increased by grinding it to a fine powder. For example, the reaction between zinc and hydrochloric acid occurs within second if the zinc metal is finely powdered while the reaction will be slower when a zinc wire is used.
- This is also true with solid catalysts, which are usually employed in finely powdered form, while carrying out a chemical reaction. For example, finely powdered nickel is used during hydrogenation of alkenes.

In most cases, effect of surface area is greater than the effect of concentration and this explain why the rate of reaction between magnesium and dilute hydrochloric acid is increased more by changing magnesium from ribbon to powder than by increasing the concentration of the acid.

- The increase in surface area increases more collision frequency between reacting particles than the increase in concentration.

Intensity of light

Reactions which occur in presence of light are known as **photochemical reactions**.

- The rate photochemical reactions, increase with increase in the intensity of suitable light used. With increase in the intensity, the number of photons in light also increases. Hence more number of reactant molecules gets energy by absorbing more number of photons and undergo chemical change. For example, the rate of photosynthesis is greater on brighter (sun) days.
- However, some photochemical reactions involving the free radicals, generated in chain process are not greatly affected by the intensity of the light. Just one photon is sufficient to cause the formation of a free radical which in turn initiate a chain process in which more free radicals are formed repeatedly in each step without the need of extra photons.

Nature solvents

The solvents are used to dissolve the reactants and while doing so they help in providing more interactive surface between reactant particles which may be otherwise different phases or strongly bonded in solid phase.

- The polar molecules and ionic compound tend to dissolve more in polar solvents while non – polar molecules tend to dissolve in polar solvent.

So the reaction involving polar or ionic reactants is faster in polar solvent and slower in non – polar solvent while the reaction involving non – polar reactants is faster in non – polar solvent and slower in polar solvent.

Example 4

For each of the following statement, say whether you **agree** or **disagree** with the given argument and give brief explanation to defend your response:

- Every chemical reaction involving gaseous reactants is favoured by high pressure.
- Exothermic reactions are always fast reactions.

Solution

- Agree

Explanation

High pressure means high collision frequency and hence high reaction rate.

- Disagree

Even exothermic reaction may have high **activation energy** leading to slow reaction.

Example 5

For each of the following reactions, list three ways in which the rate of the reaction could be increased.

- $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$
- $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

Solution

(a)

- 1) Using high temperature
- 2) Reducing particle size of CaCO_3 (increasing surface area of CaCO_3)
- 3) Using high concentration of HCl(aq)

(b)

- 1) Using high pressure
- 2) Using high temperature
- 3) Using high concentration of H_2 (or I_2)

(c)

- 1) Using high temperature
- 2) Using high concentration of H_2O_2
- 3) Addition of catalyst

DIGGING DEEPER EXERCISE 9

EXERCISE 9A: BINDER QUESTIONS

Question 1

Identify two quantities that must be measured to establish the rate of a chemical reaction.

Question 2

Average rate of reaction does not give the true picture of the reaction. Explain.

Question 3

- (a) What is meant by the terms;
- (i) Collision frequency
 - (ii) Collision energy
 - (iii) Activation energy (in terms of collision energy)
- (b) How can these be changed in a chemical system?

Question 4

How the following are related to the rate of chemical reaction?

- (i) Collision frequency
- (ii) Collision energy
- (iii) Activation energy

Question 5

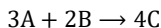
Describe how temperature, concentration, light, pressure and surface area can affect the rate of a chemical reaction.

Question 6

Why the rate of reaction does not remain constant throughout?

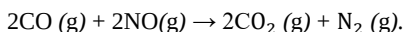
Question 7

For the reaction given below, what is the instantaneous rate for each of the reactant and product?



Question 8

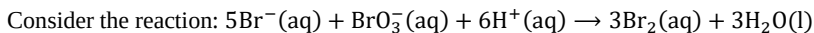
Explain why the rate of disappearance of NO and the rate of formation of N₂ are not the same in the reaction,



Question 9

For a chemical reaction $A \rightarrow B$, it was found that concentration of B increases by 0.2 mol L^{-1} in half an hour. What is the average rate of reaction?

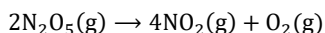
Question 10



The average rate consumption of Br⁻ is $1.06 \times 10^{-4} \text{ M/s}$ over the first two minutes, what is the average rate of formation of Br₂ during the same time interval?

Question 11

The decomposition of N₂O₅ proceeds according to the following equation;



If the rate of decomposing of N₂O₅ at particular instant in a reaction vessel is $4.2 \times 10^{-7} \text{ M/s}$, what is the rate of appearance of: (a) NO₂ (b) O₂?

EXERCISE 9B: REAL QUESTIONS

Question 12

Why keeping foods in the fridge, prevent them from spoiling?

Question 13

It takes many days for rusting of iron to be observable although the process is highly exothermic; why?

Question 14

Dropping a light stick into hot water makes it glow more intensely. Explain.

Question 15

Oxygen is available in plenty in air, yet woods do not burn by themselves at room temperature. Explain.

Question 16

A lump of coal burns at moderate rate in air while coal dust burns explosively. Explain.

Question 17

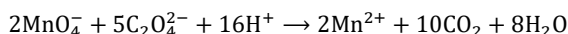
Why does coal not burn itself in air, but once initiated by flame continues to burn. Explain.

Question 18

Akilikubwa is a laboratory technician. In an effort to find the proper way of completing the reaction between magnesium and dilute hydrochloric acid quicker, he found that the time consumed for the reaction completion becomes shorter by changing magnesium from ribbon to powder than by doubling the concentration of the acid. Explain why.

Question 19

Another day, our laboratory technician, **Akilikubwa**, was doing an experiment that involved the reaction between manganate (VII) ions, MnO_4^- , and ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, in acid solution as per the following equation:



He observed that the reaction starts slowly, the rate of reaction then increases, before it decreases again. Unfortunately, **Akilikubwa** was unable to make sense of this sequence. Offer the desired help to our technician!

EXERCISE 9C: HOT QUESTIONS

Question 20

Although the reaction between H_2 (g) and O_2 (g) is highly feasible, leaving the gases in the same vessel at room temperature does not result in the creation of water. Explain.

Question 21

Consider a hypothetical reaction; $\text{P} \rightarrow \text{Q}$;

Average rates for the reaction was determined after 30min and 60min and found to be 0.08M/min and 0.03M/min respectively. Account for the difference of the average rates.

Question 22

Even a reaction with large number of colliding reactant molecules which have attained activation energy may be slow. Explain.

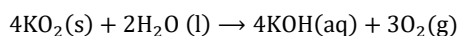
Question 23

The activation energy for forward and backward reactions for a hypothetical reaction, $\text{P} \rightarrow \text{Q}$; are 15 kJ/mol and 9 kJ/mol respectively. Potential energy of P is 10 kJ/mol. Predict:

- Threshold energy of the forward reaction.
- Potential energy of Q.
- Heat of reaction.

Question 24

Potassium superoxide(KO_2) is used to produce oxygen according to the following equation



When a sample of KO_2 was placed in water in an open flask, the following data was collected

Time in s	Mass of flask and content in g
0.0	150.00
30.0	145.50

Calculate;

- (a) The rate of O_2 production in grams of O_2 per second
- (b) The mass of KO_2 that reacted.(Atomic masses:O = 16, K = 39.1)

Question 25

Consider the following reaction: $2\text{Al}(\text{s}) + 3\text{CuCl}_2(\text{aq}) \rightarrow 2\text{AlCl}_3(\text{aq}) + 3\text{Cu}(\text{s})$

If the rate of consumption of Al is 0.46g/min, how many minutes will it take to produce 0.89g of Cu?

Chapter 10

ORDER OF CHEMICAL REACTIONS

GULDBERG AND WAAGE'S RATE LAW

In the previous chapter, we have seen that, commonly reaction rate increases as the concentration of reactants increases. However experimentally it has been found that the relationship between reaction rate and concentration is not always linear; doubling the concentration may increase reaction rate, two times (linear relationship) or four times or even eight times! The **rate law** (also known as **Guldberg and waage's rate law** in honour of people who discovered it) help us to understand specific relationship between reaction rate and concentration of reactants.

Guldberg and waage's rate law or simply **rate law** gives mathematical relationship between rates of reactions and concentrations of reactants and the law state that, *"the rate of reaction is directly proportional to the concentration of reactants each raised to its respective order."*

To understand the law, consider the reaction between reactants A and B such that: $A + B \rightarrow P$

From the rate law: $R \propto [A]^m[B]^n$

Introducing the constant of proportionality, the relationship become: $R = k[A]^m[B]^n$

And the result is known as the **rate law** (or **differential rate equation** or simply **rate equation** or **expression**) for the reaction between A and B to form P.

Where:

R = Rate of the reaction

k = Rate constant or velocity constant or rate coefficient.

m = Order of the reaction with respect to A

n = Order of the reaction with respect to B

And $m + n$ is the **overall order of the reaction** (it results from **partial orders of reaction** which are m and n).

The rate law may or may not include concentration of all the reactants. Sometimes, the rate law may include the concentration of species like catalysts, which do not appear in their stoichiometric equations.

By definition:

Rate law is the differential equation that describes the mathematical dependence of rate of reaction on the concentration terms of the reactants.

Order of the reaction is powers (exponents) of concentration of reactants in the rate law.

Order of the reaction describes the extent of which the concentration of particular reactant affects the rate of chemical reaction.

- If the order of the reaction with respect to a reactant is greater than that of another reactant, then the rate of chemical reaction is affected more by changing of the concentration of the reactant than that of another.
- That is if rate law is $R = k[A]^m[B]^n$ and $m > n$ then changing concentration of A has more effect on the rate of the reaction (value of R) than changing concentration of B.
- If the order of the reaction with respect to the particular reactant is zero, then changing concentration of the reactant has no effect on the rate of the reaction.

Overall order of the reaction is the sum of powers (exponents) of concentration of reactants in the rate law.

Overall order of the reaction expresses the extent to which the rate of the chemical reaction is affected by changing of concentration of reactants.

- If the overall order of one reaction is greater than that of another, then the rate of the reaction is affected more by changing concentration of its reactants than another reaction does.

That is if the rate law of first reaction is: $R_1 = k_1[A_1]^m[B_1]^n$

Where overall order of the reaction is $m + n$

And the rate law of second reaction is: $R_2 = k_2[A_2]^x[B_2]^y$

Where overall order of the reaction is $x + y$

Then if: $(m + n) > (x + y)$, the rate of first reaction has more dependence on concentration of reactants than the second reaction does.

- If the overall order of a reaction is zero, then the rate of the chemical reaction is not affected by changing in concentration of the reactants. For example, **when the reactant presents in excess, further increase in concentration of the reactant has no effect on the rate of the reaction and hence the reaction is always of zero order with respect to the excess reactant.**

The order of reaction may have positive, negative or zero values.

- The order with respect to an individual reactant may be sometimes fractional. However, the order of the overall reaction is usually an integer.

If the overall order of chemical reaction is:

- **Zero** then the reaction is termed as **zero order chemical reaction**.
- **One** then the reaction is termed as **first order chemical reaction**.
- **Two** then the reaction is termed as **second order chemical reaction** etc.

Very important to understand that:

For most chemical reactions order of the reaction can never be predicted from their balanced chemical equations. Determination of order of the reaction is experimental work.

Rate constant or **velocity constant** or **rate coefficient** is a temperature dependent fixed factor which gives the relationship between rate of the reaction and concentration of reactants. This is the qualitative definition of the constant.

Quantitatively, rate constant may be defined as:

The temperature dependent fixed factor which is given as a ratio of the rate of the reaction to concentration of reactants raised to their respective order.

That is if; $R = k[A]^m[B]^n$; then $k = \frac{R}{[A]^m[B]^n}$ where k is rate constant

So **rate constant** is the **specific rate** of a reaction at the unit concentration of all the reactants of the reaction and hence the term **specific rate** for the rate constant.

That is, if the rate law is, $R = k[A]^m[B]^n$

It clearly understand that, when $[A] = [B] = 1M$ (unit concentration)

$$R = k \times 1^m \times 1^n = k$$

And hence $R = k$ for unit concentration of all the reactants.

Units of rate constant

Consider **nth** order chemical reaction with the following rate law:

$$R = k[A]^n$$

It follows that:

$$\text{Units of } R = \text{units of } k \times (\text{units of } [A])^n$$

$$\text{From which, units of } k = \frac{\text{units of } R}{(\text{units of } [A])^n}$$

$$\text{Substituting units of } k = \frac{\text{mol dm}^{-3} \text{s}^{-1}}{(\text{mol dm}^{-3})^n} = (\text{mol dm}^{-3})^{1-n} \text{s}^{-1}$$

Hence unit of rate constant for the reaction is $(\text{mol dm}^{-3})^{1-n} \text{s}^{-1}$ where n is the overall order for the reaction.

Example 1

The rate constant for certain reaction is $0.01282 \text{ L mol}^{-1} \text{ s}^{-1}$. What is the order of the reaction?

Solution

The unit of rate constant for the reaction of n th order is given by $(\text{mol L}^{-1})^{1-n} \text{s}^{-1}$

$$\text{Thus, } \text{L mol}^{-1} \text{s}^{-1} = (\text{mol L}^{-1})^{1-n} \text{s}^{-1} \text{ or } \text{L mol}^{-1} = (\text{mol L}^{-1})^{1-n}$$

$$\text{It follows that } (\text{mol L}^{-1})^{-1} = (\text{mol L}^{-1})^{1-n} \text{ or } -1 = 1 - n \text{ or } n = 2$$

Hence the reaction is of the second order.

CHEMICAL REACTIONS OF ZERO ORDER

Most reactions involving a single reactant show either first order or second order kinetics. However, sometimes such a reaction can be a zero order reaction. Chemical reactions of zero order are not common reactions; are rare, but they exist. Example of zero order reaction is the decomposition of ammonia (NH_3) or hydrogen iodide (HI) on metal surface such as gold.

In zero-order reaction, the rate of reaction is not affected by the change of concentration of reactant and thus the reaction rate remain constant throughout the reaction process in contradiction to what we had studied in the introduction of the previous chapter. The graph of rate against time is horizontal while that of concentration of reactant against time is the straight line (not a curve!) with negative slope as illustrated below.

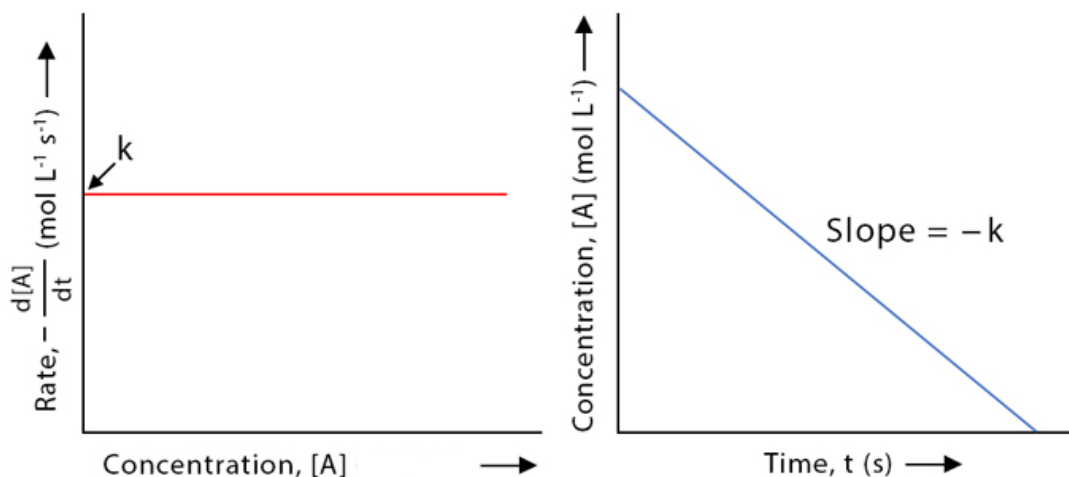
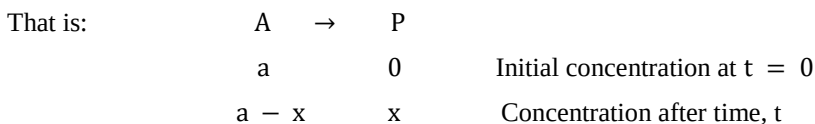


Figure 10.1: Graphs for zero order reaction

Integral equation for zero order chemical reaction

Consider the following zero order chemical reaction in which a reactant, A, reacts to give a product, P.



From the rate law: $R = k[A]^n$ (Where [] stands for molar concentration in mol/dm³)

But for the zero order chemical reaction, $n = 0$

Thus the rate law (differential rate equation) of the reaction becomes: $R = k$

Using Rate, $R = \frac{\text{change in concentration}}{\text{change in time}} = \frac{-d[A]}{dt}$

(The negative sign indicate that the concentration is continuously decreasing as the reaction proceed)

But $-\frac{d[A]}{dt} = \frac{d[P]}{dt} = \frac{dx}{dt}$

Substituting $\frac{dx}{dt}$ for R in $R = k$, gives $\frac{dx}{dt} = k$

Then $\frac{dx}{dt} = k$ or $dx = kdt$ (i)

Integrating throughout the equation (i) $\int dx = \int kdt$ OR $x = kt + c$

When $t = 0$ and $x = 0$

Hence $x = kt$(ii)

Now let:

$a - x = [A]_t$ (concentration of A present after anytime, t.

And $a = [A]_0$ (Initial concentration of A at the reaction beginning)

Then $[A]_t = [A]_0 - x$ or $x = [A]_0 - [A]_t$(iii)

Substituting (iii) into (ii) gives;

$$[A]_0 - [A]_t = kt \text{ or } [A]_t = -kt + [A]_0$$

Hence integral equation for zero order chemical reaction is $[A]_t = -kt + [A]_0$

Where:

$[A]_0$ is the initial concentration of the reactant.

$[A]_t$ is the concentration of the reactant remained after any time, t.

k is the rate constant (or velocity constant).

Units of rate constant for zero order reactions

Consider the first order chemical reaction with the following rate law: $R = k$

It follows that: Units of $R =$ units of k

But units of $R = \text{mol dm}^{-3} \text{s}^{-1}$

Hence units of rate constant for zero order reactions is $\text{mol dm}^{-3} \text{s}^{-1}$

Half-life of zero order chemical reactions

The half-life of a reaction, $t_{1/2}$ is the time required for the concentration of the reactant(s) to be reduced to a half of its initial concentration of the reactant (s) to react.

For zero order chemical reaction, it has been shown that; $x = kt$

But when $t = t_{1/2}$, $x = a/2$ (where a is initial concentration of reactant and $t_{1/2}$ is the half-life)

$$\text{Thus } a/2 = kt_{1/2} \text{ or } t_{1/2} = \frac{a}{2k}$$

Hence for zero order chemical reaction: $t_{1/2} = \frac{a}{2k}$

Thus the half-life for the zero order reaction increases at exact proportional as an increase in initial concentration of the reactant. For example, if the initial concentration is doubled, the half-life will double too or if the concentration is increased by a factor of 5, the half-life will increase by the same factor.

Time for completion of zero order chemical reaction

From the integral rate equation of zero order reaction: $[A]_t = -kt + [A]_0$

Upon reaction completion, the reactant is entirely consumed and therefore $[A]_t = 0$

$$\text{Substituting } 0 = -kt + [A]_0 \text{ or } t = \frac{[A]_0}{k}$$

Hence **the zero order reaction can reach completion** and the time required to have zero concentration of reactant is given by;

$$t = \frac{[A]_0}{k}$$

Example 2

In the reaction, $A \rightarrow \text{products}$, with the initial concentration, $[A]_0 = 1.512 \text{ M}$, $[A]$ is found to be 1.496 M at $t = 30 \text{ s}$. With the initial concentration $[A]_0 = 2.584 \text{ M}$, $[A]$ is found to be 2.552 M at $t = 1 \text{ min}$. What is the order of this reaction?

$$\text{Using; average rate} = \frac{\text{change in concentration}}{\text{time taken}} = \frac{C_{t_2} - C_{t_1}}{t_2 - t_1}$$

$$\text{Then using first set of values; average rate, } R_1 = \frac{(1.512 - 1.496) \text{ M}}{(30 - 0) \text{ s}} = 5.33 \times 10^{-4} \text{ M/s}$$

$$\text{And from second set of values; average rate, } R_2 = \frac{(2.584 - 2.552) \text{ M}}{(60 - 0) \text{ s}} = 5.33 \times 10^{-4} \text{ M/s}$$

Since the reaction rate remained the same even after changing initial concentration, the order of the reaction is zero order.

Example 3

The decomposition of hydrogen iodide on gold at 323 K is zero order reaction and the rate constant is $1.2 \times 10^{-4} \text{ Ms}^{-1}$.

- If the initial concentration of hydrogen iodide is 0.5 M , calculate its concentration after $3 \times 10^3 \text{ s}$.
- How long will it take for all of the hydrogen iodide to decompose?

Solution

(a) Using integral rate equation for zero order reaction; $[A]_t = -kt + [A]_0$

$$\text{Substituting } [A]_t = (-1.2 \times 10^{-4} \text{ Ms}^{-1} \times 3 \times 10^3 \text{ s}) + 0.5 \text{ M} = 0.14 \text{ M}$$

The concentration is 0.14 M

(b) The time required is given by; $t = \frac{[A]_0}{k}$

$$\text{Substituting } t = \frac{0.5M}{1.2 \times 10^{-4} \text{Ms}^{-1}} = 4.17 \times 10^3 \text{s}$$

The time required is $4.17 \times 10^3 \text{s}$.

CHEMICAL REACTIONS OF FIRST ORDER

First order chemical reaction is the reaction whose summation of powers (exponents) in the rate law is one. Thus in the chemical reaction of the first order, the rate of chemical reaction increases at equal times as the increase in the concentration e.g. if the concentration of the reactant is doubled the rate of chemical reaction is also doubled. Most of first order chemical reactions are **decomposition reactions** e.g. decomposition of hydrogen peroxide (H_2O_2) into water and oxygen gas. All radioactive disintegrations are first order reactions.

Relationship between the initial concentration of the reactant and time for forming given amount of product in the first order chemical reaction

The rate of first order reaction varies directly proportional to the concentration of the reactant (raised to one).

Thus if: R is the rate of the reaction and C is the original concentration of the reactant.

Then $R \propto C$

Introducing constant of proportionality: $R = kC$

From which: $\frac{R}{C} = k$

Therefore $\frac{R_1}{C_1} = \frac{R_2}{C_2} = k$ or (by rearranging the equation) $\frac{R_1}{R_2} = \frac{C_1}{C_2}$

But the rate of the chemical varies inversely to the time taken for the reaction to take place.

Thus if t is the time taken for the reaction to form given amount of product:

$$R \propto \frac{1}{t} \quad \text{or} \quad R = \frac{k}{t}; \quad \text{then} \quad \frac{R_1}{R_2} = \frac{k/t_1}{k/t_2} = \frac{t_2}{t_1}$$

Substituting $\frac{R_1}{R_2} = \frac{t_2}{t_1}$ in $\frac{R_1}{R_2} = \frac{C_1}{C_2}$ gives $\frac{t_2}{t_1} = \frac{C_1}{C_2}$ From which $C_1 t_1 = C_2 t_2$

Hence for first order chemical reaction; **Ct = constant**

i.e. $C_1 t_1 = C_2 t_2 = C_3 t_3 = \dots = C_n t_n$

Where C is the initial concentration of the reactant

t is the time taken for the reaction to form given amount of product.

Integral equation for first order chemical reaction

Most of the first order chemical reactions have single reactants.

So they in the form of: $A \rightarrow P$

$a \qquad 0 \qquad \text{Initial concentration at } t = 0$

$a - x \qquad x \qquad \text{Concentration after time, } t$

From the rate law: $R = k[A]^n$

But for the first order chemical reaction, $n = 1$

Thus the rate law (differential rate equation) of the reaction becomes: $R = k[A]$

Where $[]$ stands for molar concentration in mol/dm^3

$$\text{Using Rate, } R = \frac{\text{change in concentration}}{\text{change in time}} = \frac{-d[A]}{dt}$$

(The negative sign indicate that the concentration is continuously decreasing as the reaction proceed)

$$\text{But } -\frac{d[A]}{dt} = \frac{d[P]}{dt} = \frac{dx}{dt}$$

$$\text{Substituting } \frac{dx}{dt} \text{ for } R \text{ in } R = k[A] \text{ gives } \frac{dx}{dt} = k[A]$$

But $[A]$ after any time, t is $(a - x)$

$$\text{Then } \frac{dx}{dt} = k(a - x) \text{ or } \frac{dx}{(a-x)} = k dt \dots \dots \dots (i)$$

$$\text{Integrating throughout the equation (i) } \int \frac{dx}{(a-x)} = \int k dt \text{ Or } -\ln(a - x) = kt + c$$

When $t = 0$ and $x = 0$; then $-\ln(a - x) = k \times 0 + c$; from which $c = -\ln a$

$$\text{Thus } -\ln(a - x) = kt - \ln a \text{ or } \ln a - \ln(a - x) = kt$$

$$\text{Then } \ln\left(\frac{a}{a-x}\right) = kt$$

And by changing natural logarithm to common logarithm the equation become;

$$2.303 \log\left(\frac{a}{a-x}\right) = kt$$

$$\text{Hence for first order chemical reaction: } \log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$$

Where:

a is the initial concentration of the reactant

x is the concentration of the reactant decreased (reacted) after any time, t

$(a - x)$ is the concentration of the reactant remained after any time, t

k is the rate constant (or velocity constant)

You should understand that:

The ratio; $\left(\frac{a}{a-x}\right)$ in the above first order equation allows to substitute partial pressure (for gas phase reaction) of the reactant instead of its concentration. This can be clearly shown as follows:

$$\text{From an ideal gas equation: } PV = nRT \text{ or } P = \left(\frac{n}{V}\right) RT$$

$$\text{But } \frac{n}{V} = \text{Molar concentration, } []$$

$$\text{Thus } P = [] RT, \text{ from which; } [] = \frac{P}{RT} \text{ then } a = \frac{P_o}{RT} \text{ and } (a - x) = \frac{P_o - P}{RT}$$

$$\text{Thus } \frac{a}{a-x} = \frac{P_o}{RT} \div \frac{P_o - P}{RT} = \frac{P_o}{P_o - P}$$

$$\text{Substituting } \frac{P_o}{P_o - P} \text{ for } \frac{a}{a-x} \text{ in the obtained first order equation gives:}$$

$$\log\left(\frac{P_o}{P_o - P}\right) = \frac{kt}{2.303} \text{ in terms of partial pressure of the reactant}$$

Where: P_0 is the initial pressure of the reactant before the reaction starts,

P is the decrease in pressure after any time, t of the reaction,

$P_0 - P$ is the recorded pressure after any time, t of the reaction (pressure of the reactant which remains after any time, t).

Units of rate constant for first order reactions

Consider the first order chemical reaction with the following rate law: $R = k[A]$

It follows that: Units of $R = \text{units of } k \times \text{units of } [A]$

From which, unit of $k = \frac{\text{unit of } R}{\text{unit of } [A]}$

Then substituting units of $k = \frac{\text{mol dm}^{-3} \text{s}^{-1}}{\text{mol dm}^{-3}} = \text{s}^{-1}$

Hence units of rate constant for first order reaction is s^{-1} (or min^{-1} , hr^{-1} etc., depending on unit used for measuring time).

Half-life of first order chemical reactions

The half-life equation for first order reaction can be derived from the first order equation as follows:

From $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$; $t = \frac{2.303}{k} \log\left(\frac{a}{a-x}\right)$: When $t = t_{1/2}$, $x = a/2$

$$\text{Thus } t_{1/2} = \frac{2.303}{k} \log\left(\frac{a}{a-a/2}\right) = \frac{2.303}{k} \log 2 = \frac{0.693}{k}$$

Hence the half life for the first order chemical reactions is given by: $t_{1/2} = \frac{0.693}{k}$

Thus the half-life for the first order reaction is always constant and does not depend on initial concentration of the reactants.

Understand this interesting fact!

Not only the time required for a half of reactant to react (or to remain) which is constant but the rule holds for any fraction amount, whether it is $t_{1/4}$, $t_{3/4}$, $t_{2/3}$ etc. To understand this, consider the following general scenario;

Let us assume f represents fraction of initial concentration of reactant that remains after anytime, t .

Then $f = \frac{a-x}{a}$ or $a-x = af$

Then the equation $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$ becomes;

$$\log\left(\frac{a}{af}\right) = \frac{kt}{2.303} \text{ or } \log\left(\frac{1}{f}\right) = \frac{kt}{2.303}$$

From which; $t = \frac{2.303}{k} \log \frac{1}{f}$ or $-\frac{2.303}{k} \log f$

Hence the time required (t) for any fraction of reactant (f) to remain is given by;

$$t = \frac{-2.303}{k} \log f$$

From the above equation, there is no term for initial concentration and thus it is clearly understood that the time required for the given fraction amount of reactant to remain (or react) is constant at given temperature.

Also from the above equation, the equation of half-life can be easily deduced as follows:

$$\text{If } t = t_{1/2}, f = \frac{1}{2}$$

Then our bolded equation becomes;

$$t_{1/2} = \frac{-2.303}{k} \log \frac{1}{2} = \frac{0.693}{k} \text{ (As we have seen earlier)}$$

Time for completion of first order chemical reaction

From the integral rate equation of first order reaction: $\log \left(\frac{a}{a-x} \right) = \frac{kt}{2.303}$

Upon reaction completion, the reactant is entirely consumed and therefore $x = a$ and $a - x = 0$

$$\text{Substituting } \log \left(\frac{a}{0} \right) = \frac{kt}{2.303} \text{ or } t = \frac{2.303}{k} \log^{-1} \left(\frac{a}{0} \right)$$

Since $\log^{-1} \left(\frac{a}{0} \right)$ is undefined, the value of t is undefined (cannot be found) too and hence **the first order reaction can never reach completion by 100% and the concentration of reactant cannot be exactly zero (will be zero at infinite time)!**

Example 4

Consider a first order reaction: $A \rightarrow P$

The rate constant at 298K is $2 \times 10^{-3} \text{ sec}^{-1}$. If the initial concentration of A is 0.8M, calculate:

- Amount of A present after 9 minutes of the reaction
- The percentage of A which has reacted after 100 seconds
- The time required for 60% to react.

Solution

Using the equation

$$\log \left(\frac{a}{a-x} \right) = \frac{kt}{2.303} \text{ where } k = 2 \times 10^{-3}, t = 9 \text{ minutes} = 9 \times 60 \text{ sec} = 540 \text{ sec}$$

$$\text{Then } \log \left(\frac{a}{a-x} \right) = \frac{2 \times 10^{-3} \times 540}{2.303} = 0.47; \frac{a}{a-x} = \log^{-1}(0.47) = 2.95$$

$$\text{Then } (a-x) = \frac{a}{2.95} = \frac{0.8}{2.95} = 0.27 \text{ M}$$

- Amount of A after 9 minutes of the reaction is 0.27M

$$\text{Using: } \log \left(\frac{a}{a-x} \right) = \frac{kt}{2.303}$$

When $t = 100 \text{ sec}$

$$\log \left(\frac{a}{a-x} \right) = \frac{2 \times 10^{-3} \times 100}{2.303} = 0.0868; \frac{a}{a-x} = \log^{-1}(0.0868) = 1.2212$$

$$\text{Then } \frac{a-x}{a} = \frac{1}{1.2212} = 0.8189$$

Thus the percentage of A remained after 100s is $0.8189 \times 100\% = 81.89\%$

- Hence the percentage of A reacted is $(100 - 81.89)\% = 18.11\%$

$$\text{From } \log \left(\frac{a}{a-x} \right) = \frac{kt}{2.303}$$

$$\log \left(\frac{a-x}{a} \right)^{-1} = \frac{kt}{2.303}$$

$$\text{Then } -\log\left(\frac{a-x}{a}\right) = \frac{kt}{2.303} \text{ or } \log\left(\frac{a-x}{a}\right) = \frac{-kt}{2.303}$$

But it is given that: 60% of A reacted

$$\text{Thus } \frac{a-x}{a} \times 100\% = 40\% \text{ (Amount of A remained} = 100\% - 60\% = 40\%)$$

$$\text{Then substituting } \frac{a-x}{a} = 0.4 \text{ and } k = 2 \times 10^{-3} \text{sec}^{-1} \text{ to } \log\left(\frac{a-x}{a}\right) = \frac{-kt}{2.303};$$

$$\text{It gives: } \log 0.4 = \frac{-2 \times 10^{-3}t}{2.303} \text{ or } t = 458 \text{sec}$$

(iii) Hence the time required for 60% to react is 458seconds.

Example 5

A certain first order reaction has a half – life of 20 minutes:

(i) What is the rate constant for the reaction?

(ii) How long will it take for this reaction to be 75% complete?

Solution

For first order reaction, the half life ($t_{1/2}$) is given by: $t_{1/2} = \frac{0.693}{k}$

$$\text{From which } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20 \text{min}} = 0.03465 \text{min}^{-1}$$

(i) Thus the rate constant is 0.03465min^{-1}

$$\text{Using } \log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$$

Where:

$$a = 100$$

$$a-x = 25 \text{ ((100 - 75) as the reaction is 75\% complete)}$$

$$t = \text{time taken for the reaction to be 75\%complete}$$

$$k = \text{Rate constant} = 0.03465 \text{ min}^{-1}$$

$$\text{Substituting } \log\left(\frac{100}{25}\right) = \frac{0.03465t}{2.303}; \text{ from which } t = 40$$

(ii) Thus it will take 40 minutes for the reaction to be 75% complete.

Example 6

The first-order rate constant for the decomposition of N_2O_5 at 67°C is $5.2 \times 10^{-3} \text{s}^{-1}$.

(a) Calculate the time required for the concentration of N_2O_5 to fall to 50% of its initial concentration

(b) Without doing any further calculation, determine the time required for the concentration of N_2O_5 to decrease to one-fourth of its initial value.

Solution

(a) The time required for the reactant to fall to 50% is the half-life.

$$\text{The half life } (t_{1/2}) \text{ is given by: } t_{1/2} = \frac{0.693}{k}$$

$$\text{Substituting } t_{1/2} = \frac{0.693}{5.2 \times 10^{-3} \text{s}^{-1}} = 133 \text{s}$$

The time required is 133s

- (b) Since for the first order reaction, half-life is independent to initial concentration, the time required for the concentration to decrease to one-half (50%) is the same as the time required to decrease the concentration from one-half to one-fourth (25%). Hence the time required for the decrease in the concentration of N_2O_5 to 25% of its initial value is twice the half-life, that is 266s.

Question 7

After five half-life periods for a first order reaction, calculate fraction of reactant that remains?

Solution

Single period half-life of first order reaction is given by: $t_{1/2} = \frac{0.693}{k}$

But for first order reaction, half-life is the same irrespective to initial concentration.

Thus total time after five periods, $t = 5t_{1/2} = \frac{5 \times 0.693}{k} = \frac{3.465}{k}$

Then using; $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$;

$$\log\left(\frac{a}{a-x}\right) = \frac{k \times 3.465}{2.303 \times k} = 1.5046$$

From which; $\frac{a}{a-x} = \log^{-1}(1.5046) = 32$

Fraction that remains = $\frac{a-x}{a} = \frac{1}{\frac{a}{a-x}} = \frac{1}{32}$

Hence the fraction is $\frac{1}{32}$

CHEMICAL REACTIONS OF SECOND ORDER

Second order chemical reaction is the reaction whose summation of powers (exponents) in the rate law is two. A good example of second order reaction is the decomposition of nitrogen dioxide (NO_2) to nitrogen monoxide (NO) and oxygen (O_2).

Most of the second order reactions have two reactants of the following form: $\text{A} + \text{B} \rightarrow \text{P}$

Relationship between the initial concentration of the reactant and time for forming given amount of product in the second order reaction

The rate of second order reaction varies directly proportional to the square of concentration of the reactant.

Thus if: R is the rate of the reaction and C is the original concentration of the reactant.

Then $R \propto C^2$

Introducing constant of proportionality: $R = kC^2$

From which: $\frac{R}{C^2} = k$

Therefore $\frac{R_1}{(C_1)^2} = \frac{R_2}{(C_2)^2} = k$ or (by rearranging the equation) $\frac{R_1}{R_2} = \frac{(C_1)^2}{(C_2)^2}$

But the rate of the chemical varies inversely to the time taken for the reaction to take place.

Thus if t is the time taken for the reaction to form given amount of product:

$$R \propto \frac{1}{t} \quad \text{or} \quad R = \frac{k}{t}; \quad \text{then} \quad \frac{R_1}{R_2} = \frac{k/t_1}{k/t_2} = \frac{t_2}{t_1}$$

Substituting $\frac{R_1}{R_2} = \frac{t_2}{t_1}$ in $\frac{R_1}{R_2} = \frac{(C_1)^2}{(C_2)^2}$ gives $\frac{t_2}{t_1} = \frac{(C_1)^2}{(C_2)^2}$

From which $(C_1)^2 t_1 = (C_2)^2 t_2$

Hence for second order chemical reaction; **$C^2 t = \text{constant}$**

Where C is the initial concentration of the reactant

t is the time taken for the reaction to form given amount of product.

Integral equation for second order chemical reaction

Consider A and B with the same concentration say "a" react together to form P according to the following equation:



From the rate law: $R = k[A][B]$

Let $m = n = 1$ Such that $m + n = 2$ (for the second order chemical reaction)

Then the rate law of the reaction becomes: $R = k[A][B]$

$$\text{But } R = -\frac{d}{dt}[A] = -\frac{d[B]}{dt} = \frac{d[P]}{dt} = \frac{dx}{dt}$$

But from the rate law: $R = k[A](B) = k(a-x)(a-x) = k(a-x)^2$

$$\text{Thus } \frac{dx}{dt} = k(a-x)^2 \quad \text{or} \quad \frac{dx}{(a-x)^2} = k dt$$

$$\text{Then } \int \frac{dx}{(a-x)^2} = \int k dt \quad \text{or} \quad (a-x)^{-1} = kt + c \quad \text{or} \quad \frac{1}{(a-x)} = kt + c$$

$$\text{When } t = 0, x = 0 \text{ then } c = \frac{1}{a}$$

$$\text{Thus } \frac{1}{(a-x)} = kt + \frac{1}{a} \quad \text{or} \quad \frac{1}{(a-x)} - \frac{1}{a} = kt$$

$$\frac{a - (a-x)}{a(a-x)} = kt$$

$$\text{Hence for second order chemical reaction: } \frac{x}{a(a-x)} = kt$$

Where:

a is the initial concentration of the reactant

x is the decrease in concentration of the reactant at any time, t

(a - x) is the concentration of the reactant at any time, t

k is the rate constant of chemical reaction.

Note:

The above formula holds for second order reaction with single reactant only or for mixed reactants of the type $aA + bB \rightarrow \text{product}$, if and only if $a[A]_0 = b[B]_0$ or $[A]_0 = [B]_0$ if $a = b$.

The discussion of the integral rate equation of the type $aA + bB \rightarrow \text{product}$ where $a[A]_0 \neq b[B]_0$ is beyond the scope of this book.

Units of rate constant for second order chemical reaction

Consider the second order chemical reaction with the following rate law: $R = k[A]^2$

It follows that: Unit of $R = \text{unit of } k \times (\text{unit of } [A])^2$

From which, unit of $k = \frac{\text{unit of } R}{(\text{unit of } [A])^2}$

Then substituting units of $k = \frac{\text{mol dm}^{-3} \text{s}^{-1}}{(\text{mol dm}^{-3})^2} = (\text{mol dm}^{-3})^{-1} \text{s}^{-1}$ or $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$

Hence units of rate constant for first order reaction is $(\text{mol dm}^{-3})^{-1} \text{s}^{-1}$ or $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$

(In place for s^{-1} , min^{-1} , hr^{-1} etc., may be used depending on unit used for measuring time).

Half-life for second order chemical reaction

If the time taken for the reaction to proceed is the half life $t_{1/2}$ then $x = \frac{a}{2}$

So from $kt = \frac{x}{a(a-x)}$

$$t_{1/2} = \frac{a/2}{a(a-a/2)} = 1/a$$

$$t_{1/2} = \frac{1}{ak}$$

Hence the half-life for the second order chemical reaction is given by $t_{1/2} = \frac{1}{ak}$

Where 'a' is the initial concentration of the reactant and k is the rate constant

Thus unlike the first order chemical reaction whose half-life is independent to initial concentration, *the half-life of the second order chemical reaction depends on the initial concentration of the reactant and it is inversely proportional to the initial concentration. For example, when concentration is halved, half-life will be doubled.*

Again!

The rule holds for any fraction amount. For better understanding, consider the following general scenario;

Again, let f represents fraction of initial concentration of reactant that remains after anytime, t .

Then $f = \frac{a-x}{a}$ or $a - x = af$

Then the equation $kt = \frac{x}{a(a-x)}$ becomes;

$$kt = \frac{x}{a \times af} \text{ or } kt = \frac{x}{a^2 f} \text{ or } t = \frac{x}{a^2 kf}$$

But from $a - x = af$; $x = a - af = a(1 - f)$

$$\text{Then } t = \frac{a(1-f)}{a^2 kf} = \frac{(1-f)}{akf}$$

Hence the time required (t) for any fraction of reactant (f) to remain is given by;

$$t = \frac{(1-f)}{akf}$$

From the above equation, there is a term for initial concentration and thus it is clearly understood that the time required for the given fraction amount of reactant to remain (or react) depends on the initial concentration of the reactant and it is inversely proportional to the initial concentration.

Also from the above equation, the equation of half-life can be easily deduced as follows:

$$\text{If } t = t_{1/2}, f = \frac{1}{2}$$

Then the above equation becomes;

$$t_{1/2} = \frac{(1-\frac{1}{2})}{ak \times \frac{1}{2}} = \frac{1}{ak} \text{ (As we have seen earlier)}$$

Time for completion of second order chemical reaction

From the integral rate equation of second order reaction: $kt = \frac{x}{a(a-x)}$

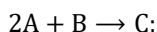
Upon reaction completion, the reactant is entirely consumed and therefore $x = a$ and $a - x = 0$

$$\text{Substituting } kt = \frac{x}{a \times 0} \text{ or } t = \frac{x}{0}$$

Since $\frac{x}{0}$ is undefined, the value of t is undefined (cannot be found) too and hence like first order reaction, **the second order reaction can never reach completion by 100% and the concentration of reactant cannot be exactly zero!**

Pseudo first order reactions

When a reaction is known to follow a rate of higher order than 1, concentration can often be adjusted to make the kinetics appear first order. To understand these, consider the reaction,



$$\text{with the rate law: } R = \frac{-1}{2} \frac{d[A]}{dt} = \frac{-d[B]}{dt} = k[A][B]$$

This rate law is second order in overall and its rate constant unit is $M^{-1}s^{-1}$.

But if we run the reaction with a very large excess of B, say $[B]_0 = 100[A]_0$ (where $[B]_0$ and $[A]_0$ stands for initial concentration of B and A respectively), then $[B]$ will change very little during the reaction; it will be nearly equal to $[B]_0$ the whole time.

That is if B present in excess;

$$[B] = \text{constant}$$

Then the equation $R = k[A][B]$ becomes;

$$R = k[A] \times \text{constant}$$

Where $k \times \text{constant}$ gives another constant, say k'

Hence we can write: (if B present in excess)

$$R = k'[A] \text{ (Where } k' = k[B])$$

Where $R = k'[A]$ is known as **pseudo first order rate law**, (**Pseudo** comes from Greek meaning *pretended* or *fake*)

k' is the **pseudo rate constant** with unit, s^{-1} .

And the reaction $2A + B \rightarrow C$ is now said to be **pseudo first order reaction**.

By definition

A pseudo first order reaction is the reaction that is truly second order but can be approximated to be the first order when one of the reactants is present so much in excess.

Most of hydrolysis reactions like hydrolysis of ester are pseudo first order reactions because in these reactions water is present in so large amount that its change in concentration can be ignored.

Example 8

The rate constant for the second order chemical reaction: $2\text{NOBr} \rightarrow 2\text{NO} + \text{Br}_2$ is $0.8 \text{ mol}^{-1} \text{ dm}^3 \text{ sec}^{-1}$ at 283K starting with initial concentration of $0.088 \text{ mol dm}^{-3}$ in NOBr. Calculate concentration of NOBr after 20 seconds of the reaction

Solution

From the second order equation: $\frac{x}{a(a-x)} = kt$

Substituting given values: $\frac{x}{0.088(0.088-x)} = 0.8 \times 20$ or $x = 0.0515$

The concentration of NOBr remained

$$= a - x = (0.088 - 0.0515) \text{ mol dm}^{-3} = 0.0365 \text{ mol dm}^{-3}$$

Hence concentration of NOBr after 20seconds is $0.0365 \text{ mol dm}^{-3}$

METHODS OF DETERMINING ORDER OF CHEMICAL REACTION

Generally, the order of the reaction can be determined from experimental data by various methods. Important methods which we are going to discuss in this book are four, namely:

- Graphical method
- Half-life method
- Integral rate equation method (calculation of the rate constant method).
- Initial rate method

Among the four methods, the graphical method and the integral method are done by trial and error and hence the two methods are collectively known as trial and error method.

Graphical method

For reactions which involve only one reactant, we can determine the reaction order by checking whether a graph of the data fits in one of the integral rate equations.

For the first order reaction

From the first order integral equation: $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

The equation can be rearranged as follows: $\log a - \log(a-x) = \frac{kt}{2.303}$

From which, $\log(a-x) = \frac{-kt}{2.303} + \log a$

The final equation corresponds to the equation of the straight line graph of the form of;

$$y = mx + c$$

With:

y corresponds to **$\log(a-x)$**

x corresponds to **t**

m (slope) corresponds to $\frac{-k}{2.303}$ (The graph has negative slope)

y-intercept corresponds to **$\log a$**

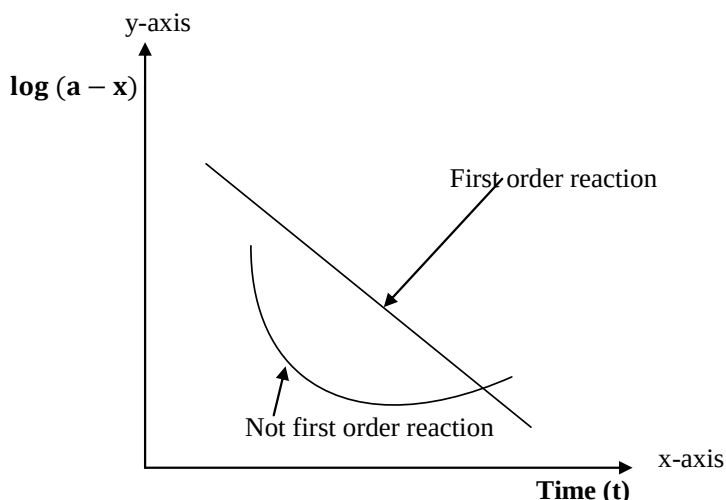


Figure 10.2 Graph of logarithm of concentration of reactant against time of the reaction

For the second order reaction

Here we are going to use this form of the second order integral equation; $\frac{1}{(a-x)} = kt + \frac{1}{a}$

Thus the graph of $\frac{1}{(a-x)}$ against t has the following characteristics (for the second order chemical reaction).

- The graph is straight line
- The slope of the graph, m is equal to the rate constant, k
That is $m = k$
- The y- intercept, c is equal to reciprocal of the original concentration
That is: $c = \frac{1}{a}$

The reader should be aware with the fact that:

The graph can also be plotted by applying rate law. For the first order reaction, the rate law; $R = k[A]$ will be used and the rate equation corresponds to the equation of straight line of the form of $y = mx$ with positive slope which corresponds to the rate constant (k) of the reaction when the graph of **Rate** (y) is plotted against **concentration** (x). The graph also passes through the origin as illustrated below:

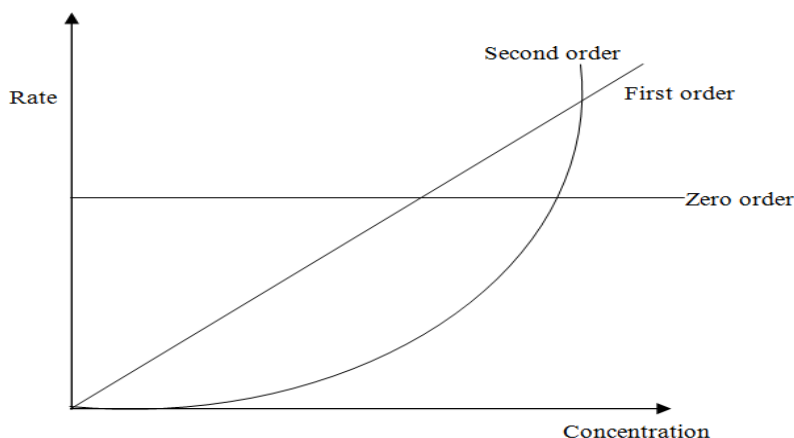


Figure 10.3 Graph of rate against concentration for different reaction orders

Summary on features of the graph

- The graph is straight line
- The graph passes through the origin
That is: $x - \text{intercept} = 0$ and $y - \text{intercept} = 0$
- The graph has positive slope such that: Slope of the graph = Rate constant.

For the second order reaction, the rate law is $R = k[A]^2$ and hence the graph of **rate (y)** against **square of concentration (x)** will be plotted to give the straight line of the form of $y=mx$.

Also the reader should understand that:

- Since rate of chemical reaction varies inversely proportional to time taken for the reaction to take place. **In most cases the reciprocal of the time (1/t) is used instead of the rate and the graph has the same features.**
- The rate of the reaction is equal to the slope of the graph of concentration plotted against time (slope of tangent lines drawn at each point of the graph).

Example 9

For the reaction: $N_2O_4(g) \rightarrow 2NO_2(g)$

Following data was collected:

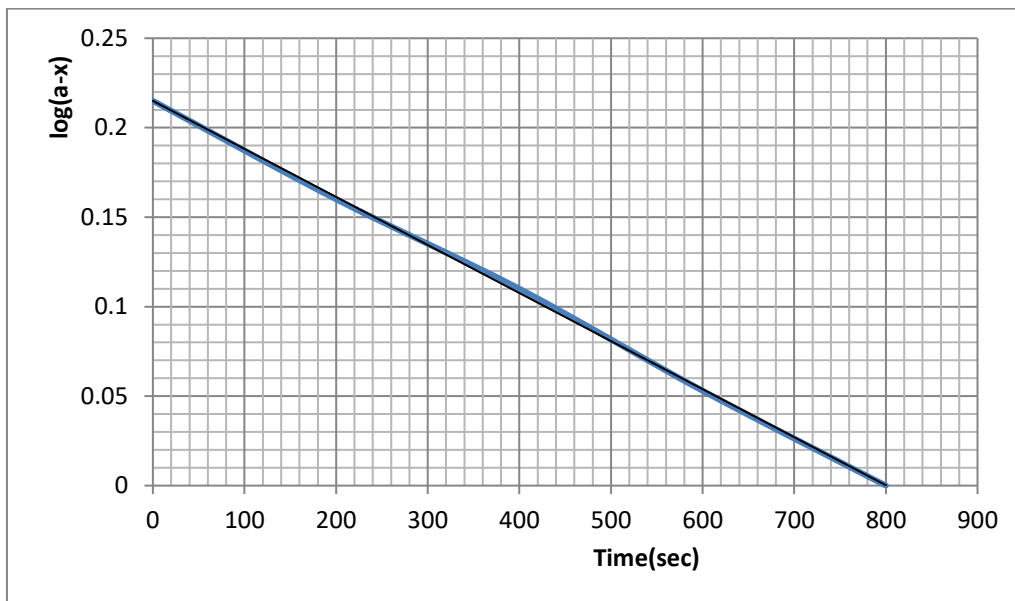
Time (sec)	0	200	400	600	800
$[N_2O_4]$	1.64	1.45	1.28	1.13	1.00

- Determine the order of the reaction graphically.
- What is the rate constant of the reaction?

Solution

A table for data analysis

Time (t)/ sec	0	200	400	600	800
$(a - x)$	1.64	1.45	1.28	1.13	1
$\log(a - x)$	0.215	0.16	0.11	0.053	0.00

GRAPH OF $\log(a - x)$ AGAINST TIME (t)

(i) Thus the reaction is of the first order since the nature of the graph agrees with the first order equation which is $\log(a - x) = \frac{-kt}{2.303} + \log a$

Comparing the equation: $\log(a - x) = \frac{-kt}{2.303} + \log a$ with the equation: $y = mx + c$

The slope, $m = \frac{-k}{2.303}$

But $m = \frac{\Delta y}{\Delta x} = \frac{\Delta \log(a-x)}{\Delta t}$

Taking any two points from the graph gives the slope, m of -0.000265

So from $m = \frac{-k}{2.303}$; $-0.000265 = \frac{-k}{2.303}$

or $k = 2.303 \times 0.000265 \text{ sec}^{-1} = 6.1 \times 10^{-4} \text{ sec}^{-1}$

(ii) Hence the rate constant of the reaction is $6 \times 10^{-4} \text{ sec}^{-1}$.

Half-life method

This method is used when there is only one concentration term in the rate law.

Consider half-life equations for various order chemical reactions as given below:

For first order chemical reaction: $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{a^0 k}$

For second order chemical reaction: $t_{1/2} = \frac{1}{ak} = \frac{1}{a^1 k}$

For third order chemical reaction: $t_{1/2} = \frac{1}{a^2 k}$

For fourth order chemical reaction: $t_{1/2} = \frac{1}{a^3 k}$

Thus from the half-life equations of various order chemical reactions, it appears that : *Half-life is inversely proportional to initial concentration, c, of the reactants raised to the order of the reaction decreased by one.*

That is: $t_{1/2} \propto \frac{1}{C^{n-1}}$

Where:

c = is the initial concentration of the reactant

n = is the order of the reaction with respect to the reactant

For two different initial concentrations, C_1 and C_2 with respective half-lives of t_1 and t_2

$$t_1 \propto \frac{1}{C_1^{n-1}} \text{ or } t_1 = \frac{1}{kC_1^{n-1}} \dots\dots\dots (i)$$

$$t_2 \propto \frac{1}{C_2^{n-1}} \text{ or } t_2 = \frac{1}{kC_2^{n-1}} \dots\dots\dots (ii)$$

$$\text{Taking (i) } \div \text{ (ii) gives: } \frac{t_1}{t_2} = \frac{C_2^{n-1}}{C_1^{n-1}} \text{ or } \frac{t_1}{t_2} = \left(\frac{C_2}{C_1}\right)^{n-1} = \left(\frac{C_1}{C_2}\right)^{1-n}$$

$$\text{Hence; } \frac{t_1}{t_2} = \left(\frac{C_2}{C_1}\right)^{n-1} = \left(\frac{C_1}{C_2}\right)^{1-n}$$

Where t_1 is the half life when the initial concentration is C_1

t_2 is the half life when the initial concentration is C_2

n is the order of the reaction

The reader should understand that:

First order of chemical reaction can also be spotted by studying half-lives of the reaction at different concentration. In this case graph of concentration against time is plotted. From the graph, several half-lives at different concentration are determined and compared. The graph of concentration plotted against time has always the nature given below: **(Except for zero order chemical reaction where the graph is straight line with negative slope which is equal to the rate constant).**

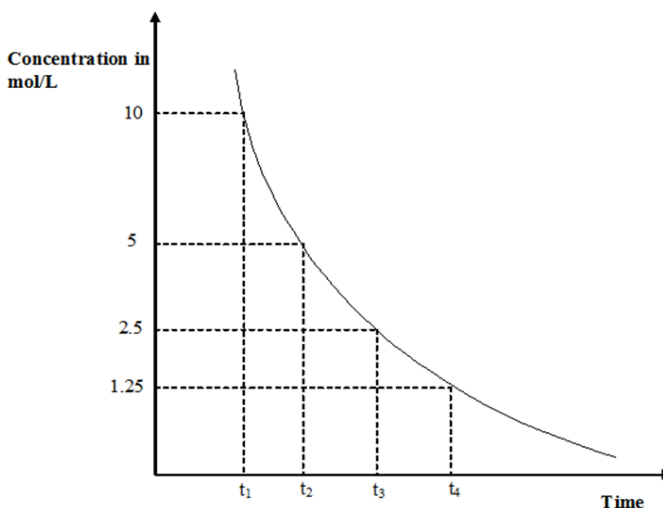


Figure 10.3 Graph to illustrate determination of reaction order by half-life method

Where:

$t_2 - t_1$ is the half life at concentration of 10 mol/dm^3 (The time taken for concentration to decrease from 10 to 5 mol/dm^3 in the reaction)

Similarly:

$t_3 - t_2$ is the half at concentration of 5 mol/dm^3 (The time taken for the concentration to decrease from 5 to 2.5 mol/dm^3) And $t_4 - t_3$ is the half life at concentration of 2.5 mol/dm^3 (The time taken for the concentration to decrease from 2.5 to 1.25 mol/dm^3)

Then from the graph, if the reaction is the first order the half-lives determined at different concentration will almost be equal. If the half-lives varies greatly the reaction is not of the first order.

Thus: If $t_2 - t_1 = t_3 - t_2 = t_4 - t_3$ then the reaction is of the first order.

But if $t_2 - t_1 \neq t_3 - t_2 \neq t_4 - t_3$ then the reaction is not of the first order.

Example 10

Decomposition of hydrogen peroxide obey first order reaction when started with 1.33M of H_2O_2 ; its half life was found to be 90sec . What would be the half life if one started with 0.57M of H_2O_2 under the same conditions.

Solution

Since the half-life of the first order chemical reaction does not depend on the initial concentration of the reactants, the half-life remains constant (unchanged).

Hence the half-life if one started with 0.57M of H_2O_2 is 90sec .

Alternative solution:

Using: $\frac{t_1}{t_2} = \left(\frac{C_2}{C_1}\right)^{n-1}$ Where $t_1 = 90\text{sec}$, $C_1 = 1.33\text{M}$, $C_2 = 0.57\text{M}$, $n = 1$

Then: $\frac{90}{t_2} = \left(\frac{1.33}{0.57}\right)^{1-1} = 1$ or $t_2 = 90 \text{ sec}$

Hence the half-life if one started with 0.57M of H_2O_2 is 90sec .

Example 11

In a simple conversion reaction: $\text{G} \rightarrow \text{P}$ when concentration of G was changed from 0.52M to 1.03M , the half life dropped from 150sec to 75sec

- What is the order of this reaction?
- Calculate the rate constant of this reaction

Solution

(a) Using $\frac{t_1}{t_2} = \left(\frac{C_1}{C_2}\right)^{1-n}$

Where $t_1 = 150\text{sec}$, $t_2 = 75\text{sec}$, $C_1 = 0.52\text{M}$, $C_2 = 1.03\text{M}$

$\frac{150}{75} = \left(\frac{0.52}{1.03}\right)^{1-n}$ or $n - 1 = 1$ or $n = 2$

Hence the reaction is of the second order

(b) Using $t_{1/2} = \frac{1}{ak}$ (for second order reaction)

Then: $t_1 = \frac{1}{kC_1}$ or $k = \frac{1}{t_1 C_1}$

So $k = \frac{1}{150 \times 0.52} \text{M}^{-1}\text{sec}^{-1} = 0.01282\text{M}^{-1}\text{sec}^{-1}$

Hence the rate constant for the reaction is $0.01282\text{M}^{-1}\text{sec}^{-1}$

Integral rate equation method

This method is also known as simply **integral method**. It is suitable when there is only one reactant. In this case, the integral rate equation of is used to calculate rate constant and hence the method is also known as **calculation of rate constant method**. This is done by taking different initial concentrations of the reactant (**a**) and noting the concentration (**a – x**) after regular time intervals (**t**). The experimental values of a, (a – x) and t are then substituted into the integral rate equations for the first, second and third order reactions to check whether the equation will give uniform value of k or not. **The rate equation which yields a constant value of k corresponds to the correct order of the reaction.**

As an example, for first order reaction; several rate constants are calculated at different concentrations by using first order equation.

$$\text{That is; } \log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$$

$$\text{From which; } k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$$

If the rate constants obtained (by using the above final rearranged equation) at different concentrations are equal, then the reaction is of the first order but if are different (vary greatly), the reaction is not of the first order.

Example 12

Experimental studies on the rearrangement of methylene nitrite to cotonitrite at 20°C yielded the following results:

Time	0	1000	2000	5000	10000	15000
Pressure of methylene nitrite in mmHg	150	142	135	115	88.8	68.2

Use the data above to determine the order of the reaction by calculation of the rate constant method. What is the rate constant of this reaction?

Solution

From $\log\left(\frac{P_0}{P_0 - P}\right) = \frac{kt}{2.303}$ which is first order equation in terms of pressures

$$k = \frac{2.303}{t} \log\left(\frac{P_0}{P_0 - P}\right) \text{ where } P_0 = 150\text{mmHg (when } t = 0)$$

When $t = 1000\text{sec}$, $P_0 - P = 142\text{mmHg}$

$$k_1 = \frac{2.303}{1000} \log\left(\frac{150}{142}\right) = 5.48 \times 10^{-5}\text{sec}^{-1}$$

When $t = 2000\text{sec}$, $P_0 - P = 135\text{mmHg}$

$$k_2 = \frac{2.303}{2000} \log\left(\frac{150}{135}\right) = 5.27 \times 10^{-5}\text{sec}^{-1}$$

When $t = 5000\text{sec}$, $P_0 - P = 115\text{mmHg}$

$$k_3 = \frac{2.303}{5000} \log\left(\frac{150}{115}\right) = 5.32 \times 10^{-5}\text{sec}^{-1}$$

When $t = 10000$, $P_0 - P = 88.8\text{mmHg}$

$$k_4 = \frac{2.303}{10000} \log\left(\frac{150}{88.8}\right) = 5.24 \times 10^{-5}\text{sec}^{-1}$$

When $t = 15000$, $P_0 - P = 68.2\text{mmHg}$

$$k_5 = \frac{2.303}{15000} \log \left(\frac{150}{68.2} \right) = 5.26 \times 10^{-5} \text{sec}^{-1}$$

Since rate constants for given reaction do not differ much, the reaction is of the first order.

$$\text{Rate constant, } k = \frac{k_1 + k_2 + k_3 + k_4 + k_5}{5} = \frac{(5.48 + 5.27 + 5.32 + 5.24 + 5.26) \times 10^{-5}}{5} \\ = 5.31 \times 10^{-5} \text{sec}^{-1}$$

Hence the rate constant for the reaction is $5.31 \times 10^{-5} \text{sec}^{-1}$

Initial rate method

This method suits reactions with more than one reactant. In this case, initial rate of reaction is determined by varying the concentration of one of the reactants while others are kept constant.

If A reacts with B to give P the order of reaction with respect of each reactant can be determined as follows:

- Firstly the rate of chemical reaction is determined with given concentration of A and B say A_1 and B_1

$$\text{Then } R_1 = k [A_1]^x [B_1]^y \dots \dots \dots \text{(i)}$$

- To determine the order of the reaction with respect to A, the concentration of A is varied to A_2 while that of B is kept constant and then the new rate of chemical reacting, R_2 is measured

$$\text{So } R_2 = k [A_2]^x [B_1]^y \dots \dots \dots \text{(ii)}$$

$$\text{Then taking } R_2 \div R_1; \text{ gives: } \frac{R_2}{R_1} = \frac{[A_2]^x [B_1]^y}{[A_1]^x [B_1]^y} = \left(\frac{[A_2]}{[A_1]} \right)^x$$

- To determine the order of the reactions with respect to B the concentration of B is varied to B_2 while that of A is kept constant

$$\text{That is } R_3 = k [A_1]^x [B_2]^y \dots \dots \dots \text{(iii)}$$

$$\text{Then taking } R_3 \div R_1 \text{ gives: } \frac{R_3}{R_1} = \frac{[A_1]^x [B_2]^y}{[A_1]^x [B_1]^y} = \left(\frac{[B_2]}{[B_1]} \right)^y$$

Example 13

Consider the following reaction: $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}$

The following data collected:

[NO]/M	[H ₂]/M	Rate /Msec ⁻¹
0.6	0.37	0.18
1.2	0.37	0.72
1.2	0.74	0.72

Determine the order of the reaction with respect to each reactant.

Solution

$$R = k [\text{NO}]^x [\text{H}_2]^y \text{ (From the rate law)}$$

$$\text{When } R = 0.18 \text{Msec}^{-1}, [\text{NO}] = 0.6 \text{ and } [\text{H}_2] = 0.37$$

$$\text{Thus } R_1 = k [0.6]^x [0.37]^y \dots \dots \dots \text{(i)}$$

When $R = 0.72 \text{ M sec}^{-1}$ $[\text{NO}] = 1.2 \text{ M}$ and $[\text{H}_2] = 0.37$

$$\text{Thus } R_2 = k [1.2]^x [0.37]^y \dots\dots\dots (ii)$$

When $R = 0.72 \text{ M sec}^{-1}$ $[\text{NO}] = 1.2 \text{ M}$ and $[\text{H}_2] = 0.74 \text{ M}$

$$\text{Thus } R_3 = k [1.2]^x [0.74]^y \dots\dots\dots (iii)$$

To find the order of the reaction with respect to NO, $[\text{H}_2]$ must be constant while $[\text{NO}]$ is changed. So taking (ii) $\div$ (i) $\frac{R_2}{R_1} = \frac{[1.2]^x}{[0.6]^x}$

$$\text{But } R_2 = 0.72 \text{ M sec}^{-1} \text{ and } R_1 = 0.18 \text{ M sec}^{-1}$$

$$\text{Then } \frac{0.72}{0.18} = \left(\frac{1.2}{0.6}\right)^x$$

$$4 = 2^x \text{ or } 2^x \text{ or } x = 2$$

Hence the order of the reaction with respect to NO is 2

To find the order of the reaction with respect to H_2 , concentration of NO must be kept constant while $[\text{H}_2]$ is changed. So taking (iii) $\div$ (ii) gives $\frac{R_3}{R_2} = \frac{[0.74]^y}{[0.37]^y}$

$$1 = 2^y \text{ or } 2^0 = 2^y \text{ or } y = 0$$

Hence the order of the reaction with respect to H_2 is zero

It should be understood that:

The zero order reaction with respect to H_2 means that the change in concentration of hydrogen gas has no effect on the rate of the reaction e.g. in given data of above question when the $[\text{H}_2]$ is doubled from 0.37M to 0.74M (while $[\text{NO}]$ is kept constant the rate of the reaction remains unchanged with value of 0.72 M sec^{-1})

Example 14

For the reaction: $\text{PCl}_3 + \text{Cl}_2 \rightarrow \text{PCl}_5$

The following experimental data were obtained

Experiment	$[\text{PCl}_3]/\text{M}$	$[\text{Cl}_2]/\text{M}$	Rate $/\text{M min}^{-1}$
1	0.36	1.26	0.036
2	0.36	0.63	0.009
3	0.72	0.63	0.018

- Determine the rate law of the reaction
- Calculate the value of rate constant and give its units
- Calculate the rate with which $[\text{PCl}_3] = 0.04 \text{ M}$ and $[\text{Cl}_2] = 0.02 \text{ M}$

Solution

$$R = k [\text{PCl}_3]^x [\text{Cl}_2]^y$$

$$R_1 = k [0.36]^x [1.26]^y$$

$$R_2 = k [0.36]^x [0.63]^y$$

$$R_3 = k [0.72]^x [0.63]^y$$

(a) Taking (i) $\div$ (ii);

$$\frac{R_1}{R_2} = \frac{[1.26]^y}{[0.63]^y} = \left(\frac{1.26}{0.63}\right)^y = 2^y$$

$$\text{But } \frac{R_1}{R_2} = \frac{0.036}{0.009} = 4 = 2^2$$

Then $2^2 = 2^y$ or $y = 2$

Taking (iii) $\div$ (ii);

$$\frac{R_3}{R_2} = \left(\frac{0.72}{0.36}\right)^x = 2^x$$

$$\text{But } \frac{R_3}{R_2} = \frac{0.018}{0.009} = 2^1$$

Then $2^1 = 2^x$ or $x = 1$

Thus the reaction is of the second order with respect to Cl_2 and is the first order with respect to PCl_3

Hence the rate law of the reaction is $R = k[\text{PCl}_3][\text{Cl}_2]$

$$(b) \text{ From the above rate law } k = \frac{R}{[\text{PCl}_3][\text{Cl}_2]^2}$$

Substituting values of **experiment I** (You may choose any set of value from respective experiment).

$$k = \frac{0.036 \text{ Msec}^{-1}}{(0.36)(1.26 \text{ M})^2} = 6.2988 \times 10^{-2} \text{ M}^{-2} \text{ sec}^{-1}$$

Hence the rate constant is $6.2988 \times 10^{-2} \text{ M}^{-2} \text{ sec}^{-1}$

$$(c) R = k[\text{PCl}_3][\text{Cl}_2]^2$$

Where $k = 6.2988 \times 10^{-2} \text{ M}^{-2} \text{ sec}^{-1}$

And it is given that $[\text{PCl}_3] = 0.04 \text{ M}$ and $[\text{Cl}_2] = 0.02 \text{ M}$

$$R = 6.2988 \times 10^{-2} \times 0.04 \times (0.02)^2 \text{ Msec}^{-1}$$

$$R = 1.007808 \times 10^{-6} \text{ Msec}^{-1}$$

Hence the rate will be $1.007808 \times 10^{-6} \text{ Msec}^{-1}$

DIGGING DEEPER EXERCISE 10

EXERCISE 10A: BINDER QUESTIONS

Question 1

Comment on half-life of a zero order, first order and second order reaction.

Question 2

In the reaction $A \rightarrow \text{products}$, we find that when $[A]$ has fallen to half of its initial value, the reaction proceeds at the same rate as its initial rate. Is the reaction zero order, first order, or second order? Explain.

Question 3

What is wrong with the following statement; *"Zero-order reactions are independent of concentration of reactants."*

Question 4

Give at least two examples in each of the following:

- (i) Zero order reaction
- (ii) First order reaction
- (iii) Second order reaction
- (iv) Pseudo first order reaction

Question 5

A first order reaction has a rate constant $1.15 \times 10^{-3} \text{s}^{-1}$. How long will 5g of this reactant take to reduce to 3g?

Question 6

The reaction of NO with O_2 is found to be second order with respect to NO and first order with respect to O_2 .

- (i) What is the overall reaction order?
- (ii) What is the effect of doubling the concentration of each reagent on the reaction rate?

Question 7

The rate constant of a reaction is $1.2 \times 10^{-2} \text{s}^{-1}$; what is the order of the reaction?

Question 8

A reaction is 20% complete in 20 minutes. Calculate the time required for 80% completion of reaction, if the reaction is of the first order.

Question 9

The half-life of radioisotope is found to be 4.55 minutes. If the decay follows first order kinetics what percentage of isotope will remain after 2 hours?

Question 10

The rate constant of a zero order reaction in A is 0.003M/s. How long will it take for the initial concentration of A to fall from 0.10M to 0.075M?

Question 11

From the following data for a chemical reaction between A and B at 25°C.

[A]	[B]	Initial rate in $\text{molL}^{-1}\text{sec}^{-1}$
2.5×10^{-4}	3×10^{-5}	5×10^{-4}
2.5×10^{-4}	6×10^{-5}	4×10^{-3}
1×10^{-3}	6×10^{-5}	1.6×10^{-2}

Calculate:

- The order of reaction with respect to each reactant.
- The rate constant at 25°C.

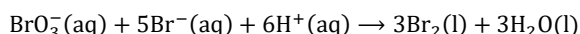
Question 12

A first order reaction, $A \rightarrow \text{products}$, has a rate of reaction of 0.00250 M s^{-1} when $[A] = 0.484 \text{ M}$.

- What is the rate constant, k , for this reaction?
- Does $t_{3/4}$ depend on the initial concentration? Explain.

Question 13

The reaction between bromate ions and bromide ions in acidic aqueous solution is

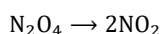


Using the data from four experiment shown below determine the orders of the rate of reaction for all the three reactants the overall reaction order, and the value of the rate constant, k .

Experiment	$[\text{BrO}_3^-]/\text{M}$	$[\text{Br}^-]/\text{M}$	$[\text{H}^+]/\text{M}$	Rate/ M s^{-1}
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

Question 14

When N_2O_4 decompose; it forms NO_2



If the half-life of this reaction is 1836seconds, how much of a 10g sample would be left after 1500seconds? State any assumption made on your calculation.

EXERCISE 10B: REAL QUESTIONS

Question 15

According to Tanzania chemistry syllabus, you are supposed to study order of chemical reactions up to second order. As a chemistry student who understand how chemical reaction occurs, suggest a possible reason of excluding reactions of higher order in the syllabus.

Question 16

You were having a discussion about chemical kinetics with your friend **Kipute**. "It is impossible for the rate of reaction to remain constant throughout." Explain to her whether you agree or disagree with her statement.

Question 17

Kipute was studying one of the book in Ngaiza book series titled physical chemistry. In the chapter of chemical kinetics, she read the following phrase; "Example of zero order reaction is the decomposition of ammonia (NH_3) or hydrogen iodide (HI) on metal surface such as gold." Unfortunately, **Kipute** was unable to make sense of how the decomposition on metal surface turns the reaction to be zero order. Since you are a good friend of **Kipute**, you decided to help her. What explanation you would give her?

Question 28

In the nuclear industry, workers use a rule of thumb that the radioactivity from any sample will be relatively harmless after 10 half-lives. Calculate the fraction of a radioactive sample that remains after this time period.

Question 19

Ngaiza Gauging Examination (NGE) is the examination conducted under Hopegen Company Limited for the aim of improving academic performance in Tanzania. In order to ensure good performance in NGE chemistry examination, student is advised to learn through reading books tilted Ngaiza's series of advanced chemistry which are under Hopegen Book Project. Assuming that the loss of ability to recall learned material in Ngaiza's series of chemistry books is a first order process with a half -life of 35days. Compute the number of days requires to forget 90% of the material that the student learned through studying Ngaiza's book series in the preparation of NGE chemistry examination.

Question 20

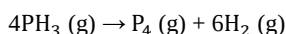
Your best friend, **Kipute**, was assigned to solve the following question:

At 700K, the rate constant for the reaction, $2HI(g) \rightarrow H_2(g) + I_2(g)$, is $1.83 \times 10^{-3} M^{-1}s^{-1}$. Calculate the time taken for $1 \times 10^{-2} M HCl$ to fall to one-eighth of its initial concentration.

Kipute blamed that the question is incomplete because it did not state whether the reaction is zero, first or second order. Do you agree with **Kipute**? If you agree, explain why and if you don't agree, help **Kipute** to solve the question.

EXERCISE 10C: HOT QUESTIONS**Question 21**

Many reactions involving heterogeneous catalysis are zero order; that is, rate = k. An example is the decomposition of phosphine (PH_3) over tungsten (W):



The rate for this reaction is independent of $[PH_3]$ as long as phosphine's pressure is sufficiently high (≥ 1 atm). Explain.

Question 22

Three-fourth of a reaction is completed in 32minutes. What is the half-life period of this reaction?

Question 23

The rate of a gaseous reaction becomes half when volume of the vessel is doubled. What is the order of reaction ?

Question 24

For the reaction in a closed vessel: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$; Rate = $k [NO]^2 [O_2]$

If the volume of the reaction vessel is doubled, how would it affect the rate of the reaction?

Question 25

A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction?

Question 26

First order reaction takes 69.3min for 50% completion. What is the time needed for 80% completion?

Question 27

The rate of decomposition of a gas was 7.25M/hr when 5% had reacted and it was 5.14M/hr in the same unit when 20% had undergone decomposition. What is the order of the reaction?

Question 28

Compounds A and B both decay by first-order kinetics. The half-life of A is 20 minutes and the half-life of B is 48 minutes. If a container initially contains equal concentrations of compounds A and B, after how long will the concentration of B be twice that of A?

Question 29

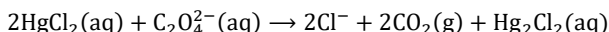
The rate of the reaction between substance A and substance B was studied in a series of experiments carried out at the same temperature. In each experiment the initial rate was measured using different concentrations of A and

B. These results were used to deduce the order of reaction with respect to A and the order of reaction with respect to B.

- When the concentrations of A and B were both doubled, the initial rate was quadrupled. Deduce the overall order of the reaction.
- In another experiment, the concentration of A was increased by factor of three and the concentration of B was halved. This caused the initial rate to increase by a factor of nine.
 - Deduce the order of reaction with respect to A and the order with respect to B.
 - Using your answer from part (i), (ii), write a rate equation for the reaction and suggest suitable units for the rate constant.

Question 30

Consider the following reaction equation:



The equation for the reaction between mercuric chloride and oxalate ion in hot aqueous solution is shown above.

The reaction rate may be determined by measuring the initial rate of formation of chloride ion, at constant temperature, for various initial concentrations of mercuric chloride and oxalate as shown in the following table.

Experiment	Initial $[\text{HgCl}_2]$	Initial $[\text{C}_2\text{O}_4^{2-}]$	Initial rate of formation of Cl^- in $\text{molL}^{-1}\text{min}^{-1}$
1	0.0836M	0.202M	0.52×10^{-4}
2	0.0836M	0.404M	2.08×10^{-4}
3	0.0418M	0.404M	1.06×10^{-4}
4	0.0316M	?	1.27×10^{-4}

- According to the data shown, what is the rate law for the reaction above?
- On the basis of the rate law determined in part (a), calculate the specific rate constant specify the units.
- What is the numerical value for the initial rate of disappearance of $\text{C}_2\text{O}_4^{2-}$ for experiment 1?
- Calculate the initial oxalate ion concentration for experiment 4.

Question 31

- The initial rate of reaction between ester A and aqueous sodium hydroxide was measured in a series of experiments at constant temperature. The data obtained are shown below.

Experiment	Initial $[\text{NaOH}]$	Initial $[\text{A}]$	Initial rate in $\text{molL}^{-1}\text{s}^{-1}$
1	0.040M	0.030M	4.0×10^{-4}
2	0.040M	0.045M	6.0×10^{-4}
3	0.060M	0.045M	9.0×10^{-4}
4	0.120M	0.060M	To be calculated

Use the data in the table to deduce the order of reaction with respect to A and the order of the reaction with respect to NaOH. Hence calculate the initial rate of reaction in experiment 4.

- In a further experiment at different temperature the initial rate of reaction was found to be $9.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the initial concentration of A was 0.02 mol dm^{-3} and the initial concentration of NaOH was 2.00 mol dm^{-3} .
 - Write a rate equation for the reaction under these new conditions
 - Calculate a value for the rate constant under these new conditions and state its units
 - Suggest why the order of reaction with respect to sodium hydroxide appears to be zero under these new conditions.

Chapter 11

TEMPERATURE AND CATALYST ON RATE OF REACTION**TEMPERATURE ON RATE OF REACTION**

Without any doubt, you know that papers which have been used to make a book which you are reading right now, are highly combustible material. But you are using this wonderful book comfortably without any worry, why? This is simply because, the activation energy for the reaction is too high to be achieved by temperature of the room. Most of collisions between oxygen molecules in the room and papers of your book are ineffective. However, when those papers are heated (temperature is raised) by flame from a match, it reaches a point where the molecules attain heat energy which is enough to overcome the activation energy and therefore they react. The reaction is highly exothermic, so the heat released in the initial stages of reaction will provide further energy to allow reaction to continue until your book turns to ashes! That is how temperature is involved in reaction rate; it affects number of collisions with activation energy and remember that only collisions with at least activation energy have possibility to react.

Generally, the rate of chemical reaction increases with rise in temperature because rise in temperature, increases the frequency of collision of reacting particles and makes the collisions more energetic (by increasing speed of reacting particles) thus increasing numbers of reacting particles which attains activation energy.

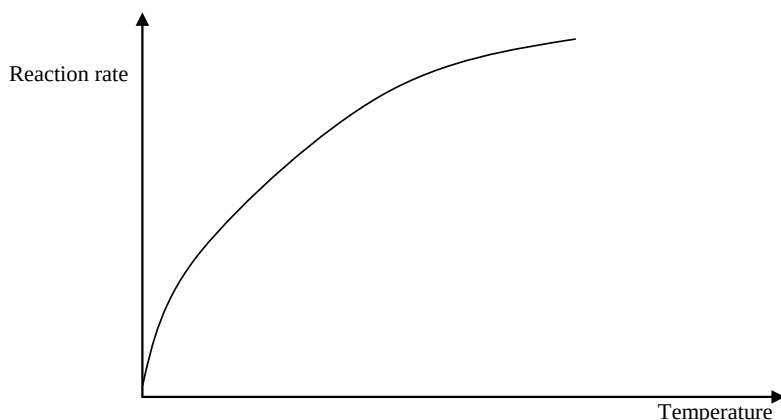


Figure 11.1 Graph to show relation between temperature and reaction rate

The effect of temperature on the reaction rate can well be illustrated by using **Maxwell Boltzmann's distribution curve**.

Understanding the Maxwell Boltzmann's curve

In any system, the particles present will have a wide range of energies. For gases, this can be shown on a graph called the **Maxwell-Boltzmann distribution curve** which is *a plot of the number of particles having each particular energy*.

The following is the sketch of the Boltzmann distribution curve.

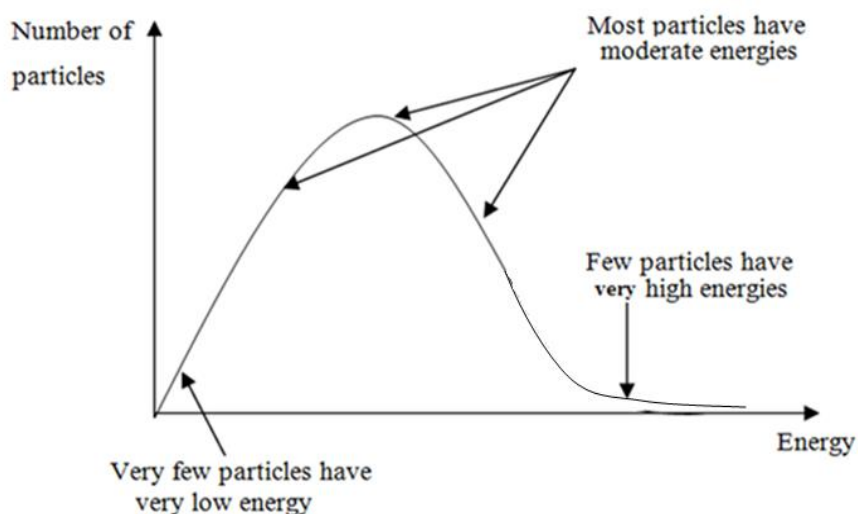


Figure 11.2 Maxwell Boltzmann's distribution curve

The area under the curve is a measure of the total number of particles present.

The reader should understand that:

Although the Maxwell-Boltzmann distribution curve applies to gases, the conclusions that we can make from it can also be applied to reactions involving liquids.

The Boltzmann distribution curve and activation energy:

Remember that for a reaction to happen, particles must collide with energies equal to or greater than activation energy for the reaction. We can mark the activation energy on the Maxwell-Boltzmann distribution curve as follows:

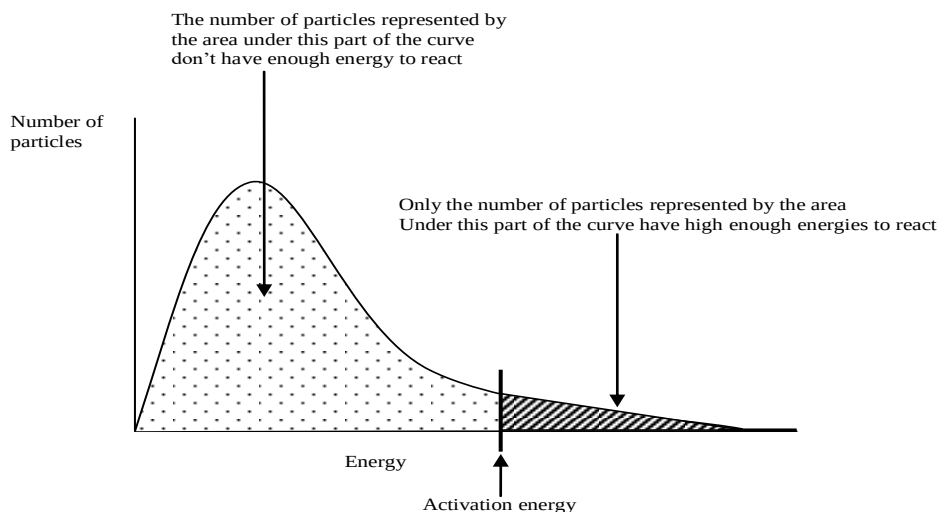


Figure 11.3 Activation energy on the Boltzmann distribution curve

Things to note from the above Maxwell-Boltzmann distribution curve:

- Most of particles have lower energy than E_a (the area under the curve which represents total number of particles is larger at the left of E_a than at the right of it).
- This means that most of collisions between particles are ineffective. They do not lead to the reaction.

- Only few particles have kinetic energy greater than E_a , (at the right of E_a mark). This means that only few collisions are effective.

Only those particles represented by the area to the right of the activation energy mark will react when they collide. The majority of particles does not have enough energy, and will simply bounce apart.

- If we increase the temperature from T_1 to T_2 , more molecules are energetic enough to achieve the activation energy, thus more molecules react and overall reaction rate increases. This is illustrated in the Maxwell-Boltzmann distribution diagram below.

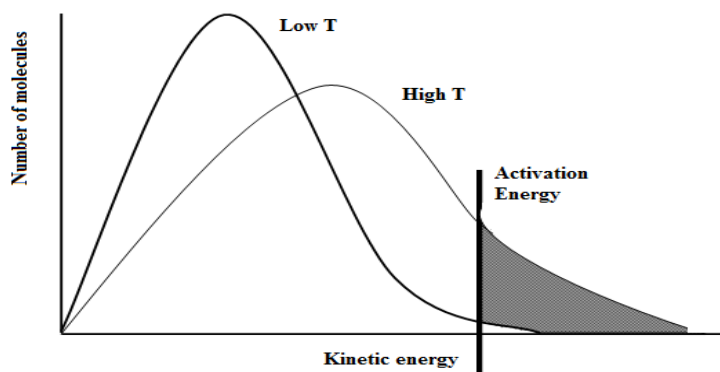


Figure 11.4 Boltzmann distribution curve to show effect of temperature on the reaction rate

Things to note from the Maxwell-Boltzmann distribution curve

- At higher temperature (T_2), fewer particles will have lower energy (at the left side of E_a mark).
- At higher temperature (T_2), greater number of particles will have higher energy than E_a . This is justified by the area under curve of T_2 at the right hand side of E_a mark which is greater than the area under curve of T_1 .

Conclusion

Since more particles have energy greater than E_a at T_2 , the increase in temperature (from T_1 to T_2) increases the rate of reaction.

Arrhenius equation

Arrhenius equation gives mathematical relationship between temperature and rate constant. It expresses quantitatively how the rate constant is affected by the change in the temperature

According to Arrhenius: $k \propto e^{-\frac{E_a}{RT}}$ or $k = Ae^{-\frac{E_a}{RT}}$

Where:

k is the rate constant

E_a is the activation energy

R is the molar gas constant

T is the absolute temperature

e is the natural number = 2.71828

A is the Arrhenius constant or pre exponential factor or simply pre factor. Its units are identical to those of the rate constant and will vary depending on the order of reaction, e.g. if the reaction is of the first order its unit will be sec^{-1} which is also the unit of frequency hence the name *frequency factor* or *attempt frequency* of the reaction for A . $e^{-E_a/RT}$ is the Boltzmann's constant

Significance of Arrhenius Constant (A)

It gives the total number of proper oriented collisions that result in a reaction (leading to reaction or not) per unit time.

Significance of Boltzmann's constant, $e^{-E_a/RT}$

It gives the probability that any given collision will result will result to reaction. That it is gives a fraction of number of collisions which have attained activation energy.

Generally $e^{-E/RT}$ is the fraction of molecules with at least energy, E (equal or greater than E and not necessary to be E_a) at temperature T.

Significance of rate constant (k or $Ae^{-E_a/RT}$)

It gives the number of collisions that result to reaction per second; that is, it gives number of proper oriented collisions which attain activation energy per unit time.

Understanding Arrhenius constant (A)

From $k = Ae^{-E_a/RT}$;

$$A = pz$$

Where; **p** is a **probability factor** or **steric factor** or **orientation factor**. *It represents the probability that the collision will have good orientation. Steric factor can be defined as the fraction of all collisions which have proper orientation for the reaction to take place.*

z is a total number of binary collisions per unit time. *It represents total number of collisions whether they have proper orientation or not or whether they have activation energy or not.*

So **A** will represent total number of binary collisions with proper orientation.

Thus in words Arrhenius equation may be written as:

$$\text{Number of binary collisions with with energy equal to or greater than activation energy} \\ = \text{Total number of proper oriented collisions} \times e^{-E_a/RT}$$

If it is assumed that all collisions are proper oriented, **p** = 1 and therefore **A** = **z** and in this case the Arrhenius constant will represent total number of binary collisions occurred per unit time.

Simplified Arrhenius equation

Also from the Arrhenius equation: $k = Ae^{-E_a/RT}$

Introducing natural logarithm both sides: $\ln k = \ln Ae^{-E_a/RT}$

$$\ln k = \ln A + \ln e^{-E_a/RT};$$

$$\ln k = \ln A + \frac{-E_a}{RT} \ln e$$

But $\ln e = 1$

$$\text{Then } \ln k = \ln A + \frac{-E_a}{RT}$$

Changing natural logarithms to common logarithm:

Using $\ln x = 2.303 \log x$

$$\text{Then the above equation become } 2.303 \log k = \frac{-E_a}{RT} + 2.303 \log A$$

$$\text{Hence, } \log k = \frac{-E_a}{2.303RT} + \log A$$

So the simplified linear equation is in the form of $y = mx + c$ with $y = \log k$ and $x = 1/T$

Hence the graph of $\log k$ against $1/T$ has the following characteristics:

- The graph is straight line
- The slope of the graph, $m = \frac{-E_a}{2.303R}$

From which $E_a = -2.303mR$ where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

It should be noted that:

The value of $\log A$ should be equal to the y – intercept of the graph and hence the value of Arrhenius constant could be found directly from the graph. However y - intercept is found when $x = 0$ and in the equation $x = 1/T$ which can never be zero. Therefore to find the value of Arrhenius constant we must take any one point from the graph and then substituting its corresponding coordinates which are $\log k$ and $1/T$ in the equation after calculating the value of activation energy (E_a) from the slope of the graph

The reader should understand that:

Practically it is difficult to determine the rate constant directly. Alternatively the rate constant is always expressed in terms of time by using the fact that the rate constant varies directly proportional to the rate of the reaction which also varies inversely proportional to the time (t) and hence the rate constant varies inversely proportional to the time (t); so the graph of $\log 1/t$ against $1/T$ has the same characters as the graph of $\log k$ against $1/T$.

$$\text{Also from the simplified Arrhenius equation: } \log k = -\frac{E_a}{2.303RT} + \log A$$

If the rate constant changes from k_1 to k_2 when the temperature changes from T_1 to T_2 respectively

$$\text{Then } \log k_1 = -\frac{E_a}{2.303RT_1} + \log A \dots\dots\dots (i)$$

$$\text{And } \log k_2 = -\frac{E_a}{2.303RT_2} + \log A \dots\dots\dots (ii)$$

Taking (i) – (ii)

$$\log k_1 - \log k_2 = \frac{E_a}{2.303RT_2} - \frac{E_a}{2.303RT_1}$$

$$\log \left(\frac{k_1}{k_2} \right) = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\text{Hence, } \log \left(\frac{k_1}{k_2} \right) = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{E_a}{2.303R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

If time is used instead of rate constant the equations become:

$$\log \left(\frac{t_2}{t_1} \right) = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{E_a}{2.303R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

Example 1

The rate constant of a simple conversion reaction $A \rightarrow P$ at 27°C is $2 \times 10^{-3} \text{ Sec}^{-1}$. Activation energy of the reaction is 15.2 kJ/mol . Calculate the rate constant of this reaction at 127°C .

Solution

$$\text{Using: } \log \left(\frac{k_1}{k_2} \right) = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log\left(\frac{k_1}{k_2}\right) = \frac{15200}{2.303 \times 8.314} \left(\frac{1}{300} - \frac{1}{400}\right)$$

$$\frac{k_1}{k_2} = \log^{-1}(-0.66) = 0.22$$

$$k_2 = \frac{k_1}{0.22} = \frac{2 \times 10^{-3}}{0.22} \text{sec}^{-1} = 9.1 \times 10^{-3} \text{sec}^{-1}$$

Hence the rate constant for the reaction at 127°C is $9.1 \times 10^{-3} \text{sec}^{-1}$

Example 2

Boiling an egg denatures protein the process which has activation energy of $5.11 \times 10^2 \text{kJmol}^{-1}$. At sea level and 100°C a favoured boiling time is 3 minutes. How long it is required for the same stage to be reached at the top of the mountain of 2440m high where the boiling point of water is 95°C?

Solution

$$\text{Using: } \log\left(\frac{t_2}{t_1}\right) = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\text{Then } \log\left(\frac{t_2}{t_1}\right) = \frac{5.11 \times 10^5}{2.303 \times 8.314} \left(\frac{1}{368} - \frac{1}{373}\right) = 0.972$$

$$\frac{t_2}{t_1} = \log^{-1}(0.972)$$

$$\text{Or } t_2 = 9.37562t_1$$

$$\text{But } t_1 = 3 \text{ minutes}$$

$$\text{So } t_2 = 9.37562 \times 3 \text{ minutes} = 28.1 \text{ minutes}$$

Hence it will consume 28.1 minutes

Example 3

- Under acidic conditions sucrose (table sugar) can be broken down into its individual sugars, glucose and fructose. At 27°C, it takes 54.5 minutes to convert half the sucrose to glucose and fructose and at 37°C it takes 13.7 minutes. Estimate the activation energy for the breakdown of sucrose.
- The above reaction is known to be second order which means that the half-life is dependent on the initial concentration. Will this affect your calculation of the activation energy above? Why or why not?

Solution

$$(a) \text{ Using } \log\left(\frac{k_1}{k_2}\right) = \frac{E_a}{2.303R} \left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

Since half-life varies inversely to the rate constant; $\frac{k_1}{k_2} = \frac{t_2}{t_1}$ where t_1 and t_2 are half lives at T_1 and T_2 respectively

$$\text{Then } \log\left(\frac{t_2}{t_1}\right) = \frac{E_a}{2.303R} \left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

$$\text{Substituting } \log\left(\frac{13.7}{54.5}\right) = \frac{E_a}{2.303 \times 8.314} \left(\frac{300 - 310}{300 \times 310}\right)$$

From which $E_a = 106783 \text{J/mol}$ or 106.783kJ/mol

- No; it makes no difference.

Half-life for the first order reaction is given by $t_{1/2} = \frac{0.693}{k}$

From which it clearly understood that, $\frac{1}{k}$ can be substituted by $t_{1/2}$, that is $\frac{t_2}{t_1} = \frac{0.693}{K_2} \div \frac{0.693}{K_1} = \frac{K_1}{K_2}$

Half-life for the second order reaction is given by: $t_{1/2} = \frac{1}{[A]K}$ Where $[A]$ is the initial concentration?
 From which you can also substitute $\frac{1}{k}$ by $t_{1/2}$ as long as $[A]$ is the same for all runs;

$$\text{That is } \frac{t_2}{t_1} = \frac{1}{[A]K_2} \div \frac{1}{[A]K_1} = \frac{K_1}{K_2}$$

Hence in both cases (Whether the reaction is first order or second order); $\frac{t_2}{t_1} = \frac{k_1}{k_2}$ giving the same result for activation energy with the given data.

Example 4

A particular reaction in the gas phase has activation energy of 8kJ/mol. For 1 mole of gas, calculate the number of molecules which exceed activation energy at:

- (a) 300K
- (b) 400K

Solution

Fraction of number of molecules which have been attained activation energy is given by $e^{-E_a/RT}$ (from the Arrhenius equation).

Thus total number of molecules with energy greater than activation energy = Total number of molecules $\times e^{-E_a/RT}$ (under assumption that all collisions have proper orientation).

But with given number of moles, total number of molecules = nN_A where n is the number of moles of gas and N_A is the Avogadro's constant.

Thus number of molecules with energy greater than E_a

$$= nN_A \times e^{-\frac{E_a}{RT}} = 1 \times 6.02 \times 10^{23} \times e^{-\frac{8000}{8.314T}}$$

- (a) When $T=300K$

$$\text{The number of molecules} = 6.02 \times 10^{23} \times e^{-\frac{8000}{8.314 \times 300}} = 2.4 \times 10^{22} \text{ molecules}$$

Hence number of molecules with energy greater than E_a at 300K is 2.4×10^{22} molecules

- (b) When $T = 400K$

$$\text{The number of molecules} = 6.02 \times 10^{23} \times e^{-\frac{8000}{8.314 \times 400}} = 5.43 \times 10^{22} \text{ molecules}$$

Hence number of molecules with energy greater than E_a at 400K is 5.43×10^{22} molecules

The answer is convincing! Number of molecules with energy greater than E_a increases as the temperature increases (from 2.4×10^{22} molecules 300K to 5.43×10^{22} molecules at 400K).

Example 5

At 250K, the activation energy for a gas phase reaction was determined to be 6.5kJ/mol. what percentage of gaseous molecules would be expected to have less than this energy at 250K.

Solution

Fraction of molecules with energy equal or greater than E_a (6.5kJ/mol)

$$= e^{-E_a/RT} = e^{-\frac{6500}{8.314 \times 250}} = 0.0438 \text{ or } 4.38\%$$

Thus the percentage of molecules with energy less than $E_a = (100 - 4.38)\% = 95.62\%$

CATALYST ON RATE OF REACTION

Catalysis is the change in rate of a chemical reaction due to the participation of a substance called a **catalyst**. While the **catalyst** is a substance which alters the rate of reaction and itself remains unchanged at the end of the reaction.

According to physical states of catalysts and those of reactants; catalysts can be classified into

- Homogeneous catalyst
- Heterogeneous catalyst

Homogenous catalyst is the catalyst which functions in the same phase as the reactants. One example of homogeneous catalyst involves the influence of *acidic medium on esterification*.

Homogeneous catalyst actually appears in the rate law because their concentration affects the rate of reaction.

Heterogeneous catalyst is the catalyst which functions in different phase to the reactants. Example in *Haber process*, finely divided reduced iron which is solid serves as a catalyst for the synthesis of ammonia from nitrogen gas and hydrogen gas. Another place where a heterogeneous catalyst is applied is in *contact process*.

Heterogeneous catalyst has the following advantages:

- Product are easily separated from the heterogeneous catalyst
- Heterogeneous catalysts are often more stable and degrade much slower than homogeneous catalyst.

Heterogeneous catalyst usually involves gaseous reactants **adsorbed** (not **absorbed**!) on the surface of a solid catalyst.

Don't confuse the use of absorption and adsorption!

Adsorption refers to the collection of one substance on the surface of another.

Absorption refers to the penetration of one substance into another. (For example, water is absorbed by sponge).

Positive and negative catalysts

Depending on whether the catalyst speed up or slow down the rate of chemical reaction; catalysts can be classified into

- Positive catalyst
- Negative catalyst

Positive catalysts are those which speed up the rate of the reaction. Positive catalysts increase the rate of chemical reaction by providing alternative route of the reaction which has lower activation energy. In some cases, the chemical structure of the catalyst may enhance proper orientation of reactants in a manner conducive to reaction and whence the steric factor is increased.

So positive catalysts can increase the rate of reactions in two ways:

- 1) They can lower the activation energy by providing the alternative mechanism (route) for the reaction with smaller activation energy.
- 2) They can properly orient reactants, thereby increasing the steric factor.

Generally, activation energy of catalysed (positive catalysis) is lower than that of uncatalysed reaction as verified in the energy profile graph shown below.

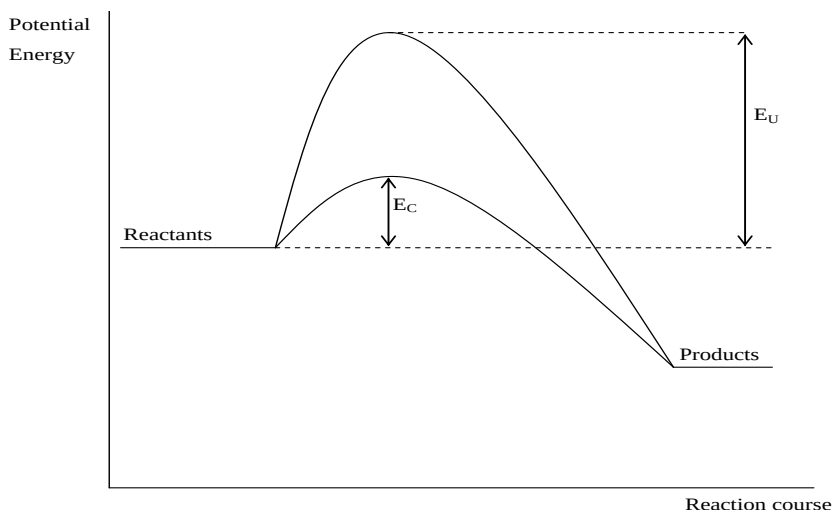


Figure 11.5 Energy profile diagram for catalysed and uncatalysed reaction

Where: E_C is the activation energy of catalysed reaction

E_U is the activation energy of uncatalysed reaction

And it is clearly seen that $E_U > E_C$

So due to the decrease in the activation energy, the addition of catalyst increases number of reactant particles with kinetic energy equal to or greater than activation energy as illustrated in the Boltzmann distribution curve below.

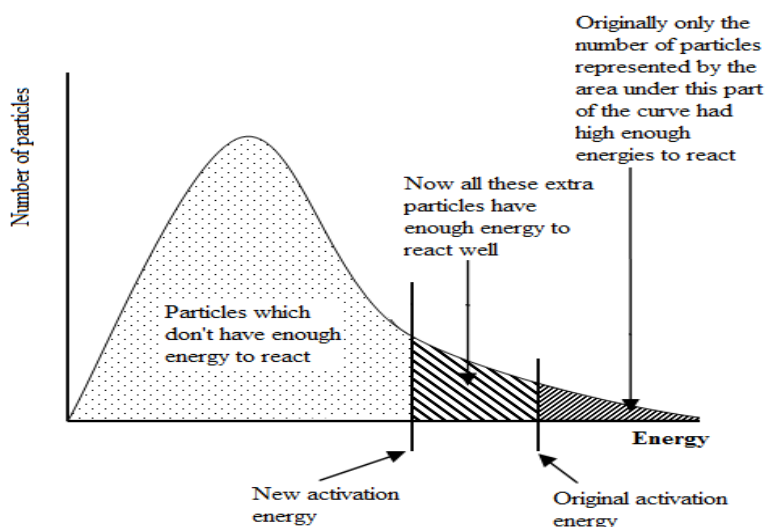


Figure 11.6 Boltzmann distribution curve to show effect of catalyst on the reaction rate

From the curve above it is clearly seen that due to decrease of activation energy, area under the curve to the right hand side of the lower activation energy mark is greater than that of higher activation energy mark (before introduction of catalyst). This means that number of molecules with kinetic energy equal to or greater than activation energy is greater than that obtained before the introduction of the catalyst.

Substances that increase the activity of positive catalysts are called **promoters**.

On another hand, substances that deactivate (decrease the activity of) the catalysts are called **catalytic poisons**.

Negative catalysts are those which slow down the rate of reaction. Negative catalysts are also known as **inhibitors**

The reader should understand that: in most cases positive catalysts are used thus *the term catalyst is commonly used to mean positive catalyst.*

Autocatalysis

A single chemical reaction is said to have undergone **autocatalysis**, or to be **autocatalytic** if the reaction product itself is the catalyst for that reaction.

So **autocatalyst** is the catalyst of a certain reaction which is automatically produced as the product of the same reaction.

Understanding factors affecting rate constant

We have seen that rate constant represents total number of **proper oriented** binary collisions which have attained **activation energy**. With this understanding we can deduce the following useful facts:

- If the collision energy is increased, number of collisions which have attained activation energy will also increase and thus the value of rate constant will increase as well.
- If the activation is lowered, number of collisions which have attained activation energy will also increase and thus the value of rate constant will increase as well.
- If orientation of reactants has been improved, number of collisions with proper orientation will also increase and thus the value of rate constant will increase as well.

The three facts are better understood if we return to our Arrhenius equation.

From the equation; $k = Ae^{-E_a/RT}$

But $A = pz$;

So the Arrhenius equation may be re-written as;

$$k = pz \times e^{-E_a/RT}$$

From which it is clearly understood that, the value of k will be affected by two probabilities:

- The probability of having proper orientation (orientation factor, p) whereby greater value of p , means greater value of k . You are not supposed to forget the fact that *catalyst may increase the chance of having proper orientation and therefore increasing the value of orientation factor.*
- The probability of attaining activation energy ($e^{-E_a/RT}$) which in turn depends on temperature (T) and activation energy (E_a) of which, greater value of T or smaller value of E_a means greater value of $e^{-E_a/RT}$ and hence greater value of k . In this case, you have to remember that catalyst *makes the activation energy smaller.*

After this discussion, we may conclude that, *the value of rate constant is affected by catalyst and temperature.*

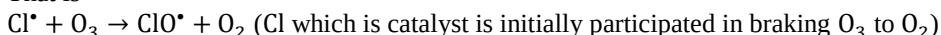
- The use of catalyst, increases the value of rate constant by reducing activation energy and enabling reactants to have proper orientation.
- The increase in temperature, increases the value of rate constant by increasing collision energy of reactants and therefore increasing number of reactants particles with activation energy.

Application of catalysis

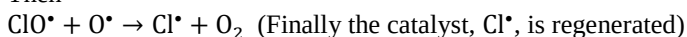
Catalysis is significant in various ways including the following:

- 1. Energy processing:** Petroleum refining makes intensive use of catalysis for *alkylation*, *catalytic cracking*, *naphtha reforming* and *steam reforming* (conversion of hydrocarbon into synthesis gas)
- 2. Bulk chemicals:** Some of the largest – scale are produced via catalytic oxidation, often using oxygen. Example, manufacture of sulphuric acid (from SO_2 to SO_3) in *contact process*. Many other chemical products are generated by large scale reduction; often via hydrogenation. The largest scale example is the manufacture of ammonia in *Haber process* from nitrogen.
- 3. Fine chemicals:** Many fine chemicals are prepared via catalysis methods include those heavy industry as well as more specialized process that could be prohibitively expensive on large scale. Examples include *olefin metathesis* using *Grubb's catalyst*
- 4. Food processing:** One of the most obvious applications of catalysis is *hydrogenation of fats* using *nickel catalyst* to produce *margarine*.
- 5. Biology:** In nature *enzymes* are catalysts in *metabolism* and *catabolism*. Enzymes are also known as **biocatalysts**.
- 6. In the environment:** Catalysis impacts the environment by increasing the efficiency of industrial processes. But catalysis also plays a direct role in the environment. A notable example is the catalytic role of chlorine free radicals in the breakdown of **ozone** (These radicals are formed by the action of ultraviolet radiation on chlorofluorocarbons)

That is



Then



Example 6

The energy of activation for a chemical reaction is 100 kJ/mol. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on the rate of reaction at 20°C, if other factors remains unaltered?

Solution

From the simplified Arrhenius equation: $\log k = -\frac{E_a}{2.303RT} + \log A$

If the rate constant changes from k_1 to k_2 when the activation energy changes (due to the application of catalyst) from E_1 to E_2 respectively at temperature, T.

$$\text{Then } \log k_1 = -\frac{E_1}{2.303RT} + \log A \dots\dots\dots (i)$$

$$\text{And } \log k_2 = -\frac{E_2}{2.303RT} + \log A \dots\dots\dots (ii)$$

Taking (ii) – (i)

$$\log k_2 - \log k_1 = \frac{E_1}{2.303RT} - \frac{E_2}{2.303RT}$$

$$\log \left(\frac{k_2}{k_1} \right) = \frac{E_1 - E_2}{2.303RT}$$

$$\text{Where: } E_1 - E_2 = \frac{75}{100} \times 100 \text{ kJ/mol} = 75 \text{ kJ/mol} = 75000 \text{ J/mol} \quad (E_a \text{ decreased by 75\%})$$

$$\text{And } T = 20^\circ\text{C} = (20 + 273)\text{K} = 293\text{K}, R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\text{Substituting } \log \left(\frac{k_2}{k_1} \right) = \frac{75000 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 293 \text{ K}} = 13.3687$$

From which;

$$\frac{k_2}{k_1} = \log^{-1}(13.3687) = 2.34 \times 10^{13} = \frac{R_2}{R_1} \text{ (Reaction rate is directly proportional to rate constant).}$$

Hence the reaction rate will increase by a factor of 2.34×10^{13} after application of catalyst.

Example 7

A hydrogenation reaction is carried out at 550K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20kJ/mol.

Solution

From the simplified Arrhenius equation: $\log k = -\frac{E_a}{2.303RT} + \log A$

If the temperature changes from T_1 to T_2 when the activation energy changes (due to the application of catalyst) from E_1 to E_2 respectively with rate constant, k (the same reaction rate means the same rate constant).

$$\text{Then } \log k = -\frac{E_1}{2.303RT_1} + \log A \dots\dots\dots (i)$$

$$\text{And } \log k = -\frac{E_2}{2.303RT_2} + \log A \dots\dots\dots (ii)$$

Taking (ii) – (i)

$$0 = \frac{E_1}{2.303RT_1} - \frac{E_2}{2.303RT_2} \text{ or } \frac{E_2}{T_2} = \frac{E_1}{T_1}$$

But $E_1 - E_2 = 20\text{kJ/mol}$ or $E_2 = E_1 - 20$

$$\text{Substituting } \frac{E_1 - 20}{T_2} = \frac{E_1}{T_1} \text{ or } \frac{E_1 - 20}{400} = \frac{E_1}{550}$$

Solving the above equation gives $E_1 = 73.33\text{kJ/mol}$ (Actual activation energy without catalyst).

The activation energy is 73.33kJ/mol

DIGGING DEEPER EXERCISE 11

EXERCISE 11A: BINDER QUESTIONS

Question 1

Write down factor (s) which affects both rate of chemical reaction and rate constant.

Question 2

The rate constant of a reaction is given by the expression;

$$k = Ae^{-E_a/RT}$$

Which factor in this expression should register a decrease so that the reaction proceeds rapidly?

Question 3

Suggest an appropriate reason for the observation: "On increasing temperature of the reacting system by 10 degrees, the rate of reaction almost doubles or even some times becomes five folds."

Question 4

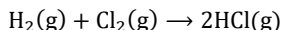
If the activation energy for reaction is zero; what does this tell about the effect of temperature on the reaction rate and rate constant?

Question 5

Which parameters in the Arrhenius equation are affected by nature of reactants?

Question 6

The gas-phase reaction between hydrogen and chlorine is very slow at room temperature.



- Give one reason why the reaction between hydrogen and chlorine is very slow at room temperature
- Explain why an increase in pressure, at constant temperature, increases the rate of reaction between hydrogen and chlorine.
- Explain why a small increase in temperature can lead to a large increase in the rate of reaction between hydrogen and chlorine.
- Suggest one reason why a solid catalyst for a gas-phase reaction is often in the form of powder

Question 7

Changing the temperature and no other conditions changes the rates of most chemical reactions. Two factors are commonly cited as accounting for the increased rate of chemical reaction as the temperature is increased.

- State and briefly discuss the two factors
- Which of the two is more important?

Question 8

The gas reaction: $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$;

Follows the Arrhenius question, $K = Ae^{-E_a/RT}$ where $R = 8.314\text{J K}^{-1}\text{mol}^{-1}$ and 1 calorie = 4.18KJ. At the temperature $T = 273\text{K}$, $k = 3.46 \times 10^{-5}\text{s}^{-1}$, whereas at $T = 298\text{K}$, $k = 8.87 \times 10^{-3}\text{s}^{-1}$. What is the value of the activation energy in kcal/mol.

Question 9

For the reaction; $(\text{A} + \text{B} \rightarrow \text{C})$, the rate constant at 215°C is 5×10^{-3} and the rate constant at 452°C is 1.2×10^{-1}

- What is the activation energy in kJ/mol
- What is the rate constant at 100°C

Question 10

What will be the temperature at which the rate constant is $15\text{M}^{-1}\text{s}^{-1}$ while temperature 389K the rate constant is $7\text{M}^{-1}\text{s}^{-1}$, the activation energy is 600kJ/mol .

Question 11

The activation energy of reaction is 94.14kJ/mol and the rate constant at 313K is $1.8 \times 10^{-1} \text{ sec}^{-1}$, calculate the Arrhenius constant for given reaction.

Question 12

Given that the rate constant is $11\text{M}^{-1}\text{s}^{-1}$ at 345K and the pre-exponential factor is $20\text{M}^{-1}\text{s}^{-1}$. Calculate the activation energy.

EXERCISE 11B: REAL QUESTIONS**Question 13**

Give at least two examples of catalysts which are common in daily life. In each case, give its main use.

Question 14

"Rate of a chemical reaction increases as temperature increases." Just this statement by using two examples which are common in daily life.

Question 15

You were discussing about Arrhenius equation with your dearest friend, **Kipute**. **Kipute** wrote down the following equation:

$$k = Ae^{-E_a/RT}$$

"From this equation, it is clear that the value of rate constant varies when activation energy and temperature changes. So, I think two reactions having identical values of activation energy will have the same rate constant if they run at the same temperature." She said.

Did you agree or disagree with her? Explain.

Question 16

Kipute was asked the following question in the examination:

The rate constant of a simple conversion reaction $A \rightarrow P$ at 27°C is $2 \times 10^{-3} \text{ sec}^{-1}$. Activation energy of the reaction is 15.2kJ/mol . Calculate the rate constant of this reaction at 127°C .

After solving, she found the rate constant to be $8 \times 10^{-4} \text{ sec}^{-1}$.

Without doing any calculation, explain to Kipute that the answer she got, it is **not** correct.

Question 17

Your friend, **Kipute**, was given the following problem:

The rate of a reaction triples when the temperature changes from 20°C to 50°C . Calculate the activation energy of the reaction.

After solving, she found the activation energy to be 284.24J/mol . How could help your friend to show that she got the wrong answer without re-working the problem?

Question 18

The wrong answer **Kipute** got in question 4 above was due to the fact that she used the value of universal gas constant (**R**) as 0.082 instead of 8.314. Without re-working the problem, help your friend to get the correct value of activation energy.

EXERCISE 11C: HOT QUESTIONS**Question 19**

An increase of 10°C in temperature rarely doubles the kinetic energy of particles but doubles the rate of reaction, why.

Question 20

The diagram below shows the Maxwell – Boltzman distribution of molecular energies in a sample of a gas;

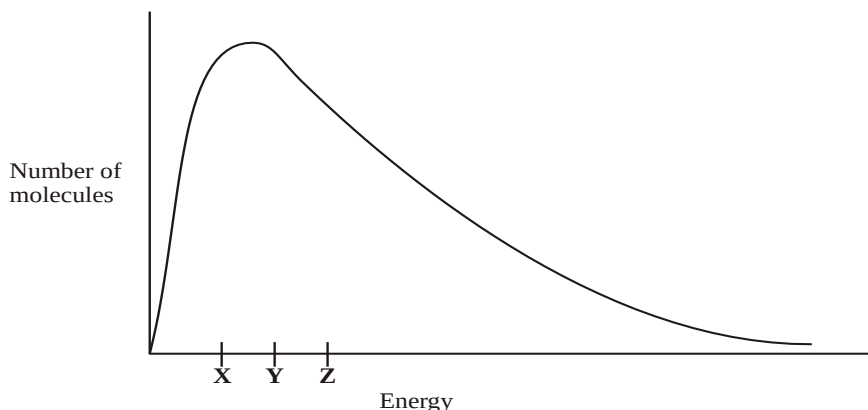


Figure 11.7 Maxwell-Boltzmann distribution for question 20

- (a) Explain the process of that causes some molecules in this sample to have very low energies.
- (b) On the diagram above, sketch a curve to show distribution of molecular energies in the same sample of gas at higher temperature.
- (c)
 - (i) Explain why, even in a fast reaction, a very small percentage of collisions lead to a reaction.
 - (ii) Other than by changing the temperature, state how the proportion of successful collisions between molecular can be increased. Explain why this method causes an increase in the proportion of successful collisions.

Question 21

For the reaction: $2\text{NH}_3(\text{g}) \rightarrow 3\text{H}_2(\text{g}) + \text{N}_2(\text{g})$

The rate constant is measured at two different temperatures.

$T_1 = 500\text{K}$, $K = 9.51 \times 10^{-9} \text{Lmol}^{-1}\text{s}^{-1}$ and $T_2 = 600\text{K}$, $K = 1.1 \times 10^{-5} \text{Lmol}^{-1}\text{s}^{-1}$

Using the above information, calculate;

- (a) The activation energy and
- (b) The value of the pre-exponential Arrhenius factor

Question 22

A certain reaction is 50% complete in 20min at 27°C and the same reaction is again 50% complete in 5min at 77°C. Calculate the activation energy if it is a first order reaction.

Question 23

The experimental rate constant for the reaction of iodide ion with methyl bromide is $7.7 \times 10^{-3} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ at 100°C and $4.25 \times 10^{-5} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ at 0°C. Calculate the frequency factor and activation energy.

Question 24

According to the Farmer's Almanac, one can tell the temperature according to how fast crickets chirp. It has been scientifically proven that cricket chirp is directly related to the temperature. At 10°C, the average rate of chirping is 20chirps/min. When the temperature rises to 20°C, the average rate of chirping is 120chirps/min. Based on this data, what is the activation energy for crickets to chirps?

Question 25

A cook finds that it takes 30minutes to boil potatoes at 100°C in an open sauce pan and only 12minutes to boil them in a pressure cooker at 110°C. Estimate the activation energy for cooking potatoes, which involves the conversion of cellulose into starch.

Chapter 12

MECHANISM OF CHEMICAL REACTIONS

One of the main goals of chemical kinetics is to understand the steps by which a reaction takes place. This series of steps is called the reaction mechanism. Understanding the mechanism allows us to find ways to facilitate the reaction. Below are terms associated with reaction mechanism whose understanding is crucial in mastering reaction mechanism.

Reaction mechanism is steps involved in the chemical reaction. It shows the path followed by the reaction course in forming products.

Elementary reaction is the reaction of particular step in the reaction mechanism. So the reaction mechanism is the combination of various elementary reactions involved in the reactions.

Intermediate product (reaction intermediate or simply intermediate) is the product of a particular step of reaction mechanism, i.e. it is the product of elementary reaction.

- Reactions intermediate are always unstable and therefore they undergo further change (chemical reaction) to give final products.

MOLECULARITY

Molecularity is the total number of reactant molecules which take part in a particular elementary reaction. Example if the elementary reaction is $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$, then its molecularity is 2 because **one** molecule of NO_3 and **one** molecule of CO react making a total of **two** molecules which react. So unlike the **reaction order** (which is determined experimentally) the molecularity can be deduced from the balanced chemical equation and it must be whole number while order of chemical reaction may take fraction.

- The molecularity of elementary reaction may be **unimolecular**, **bimolecular** or **termolecular**.

Unimolecular involves one reactant molecule that collides with a solvent or background molecule thereby becoming collisionally activated.

- In this state, the reactant molecule is thermodynamically favourable for converting into product.

Bimolecular involves collision between two reactant particles.

- Bimolecular reaction may become **pseudo-unimolecular** if one of the reactant is present so much in excess.

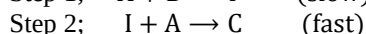
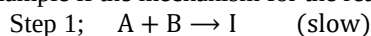
Termolecular involves simultaneous collision between three reactant particles.

- Since it is very difficult for three molecules to collide at the same time, termolecular is very rare. For similar reason, it is practically impossible to have molecularity of greater than three.

DEDUCING ORDER OF REACTION FROM REACTION MECHANISM

In a multistep reaction each step will have its own rate constant (and of course its activation energy).

For example if the mechanism for the reaction $2\text{A} + \text{B} \rightarrow \text{C}$ is thought to be;



Then the rate law for each step will be:

$$R_1 = k_1[\text{A}][\text{B}] \quad (\text{for step 1})$$

$$R_2 = k_2[\text{I}][\text{A}] \quad (\text{for step 2})$$

Where k_1 and k_2 are rate constants for step 1 and step 2 respectively.

In the multistep process, one of the steps will be slower than all others.

- The overall reaction cannot occur faster than this slowest step and hence *the slowest step in the reaction mechanism* is the **rate-determining step** or the **rate limiting step** because it limits the rate of the overall reaction.

Thus from the above mechanism, because step 1 is the slowest one, the rate law of the overall reaction will be equal to the rate law of step 1.

- That is the rate law of the overall reaction will be: $R = k[A][B]$.

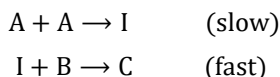
The trick of deducing rate law depends whether the slowest step contains an intermediate as its reactant or not.

If the slowest step does not contain an intermediate as reactant:

The rate law of the overall reaction must contain species which appears in the overall reaction equation.

- So if all reactants of the slowest step appear in the overall reaction (which in turn means there is no any intermediate in the reactants side of the step) there is no any special trick in deducing the required rate law! **The rate law of the slowest step will be the rate law of the overall reaction without any modification.**

For example, if the reaction $2A + B \rightarrow C$ is supposed to take place under the following mechanism:

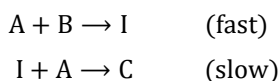


Then the rate law of the overall reaction will simply be:

$$R = k[A][A] = k[A]^2$$

If the slowest step does not contain an intermediate as reactant:

Now consider the same reaction, $2A + B \rightarrow C$ is now supposed to take place under the following mechanism:



Considering the slowest step (rate determining step), one may suggest the rate law of the overall reaction to be:

$$R = [I][A]$$

However, there is one problem, with the above rate law. The intermediate, I, do not appear in the overall reaction, so in reality its concentration does not affect the rate of overall reaction. *How can we get more correct rate law?*

To get correct rate law, one must assume the first step forms the rapid (very fast) equilibrium.

That is, $A + B \rightleftharpoons I$

Then we can use the above rapid equilibrium to eliminate, I, in the suggested rate law as follows:

- If the first step is considered to form the rapid equilibrium.

$R_f = R_b$ (At equilibrium of the first step rates of forward and backward reactions are equal)

But $R_f = k_f[A][B]$ and $R_b = k_b[I]$

Then $k_f[A][B] = k_b[I]$ (At equilibrium)

From which; $[I] = \frac{k_f}{k_b} [A][B]$

Substituting $[I] = \frac{k_f}{k_b} [A][B]$ to the suggested rate law ($R = [I][A]$) gives;

$$R = \frac{k \times k_f}{k_b} [A][B][A] = \frac{k \times k_f}{k_b} [A]^2[B]$$

But $\frac{k \times k_f}{k_b}$ gives another constant, say k'

$$\text{Thus } R = k'[A]^2[B]$$

Hence the correct rate law of the overall reaction from the above mechanism will be:

$$R = k[A]^2[B]$$

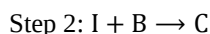
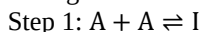
The situation where the slowest step contains the intermediate as the reactant occurs when the slowest step is not the first step. Since the intermediate must be formed in the elementary reaction (the intermediate can never be present at the beginning of the reaction as the initial reactant) there is no possibility of meeting with this situation when the slowest step is the first step.

To insist, if the slowest step is the first step in the reaction mechanism, no need of any special treatment of its obtained rate law; its rate law will automatically be the rate law of the overall reaction.

The reader should note that:

Even if it is not stated whether the elementary step is fast or not, as long as there is a sign of reversible reaction in the step, that step must be fast.

For example; if you are given with the following mechanism:



Even if it is not stated, there is no way the step 1 will be slower than step 2. This is because the intermediate formed in the step 1 is one required as reactant for step 2 to occur. The only way to make this possible is for step 1 to form very fast (rapid) equilibrium while step 2 occurs very slowly. Hence the step 2 will be the rate –determining step.

However, the reader should know that the rate law (and hence order of chemical reaction) cannot be deduced from the reaction mechanism when one of the following conditions occurs:

- If there is no slowest step.
- If all molecules appearing in the slowest step do not appear in the overall reaction.

Understand this fact!

For the reaction which takes place in single step, the rate law may be deduced from the balanced chemical equation where:

Molecularity of the reaction = order of the reaction

Stoichiometric coefficients of the reaction equation are powers of the concentration in the rate law.

For example; if the hypothetical reaction $A + B \rightarrow C$ is found to undergo in the single step, then the rate law of the reaction will be: $R = k[A][B]$

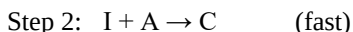
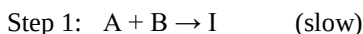
DEDUCING REACTION MECHANISM FROM RATE LAW

With given experimental rate law of a given chemical reaction, the mechanism from the reaction can be deduced. For the reaction mechanism to be plausible, it must agree with the two conditions as explained below.

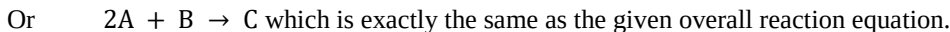
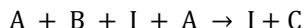
First condition: the summation of all steps in the reaction mechanism must agree with the stoichiometry of the overall reaction.

This means that the sum of all elementary reaction equations must give the correct balanced equation of the overall reaction.

For example, if the overall reaction equation is $2A + B \rightarrow C$, and one suggest the mechanism for the reaction to be:



This mechanism satisfy the **first condition** because step 1 + step 2 gives;



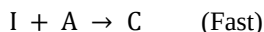
Second condition: the suggested mechanism must agree with the experimental rate law of the overall reaction.

This means that if one follows the procedures of deducing the rate law from the suggested mechanism, the deduced rate law must be the same as the experimental rate law of the reaction.

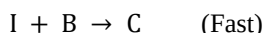
To have better understanding of this, consider again our hypothetical reaction, $2A + B \rightarrow C$; then assume we have $R = k[A][B]$ as the experimental rate law of the reaction.

And also assume we have two suggestions of the mechanism for the reaction.

First suggestion:



Second suggestion:



Now consider the following analysis of the suggested mechanisms.

- Both of the two suggested mechanisms satisfy the first condition because the summation of steps in either mechanism gives $2A + B \rightarrow C$ which is the overall reaction equation.
- However the rate determining step of the second suggestion gives the rate law of $R = k[A]^2$ which is different to the given experimental rate law while that of first suggestion gives $R = k[A][B]$ which is equal to the given experimental rate law. Thus the first suggestion has satisfied second condition while the second suggestion has not.

Conclusion from the analysis

The first suggested mechanism is the plausible mechanism for the reaction $2A + B \rightarrow C$ because:

- Summation of its steps gives $2A + B \rightarrow C$ which is equal to the given overall reaction equation, and
- Rate law of the overall reaction deduced from it ($R = k[A][B]$) is the same as the given experimental rate law of the reaction.

Don't overlook this point!

In predicting reaction mechanism, no steps can have more than molecularity of 3 (even molecularity of 3 itself is not common).

Energy profile diagram for multistep reaction mechanism

In a multistep reaction, each step will have its own activation energy and therefore its own transition state (activated complex); where the step with highest activation energy will be the slowest one and hence the rate determining step for the reaction.

For the reaction, with three steps in the reaction mechanism, its energy profile diagram will look as follows:

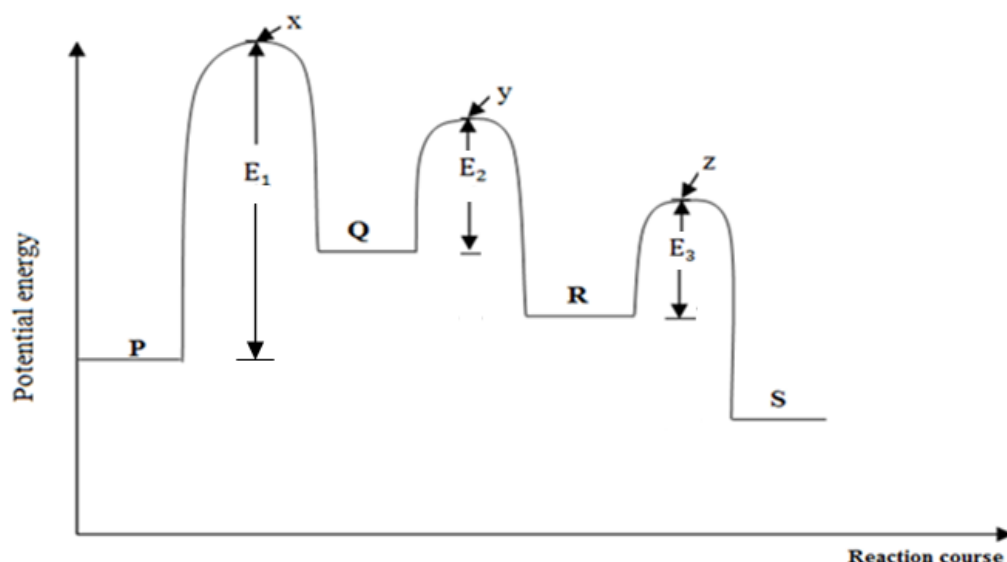


Figure 12.1 Energy profile diagram for multi-step reaction mechanism

Where: E_1 , E_2 and E_3 are activation energy for first, second and third step respectively

Q and R are reaction intermediates for first and second step respectively

X, Y and Z are transition states for first, second and third step respectively

P is the reactant for first step

S is the product for the third step

Differences between order and molecularity of reaction

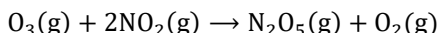
Differences between order and molecularity of reaction are summarised in the table below.

Table 12.1 Differences between order and molecularity of reaction

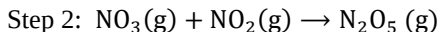
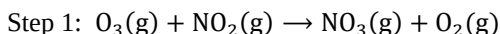
	ORDER		MOLECULARITY
01	Is the sum of the powers of concentrations in the rate law	01	Is the total number of atoms, molecules or ions taking part in an elementary reaction
02	Order corresponds to the overall reaction.	02	Molecularity is defined for elementary reactions.
03	Order of a reaction can change with the conditions such as pressure, concentration etc.	03	Molecularity is invariant for a chemical equation.
04	It may be zero, positive or negative integers	04	It may be only positive integers (1, 2 or 3)
05	It may be fraction	05	It must be whole number
06	It is determined experimentally	06	It is deduced theoretically from the mechanism of the reaction

Example 1

Ozone reacts with NO_2 to give dinitrogen pentoxide and oxygen:



The reaction occurs in the following two steps:



The experimental rate law is $\text{Rate} = k[\text{O}_3][\text{NO}_2]$

What can you say about the relative rate of the two steps of the mechanism?

Solution

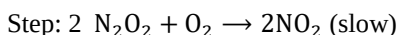
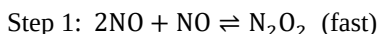
Step 1 is slower than step 2 (because rate law of step 1 is the same as experimental rate law of overall reaction and hence it must be the rate-determining step).

Example 2

Propose a mechanism for the reaction: $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ and show that the chosen mechanism is consistent with the rate law; $R = k[\text{NO}]^2[\text{O}_2]$

Solution

Mechanism



Showing that mechanism is consistent with the given rate law:

From step 2 (rate determining step)

$$R = k[\text{N}_2\text{O}_2][\text{O}_2]$$

Eliminating $[\text{N}_2\text{O}_2]$ by using the fact that:

$$k_f[\text{NO}]^2 = k_b[\text{N}_2\text{O}_2] \quad (R_f = R_b \text{ For rapid equilibrium in step 1})$$

$$\text{From which } [\text{N}_2\text{O}_2] = \frac{k_f}{k_b} [\text{NO}]^2$$

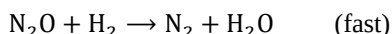
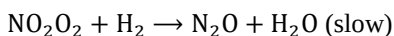
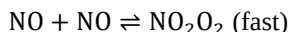
$$\text{Thus } R = \frac{k \times k_f}{k_b} [\text{NO}]^2 [\text{O}_2]$$

$$\text{But } R = \frac{k \times k_f}{k_b} \text{ gives another modified rate constant } k \text{ say } k'$$

Hence $R = k[\text{NO}]^2[\text{O}_2]$ and the given mechanism is consistent with the given rate law.

Example 3

The reaction between NO and H_2 is believed to occur in the following three-step process.



- Write a balanced equation for the overall reaction
- Identify the intermediates in the reaction. Explain your reasoning
- From the mechanism represented above, a student correctly deduced that the rate law for the reaction is; $\text{Rate} = k[\text{NO}]^2[\text{H}_2]$. The student then concluded that:

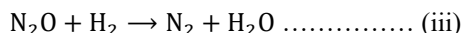
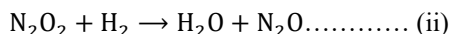
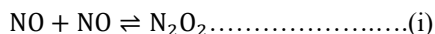
1. The reaction is third order, and
2. The mechanism involves the simultaneous collision of two NO molecules and a H₂ molecule.

Are conclusions **1** and **2** correct? Explain.

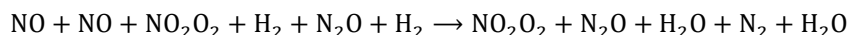
(d) Explain why an increase in temperature increases the rate constant, k, given the rate law in (c).

Solution

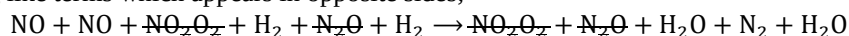
(a) Given that:



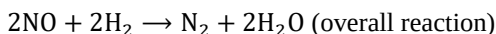
Taking (i) + (ii) + (iii);



Cancelling like terms which appears in opposite sides;



Combining like terms which appears in the same side gives overall reaction equation which is;



(b) N₂O₂ and N₂O

Reason

They appear in the elementary reactions of the mechanism but not in the overall products or reactants of the overall reaction

(c) Conclusion **1** is correct.

Explanation:

The sum of the powers (exponents) in the rate law is 2+1=3, showing the overall third order

(d) Conclusion **2** is not correct.

Explanation:

No elementary reaction (step) in the mechanism involves two NO molecules and one H₂ molecules

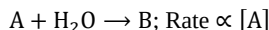
Increase in temperature, increase the rate of reaction. So from the rate law, rate = K[NO]²[H₂] as the concentration does not change with temperature the value of K must change to explain the change in the rate of reaction

DIGGING DEEPER EXERCISE 12

EXERCISE 12A: BINDER QUESTIONS

Question 1

For the elementary step of a chemical reaction:



What is the (i) Molecularity and (ii) Order of the reaction?

Question 2

Reactions of high molecularity are less in number. Explain.

Question 3

Why can't molecularity of any reaction be equal to zero or negative?

Question 4

In a reaction mechanism:

- (a) What is the difference between an **activated complex** and an **intermediate**?
- (b) What is meant by the rate-determining step?
- (c) Which elementary reaction in a reaction mechanism is often the rate-determining step?

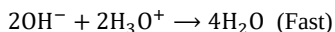
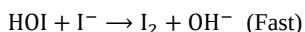
Question 5

- (i) What are the chief requirements that must be met by a plausible reaction mechanism?
- (ii) Why do we say "plausible" mechanism rather than "correct" mechanism?

Question 6

The mechanism of reaction is shown below.

- (a) What is the overall reaction?
- (b) Which compounds are intermediates?
- (c) Predict the rate law based on this mechanism
- (d) What is the overall order of reaction?



Question 7

Consider the following hypothetical reaction: $2XY \rightarrow X_2 + Y_2$

For the hypothetical reaction above:

- (a) Give a rate law that shows that the reaction is first order in the reactant XY
- (b) Give the units for the specific rate constant for this rate law
- (c) Propose a possible mechanism for the reaction.

Question 8

When we find a reaction mechanism, according to the rate law, that perfectly works to solve a complex reaction, why can we not say that the reaction mechanism proves that the rate law is right?

EXERCISE 12B: REAL QUESTIONS**Question 9**

"Understanding reaction mechanism is crucial in everyday life." Justify this statement by outlining at least three points.

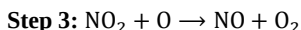
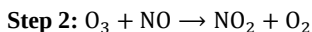
Question 10

Most of your fellow students fail to make sense of reaction mechanism. Fortunately, you are one of few students who have mastered well the concept. Your chemistry teacher, assigned you to help your classmates to understand the concept by using a process of making tea as analogy to chemical reaction. Starting with a cup of hot water, a tea bag and sugar;

- (i) Give one possible mechanism for making tea.
- (ii) Deduce overall equation for the process.
- (iii) Identify intermediate (s).

Question 11

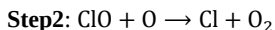
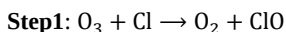
One of real reactions occurring in the atmosphere is a catalysed decomposition of ozone (O_3) which occurs in a series of steps as illustrated below;



Write the equation for the overall reaction and then identify the catalyst.

Question 12

An environment concern is the depletion of ozone O_3 , in the Earth's upper atmosphere, where O_3 is normally in equilibrium with O_2 and O . A proposed mechanism for the depletion of O_3 in the upper atmosphere is shown below.



- (a) Write balance equation for the overall reaction represented by step 1 step 2 above.
- (b) Clearly identify the catalyst in the mechanism above. Justify your answer.
- (c) Clearly identify the intermediate in the mechanism above. Justify your answer.

Question 13

You were arguing with your friend, **Kipute** about the effect of temperature on the reaction rate. **Kipute** gave a statement that was completely against your understanding. *"Temperature does not increase the rate of all reactions. There are several enzymatic reactions and even inorganic reactions whose rate tend to decrease as the temperature increases."* She said with a tone reflecting her confidence for what she is saying. *"What?! Are you kidding me? Even inorganic reactions?"* You responded with a voice of disbelief. *"I know enzymes may become inactive at high temperature; so for those biological reactions which depend on enzymes as their catalyst, their rates are lowered at high temperature; that's absolutely true. But for inorganic reactions! I don't agree at all."* Now with a tone of calmness, you added, *"Please, can you show me how this can happen? I want to make sense of it if such thing exists!"* *"Okay, I'm going to show it to you."* **Kipute** replied, she took a piece of paper and wrote the following mechanism for hypothetical reaction of A to give products:



Now, after studying above mechanism, explain how the mechanism supports **Kipute's** argument.

EXERCISE 12C: HOT QUESTIONS**Question 14**

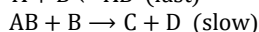
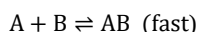
Consider the reaction: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$

- If the reaction would follow a one elementary step mechanism, what would be the rate law?
- However, the experimentally determined rate law was found to be; $\text{Rate} = k[\text{NO}_2]^2$. This suggests that the reaction must involve at least two elementary steps. Propose one mechanism which agrees with the experimental rate law.

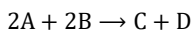
Question 15

Consider the following reaction: $\text{A}(\text{g}) + \text{B}(\text{g}) \rightarrow \text{C}(\text{g}) + \text{D}(\text{g})$ $\Delta H^\theta_{\text{reaction}} = -10\text{kJ/mol}$

- Describe the two factors that determine whether a collision between molecules A and B results in a reaction
- How would a decrease in temperature affect the rate of the reaction shown above? Explain your answer.
- Write the rate law equation that would result in the reaction proceeded by the mechanism shown below



- Explain why a catalyst increases the rate of reaction?

Question 16

The following data about the reaction above were obtained from three experiments:

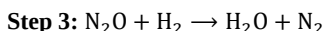
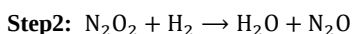
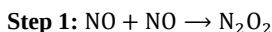
Experiment	[A]	[B]	Initial rate of formation of C in $\text{molL}^{-1} \text{min}^{-1}$
1	0.60	0.15	6.3×10^{-3}
2	0.20	0.60	2.8×10^{-3}
3	0.20	0.15	7.0×10^{-4}

- What is the rate equation for the reaction?
- What is the numerical value of the rate constant? What are its dimensions?
- Propose a reaction mechanism for this reaction

Question 17

NO reacts with H_2 according to the following equation: $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

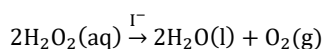
The reaction has rate law of $R = k[\text{H}_2][\text{NO}]^2$ and its proposed mechanism is as follows:



- Based on the data presented, which of the step is the rate determining step?
- Show that the mechanism is consistent with;
 - The observed rate law for the reaction, and
 - The overall stoichiometry of the reaction

Question 18

The decomposition of hydrogen peroxide is catalysed by iodide ion;



Find a possible mechanism and identify the intermediate

Question 19

Consider the following diagram:

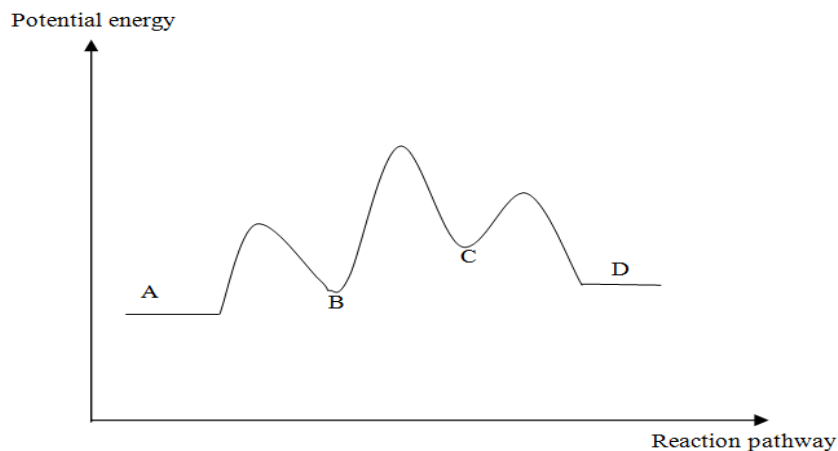


Figure 12.2 Energy profile diagram for question 12

- (i) How many elementary reactions are there in the mechanism?
- (ii) How many intermediates?
- (iii) Which step is rate limiting?
- (iv) Which is the fastest step?
- (v) Is the reaction exothermic or endothermic?

EXAMINATION QUESTIONS FOR PART THREE

Question 1

- (a) Why termolecular elementary reactions are very rare?
 (b) At 298K the following data was obtained from the following reaction $A + B \rightarrow C + D$

[A]/M	[B]/M	Rate /Ms ⁻¹
0.1	0.1	5.02×10^{-4}
0.1	0.05	2.51×10^{-4}
0.05	0.05	1.251×10^{-4}

- (i) What is the order of reaction with respect to each other?
 (ii) What is the rate constant at 298K?
 (iii) If at 342K the rate constant for the reaction was $6.71 \text{ M}^{-1} \text{ sec}^{-1}$, what was the activation energy of the reaction?
 (iv) What was the rate constant at 310K?

Question 2

- (a) Give one reason to support or oppose each of the following:
 (i) The rate of every common reaction is favoured by increasing temperature
 (ii) Catalysed reaction has higher activation energy than uncatalysed reaction
 (iii) Rate of reaction increase with concentration in a zero order reaction
 (b) The rate constant for thermal decomposition of first order reaction:

$\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$ at 593K is $2.2 \times 10^{-5} \text{ sec}^{-1}$. What percentage of the sample will decompose after heating the sample at this temperature for 1hour?

Question 3

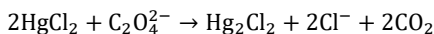
- (a) An elementary reaction is characterized by its molecularity, which is the number of particles or molecules involved in the formation of transition-state complex. Based on this statement, state types of elementary reactions.
 (b) Given the reaction between A and B;

Experiment	[A] / M	[B] / M	Rate
1	0.1	1.0	5.02×10^{-4}
2	0.2	1.0	1.004×10^{-3}
3	0.2	2.0	2.008×10^{-3}

Find the overall order of reaction.

Question 4

- (a) State the meaning of **activation energy** in terms of **threshold energy** and hence give the mathematical equation that relates the two terms.
 (b) Mercury (II) Chloride, HgCl_2 reacts with oxalate $\text{C}_2\text{O}_4^{2-}$ to give precipitate of Hg_2Cl_2



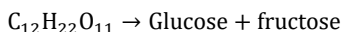
Initial rates at 373K and concentration expressed as $\text{mol dm}^{-3} \text{ min}^{-1}$ and mol dm^{-3} respectively are shown in the following table:

Experiment	$[\text{HgCl}_2]$	$[\text{C}_2\text{O}_4^{2-}]$	Rate $\times 10^{-4}$
1	0.0836	0.202	0.52
2	0.0836	0.404	2.08
3	0.0418	0.404	1.06

- (i) Deduce the order of reaction with respect to each reactant
- (ii) Write down the rate law expression for this reaction
- (iii) Calculate the value of rate constant and its correct units if any
- (iv) Determine the overall order of reaction

Question 5

- (a) Why stirring reacting mixture increases the rate of reaction?
- (b) In experimental studies on the hydrolysis of sucrose to glucose and fructose at 25°C



Time /Min	$[\text{C}_{12}\text{H}_{22}\text{O}_{11}]/\text{M}$
0.00	1.0023
30.00	0.9022
60.00	0.8077
90.00	0.7253
130.00	0.6300
160.00	0.5750
200.00	0.5010

- (i) Determine the half-life and order of reaction
- (ii) What would be the $[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$ after 4 hours of reaction

Question 6

- (a) Many coalmine disasters have resulted when a spark ignites coal dust in the air. Explain using the collision theory.
- (b) The half-life of radium is 1590 years. How long will it take for a sample of radium to decay to 25% of its original radioactivity? Assume this reaction to be first order.

Question 7

- (a) Why a lump of coal does not react with oxygen at room temperature and pressure?
- (b) If the half-life of a radioactive element is 300sec, what percentage of the isotope will remain after 1200 seconds? Assume this reaction to be first order reaction

Question 8

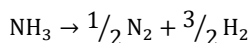
- (a) State two reasons why some collisions may not result in a chemical reaction.
- (b) Calculate the activation energy, E_a , for the reaction $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$, from the following information:

k at 20°C is $4.46 \times 10^{-5}/\text{s}$

k at 55°C is $1.5 \times 10^{-3}/\text{s}$

Question 9

- (a) "In one reaction 2g of aluminium was formed after every 5 minutes while 2g of iron was formed after the same time by another reaction." Does this mean the rate of formation of aluminium is equal to that of iron? Explain.
- (b) The table below gives the value of varying terms of the reaction rate constant for given reaction:



Temperature (K)	k(sec ⁻¹)
273	7.9×10^{-7}
298	3.5×10^{-5}
303	1.4×10^{-4}
312	5.0×10^{-4}
318	1.5×10^{-3}
320	4.9×10^{-3}

- (i) Determine the activation energy
 (ii) Arrhenius factor

Question 10

- (a) What is the difference between half-life of a zero order reaction and that of second order reaction?
- (b) Consider the following reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$
 If the rate constant, k at 317°C and 427°C is $1.4 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $6.4 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively; what is the activation energy E_a for the reaction?

Question 11

- (a) "There is more than one method which can be employed in determining order of chemical reaction from kinetic data." Justify this statement.
- (b) The reaction between compound Y and Z represented as $\text{Z}(\text{g}) + 3\text{Y}(\text{g}) \rightarrow \text{ZY}_3(\text{g})$
 The reaction produced the following experimental results show in the following table:

Experiments	Initial concentration of Z (mol dm ⁻³)	Initial concentration of Y (mol dm ⁻³)	Initial rate of formation of ZY ₃ (mol dm ⁻³ min ⁻¹)
1	0.100	0.100	0.00200
2	0.100	0.200	0.00798
3	0.100	0.300	0.01805
4	0.200	0.100	0.00399
5	0.300	0.100	0.00601

- (i) Using the results in the table calculate the order with respect to: Z, Y, and overall reaction.
 (ii) Find the rate constant for the reaction and its units.

Question 12

- (a) For each of the following reactions suggest any two properties which can be followed in measuring the rate of its reaction.
- $2\text{KMnO}_4(\text{aq}) + 5\text{H}_2\text{C}_2\text{O}_4(\text{aq}) \rightarrow \text{K}_2\text{SO}_4(\text{aq}) + 2\text{MnSO}_4(\text{aq}) + 8\text{H}_2\text{O}(\text{l}) + 10\text{CO}_2(\text{g})$
 - $\text{CuCl}_2(\text{aq}) + 2\text{AgNO}_3(\text{aq}) \rightarrow \text{CuNO}_3(\text{aq}) + 2\text{AgCl}(\text{s})$
- (b) For first order reaction at 27°C, the concentration of the reactant is reduced to half of its initial value after 5000seconds. At 37°C the concentration is halved after 1000seconds Calculate:
- The rate constant at 27°C and 37°C
 - The activation energy of the reaction

Question 13

- (a) It is known that an increase in concentration of reactant(s) tend to increase rate of chemical reactions.
- How the increase in concentration increases the rate?
 - Doubling the concentration of reactant always doubles the reaction rate. Is this true? Explain.
- (b) The rate of decomposition of hydrogen peroxide was studied by titrating known volumes of the reaction mixture with potassium permanganate at different time intervals and the results obtained were tabulated as follows:

Volume of KMnO_4 used (cm^3)	75	47	30	13	7.20
Time (minutes)	00	06	09	20	29

- Show that the reaction is first order.
- Find the rate constant.

Question 14

- (a) Activation energy plays crucial role in determining rate of chemical reactions.
- What is the relationship between activation energy and the reaction rate?
 - Explain factors affecting activation energy.
- (b) A gaseous reaction: $2\text{A} + \text{B} \rightarrow \text{A}_2\text{B}$ take place in two steps;



It was observed that when concentration of B was kept constant while that of A doubled, the rate of reaction doubled. When the concentration of A was kept constant while the concentration of B tripled, the rate of reaction was tripled.

- Out of the two steps of reaction (1) and (2) above, which one is the rate determining step?
- Write an expression representing the rate law for this gaseous reaction.

Question 15

- (a) When helium gas is added to a reaction vessel containing nitrogen and hydrogen gas under suitable condition to allow the formation of ammonia, total pressure in the vessel increases; however, the rate of formation ammonia remains the same. Explain why the rate remains constant?
- (b) For the reaction between G and F the following initial rates were measured at 25°C

S/N	Initial rates($\text{mol dm}^{-3} \text{ s}^{-1}$)	G (mol dm^{-3})	F(mol dm^{-3})
1	3.10×10^{-3}	2.0	3.0
2	7.75×10^{-4}	1.0	1.5

Calculate the overall order of reaction between G and F if the rate constant is $3.44 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$

Question 16

- (a) Is it possible to alter activation energy of given reaction? Explain.
- (b) One of the dozens of reactions that may occur in is a single ridden area is the linked oxidation of carbon monoxide and nitric oxide: $\text{CO} + \text{NO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{NO}_2$

One suggested mechanism for this reaction involves the unstable molecular fragment HO as a catalyst

- Verify that these steps add to give the correct net reaction.
- Identify the intermediates in the mechanism.
- Tell why HO is considered to be a catalyst in this reaction path way.

Question 17

- (a) In performing experiment which involves the reaction between zinc and hydrochloric acid, zinc powder is preferred to zinc wire; why?
- (b) The half-life for the disintegration of an isotope X – 210 is 3 days. Calculate the:
- Rate constant in sec^{-1}
 - Time in days needed for 0.031mg of X – 210 to disintegrate to 0.001mg

Question 18

- (a) Reaction rate is also known as reaction speed or reaction velocity. Why do you think it is more appropriate to use reaction velocity than reaction speed?
- (b) A gaseous reaction:

$2Z(g) + W(g) \rightarrow Z_2W(g)$, takes place in two steps:

$Z(g) + W(g) \rightarrow ZW \dots \dots \dots \text{I (slow)}$

$Z + ZW \rightarrow Z_2W \dots \dots \dots \text{II (fast)}$

Deduce the following:

- The rate equation of the overall reaction.
- The molecularity of slow step.

Question 19

- (a) How does a catalyst increase the rate of a chemical reaction?
- (b) The data analysis of the results of the experiment of certain reaction indicated that the graph of $\log_{10} k$ against $\frac{1}{T}$ gave a slope of $-9.8 \times 10^3 \text{K}$.
- What is the value of activation energy?
 - Calculate the factor by which the rate decreased when the rate temperature was lowered from 409K to 389K

Question 20

For a reversible reaction shown below $\Delta H^\theta = +50\text{kJ}$ and the activation energy, $E_a = 200\text{kJ}$ for the forward reaction: $A(g) + B(g) \rightleftharpoons C(g) + D(g)$

The following data was obtained experimentally on the rates of reaction under different conditions at 300K

[A] / M	[B] M	Rate / Msec^{-1}
$2 \times 10^{-2}\text{M}$	$1 \times 10^{-2}\text{M}$	1×10^2
$2 \times 10^{-2}\text{M}$	$2 \times 10^{-2}\text{M}$	2×10^2
$4 \times 10^{-2}\text{M}$	$1 \times 10^{-2}\text{M}$	2×10^2

- Write down the expression for the experimental rate equation using this data and show your reasoning.
- Calculate the rate constant at 300K and give its units.
- What is the activation energy of backward reaction?

Question 21

- (a) If a particular reactant in a chemical reaction has negative order; what does this mean?
- (b) X and Y reacts together. For a three –fold increase in the concentration of X there is a nine-fold increase in the rate of reaction. What is the order of reaction with respect to X?

Question 22

- (a) If a reactant has an order of -1 , what happens to the initial reaction rate when the concentration of that reactant is tripled?
- (b) The initial rate of a second– order reaction is $8.0 \times 10^{-3} \text{mol dm}^{-3}\text{s}^{-1}$. The initial concentrations of the two reactants, A and B are 0.2mol dm^{-3} . What is the rate constant in $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$?

Question 23

- (a) With an example in each case, give two evidences of presence of activation energy.
 (b) The following data was collected from the mode on position of acetaldehyde: $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$

Initial pressure of $\text{CH}_3\text{CHO}/\text{atm}$	Initial rate atm / sec
0.46	1.04
0.20	2.05×10^{-4}

Calculate the rate constant for this reaction.

Question 24

- (a) A large excess of zinc was added to 100cm^3 of 0.2M hydrochloric acid. After the reaction had ended, 240cm^3 of hydrogen been formed. In three further experiments, extra substances were added to the original mixture as shown in the table below. Fill in the table to show the total volume of hydrogen formed in each experiment and the qualitative effect of these additions on the initial rate of reaction compared to the original experiment.

Substances added to an excess of zinc and 100cm^3 of 0.2M hydrochloric acid	Volume of hydrogen/ cm^3	Effect on initial rate of reaction
100cm^3 water		
10g zinc		
50cm^3 0.2M hydrochloric acid		

- (b) The rate of reaction between compounds A and B was studied at a fixed temperature and some results obtained are shown in the table below.

Experiment	Initial concentration of A/ mol dm^{-3}	Initial concentration of B/ mol dm^{-3}	Initial rate/ $\text{mol dm}^{-3}\text{s}^{-1}$
1	0.16	0.20	5.0×10^{-5}
2	0.24	0.20	7.5×10^{-5}
3	0.32	0.10	5.0×10^{-5}
4	0.12	0.15	To be calculated

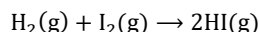
Use the data in the table to deduced the order of reaction with respect to compound A and the order of reaction with respect to compound B. Hence calculate the initial rate of reaction in experiment 4.

Question 25

- (a) How can you distinguish between an intermediate and a catalyst in the reaction mechanism?
 (b) The rate equation for the decomposition of a compound N has a rate constant with the units s^{-1} . The rate constant is $4.31 \times 10^3\text{s}^{-1}$ at 700K and $1.78 \times 10^4\text{s}^{-1}$ at a temperature T. Use this information to deduce the overall order of reaction and whether temperature T is greater or smaller than 700K.

Question 26

- (a) When you are performing titration experiment in the laboratory, how pressure affects the time taken to observe end-point? Explain.
 (b) For 1 mole of a particular gas, the average molecular energy is found to be 1.3kJ/mol at 298K. Approximately how many molecules have at least five times the average molecular kinetic energy.

Question 27

For the exothermic reaction represented above, carried out at 298K, the rate law is as follows;

$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

Predict the effect of each of the following changes on the initial rate of reaction and explain your prediction.

- Addition of hydrogen gas at constant temperature and volume
- Increase in volume of the reaction vessel at constant temperature
- Addition of catalyst. In your explanation, include diagram of potential energy versus reaction coordinate.
- Increase in temperature. In your explanation, include a diagram showing the number of molecules as a function of energy.

Question 28

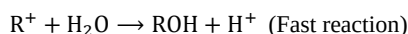
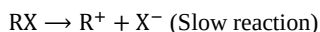
An initial- rate study was performed on the reaction system. Data for the experiment are given in the table below

Trial	$[\text{Cl}^-]$	$[\text{MnO}_4^-]$	$[\text{H}^+]$	Rate of disappearance of MnO_4^- in Ms^{-1}
1	0.0104	0.0040	3.00	2.25×10^{-8}
2	0.0312	0.0040	3.00	2.03×10^{-7}
3	0.0312	0.0020	3.00	1.02×10^{-7}

- Using the information in the table, determine the order of the reaction with respect to each of the following; justify your answer.
 - Cl^-
 - MnO_4^-
- The reaction is known to be third order with respect to H^+ . Use this information and your answers to part (a) above, complete both of the following
 - Write the rate law for the reaction
 - Calculate the value of the rate constant, k , for the reaction, including appropriate units
- Is it likely that the reaction occurs in a single elementary step? Justify your answer.

Question 29

Some alkyl halides, such as $(\text{CH}_3)_3\text{CCl}$, $(\text{CH}_3)_2\text{CBr}$ and $(\text{CH}_3)_3\text{CI}$, represented by RX are believed to react with water according to the following sequence of reactions to produce alcohols



- For the hydrolysis of RX , write a rate expression constant with the reaction sequence above
- When the alkyl halides RCl , RBr and RI are added to water under the same experimental conditions, the rates are in the order $\text{RI} > \text{RBr} > \text{RCl}$. Construct properly labelled potential energy diagrams that are consistent with the information on the rates of hydrolysis of the three alkyl halides. Assume that the reactions are exothermic.

Question 30

Consider the following reaction: $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$; $\Delta H^\theta = -137\text{kJ/mol}$

Account for the following observations regarding the exothermic reaction represented by the equation above.

- An increase in the pressure of the reactants causes an increase in the reaction rate.
- A small increase in temperature causes a large increase in the reaction rate.
- The presence of metallic nickel causes an increase in the reaction rate
- The presence of powdered nickel causes a larger increase in reaction rate than does the presence of a single piece of nickel of the same mass.

PART FOUR

CHEMICAL EQUILIBRIUM

Chapter 13

EQUILIBRIUM LAW

INTRODUCTION TO CHEMICAL EQUILIBRIUM

Chemical equilibrium deals with to what extent a chemical reaction proceeds. It is observed that, in most of the chemical reactions, the reactants are not completely converted to products. The reaction proceeds to certain extent and reaches a state at which the concentration of both reactants and product remain constant with time. This state is generally referred to as **equilibrium state**.

- In these reactions, not only the conversion of reactants to products occurs, but also the conversion of products to reactants is possible. The reactions are known as **reversible reactions**.
- Chemical equilibrium deals with these reversible reactions, which reach equilibrium state. The scope of chemical equilibrium includes the study of characteristics and factors affecting the chemical equilibrium.

Reversible and irreversible chemical reactions

Reversible chemical reaction is the reaction which can proceed in both forward and backward reaction. A good example of this, is heating of a solid calcium carbonate in the closed vessel.

That is: $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{O}_2(\text{g})$

In the above reaction, the heating must be done in the closed vessel so as to avoid the escape of the carbon dioxide gas from the container otherwise the reaction would be irreversible.

For the reversible reaction, reactants of forward reaction are products of reverse reaction and vice-versa. The symbol $\rightleftharpoons$ is used to indicate that the reaction is reversible.

Irreversible chemical reaction is the reaction which can proceed in one direction only.

A good example of this is heating of potassium chlorate thus decomposing the chlorate into potassium chloride and oxygen gas.

That is: $2\text{KClO}_3(\text{s}) \rightarrow 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g})$

In irreversible reaction, products of forward reaction at given conditions are incapable of reacting in reverse or backward reaction at the same conditions.

So it is clearly understood that, **while in the irreversible system, the reaction may reach to completion, in reversible system the reaction can never reach to completion.**

Chemical equilibrium

Chemical equilibrium is the state that occurs in the reversible reaction when the rate forward reaction is equal to the rate of backward reaction.

If A reacts with B to form C and D so that they attain chemical equilibrium according to the following equation: $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$

Initially the rate forward reaction is at maximum while that of backward reaction is zero as the only reagents present is A and B while there is no C and D at the beginning of the reaction and hence there is forward reaction only. As the reaction proceed concentration of A and B start to decrease thus lowering the rate of forward reaction while C and D start to be formed leading to backward reaction between C and D to form A and B again. But since concentration of A and B are still high forward reaction is more favoured at initial stages of the reaction. So as the reaction proceed the rate of forward reaction is continuously decreasing while that of backward reaction is continuously increasing until the rate of forward reaction is equal to that of backward reaction where it is said that the equilibrium has been attained. This can be verified graphically as follows:

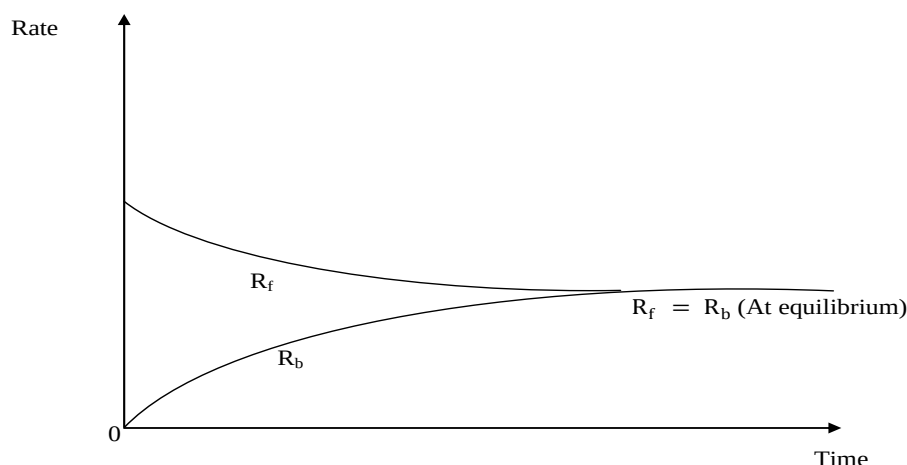


Figure 13.1 Graphical representation of formation of chemical equilibrium

Where:

R_f is the rate of forward reaction.

R_b is the rate of backward reaction

When the equilibrium has been attained the concentrations of reagents involved in the system remain unchanged. In our example, the concentration of A and B is minimum at equilibrium while that of C and D is maximum.

The reader should note that: Chemical equilibrium is also known as **dynamic equilibrium** because it involves balance of the rate of the two reactions (forward and backward reaction) which are proceeding at the same time in opposite directions, that is, **it is an equilibrium involving the constant interchange of particles in motion in opposite directions of forward and reverse reaction.**

Conditions which favour the formation of chemical equilibrium are:

- The system (reaction) must be reversible.
- The reaction should take place in a closed system, that is; no material is allowed to enter or to leave the system.

Homogeneous and heterogeneous chemical equilibrium

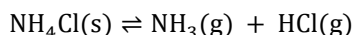
Homogeneous chemical equilibrium is the system of chemical equilibrium where by all reagents involved in the system are in the same phase.

A good example of this is the reaction between hydrogen and nitrogen gas to form ammonia gas according to the following equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

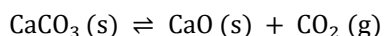
The above reactions are homogeneous chemical equilibrium because all reagents (N_2 , H_2 and $2NH_3$) are in the same gaseous phase.

Heterogeneous chemical equilibrium is the system of chemical equilibrium where by reagents involved in the system are in different phase.

A good example of this is the decomposition of solid ammonium chloride to form ammonia gas and hydrogen chloride gas.



Another example is the heating of solid calcium carbonate to form a solid calcium oxide and carbon dioxide gas.



Characteristics of chemical equilibrium

- 1) At equilibrium state, the rates of forward and backward reactions are equal.
- 2) The observable properties such as pressure, concentration, colour, density, viscosity etc., of the system remain unchanged with time once the system has attained chemical equilibrium.
- 3) The chemical equilibrium is a **dynamic equilibrium** because both the forward and backward reactions continue to occur even though it appears static externally.
In other words: the concentration of reactions and products do not change with time but their inter-conversion continues to occur.
- 4) The chemical equilibrium can be reached by starting the reaction either from the reactants side or from the product side.
- 5) Both pressure and concentration affect the position of equilibrium but do not affect the equilibrium constant (the concept of **equilibrium constant** will be discussed in the later).
- 6) The temperature can affect both the position of equilibrium as well as the equilibrium constant.
- 7) A positive catalyst can increase the rates of both forward and backward reactions and thus helping the system to attain the equilibrium faster. But it does not affect the position of equilibrium and equilibrium constant.

EQUILIBRIUM LAW

We have seen that when the reversible reaction is allowed to attain equilibrium, the concentration of reactants and products remains unchanged. Equilibrium law helps us to understand these equilibrium concentrations better. It states that: *When a chemical system is allowed to reach the equilibrium at a particular temperature, there is a fixed ratio of product of concentration of products to that of reactants raised to powers equals to stoichiometric coefficients regardless to the original concentration of the reagents present in the system.*

The equilibrium law is also known as the **law of mass action** because in the early days of chemistry concentration was called 'active mass'.

However strictly speaking, equilibrium law is just a special case of law of mass action. The more general form of law of mass action may be stated as: *The rate of reaction at an instant of time is proportional to the product of active masses of reactants at that instant of time under given conditions.* This law is the basis of derivation of equilibrium stated above.

The active masses for different substances and systems can be expressed as mentioned below.

- 1) For dilute solution, the molar concentrations are taken as active masses.
- 2) For gases at low pressure, the partial pressures are taken as active masses. However, the molar concentration can also be taken as active masses.
- 3) The active masses of pure solids and pure liquids are taken as unity (1) since their active masses (or concentration) are independent of their quantities taken.

Equilibrium constant

The equilibrium law has introduced an idea of having fixed ratio of equilibrium concentrations. The fixed ratio is known as **equilibrium constant**. It can be defined as *the temperature dependent fixed ratio which is obtained as the quotient of the product of the equilibrium concentration of products to that of reactants raised to powers equal to their stoichiometric coefficients.*

Thus the equilibrium constant is the fixed ratio which is obtained according to the law of mass action (equilibrium law)

For the reaction: $aA + bB \rightleftharpoons cC + dD$

$$\text{Then } K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Where: Where K is equilibrium constant

c (subscript in K) insists that the equilibrium constant is in terms of concentration.

$\frac{[C]^c[D]^d}{[A]^a[B]^b}$ is equilibrium constant expression

And the whole equation $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ is known as equilibrium constant equation

[] is the molar concentration at equilibrium (equilibrium concentration)

a, b, c and d are stoichiometric coefficients of A, B, C and D respectively

K_c is more commonly given in units of $\text{mol dm}^{-3}(\text{M})$ raised to certain powers; so whenever its units are deliberately omitted in the examination question, you must insert appropriate units in terms of mol dm^{-3} in your calculations.

It should be understood that:

The value of equilibrium constant does not depend on the original concentration of the reagents in the system, it is only temperature dependent.

Significance of equilibrium constant

The value of equilibrium constant K_c is important in predicting the extent of forward reaction or backward reaction of which a particular reaction proceeds:

- If K_c is too large then the reaction is more forward (the reaction will reach equilibrium when most of the reactant has been converted to product).
- If K_c is too small then the reaction is more backward (the reaction achieves equilibrium after very little reactant has been converted to product).

We can make the following generalisation concerning the composition of equilibrium mixtures:

- If $K_c > 10^3$, products predominate over reactants.
- If K_c is very large (approaches infinity), the reaction proceeds nearly to completion.
- If $K_c < 10^{-3}$, reactants predominate over products.
- If K_c very small (approach zero), there is almost no reaction
- If $10^{-3} \leq K_c \leq 10^3$, appreciable concentration of both reactants and products are present.

Keep in mind that the magnitude of equilibrium constant (K_c) does not indicate how rapidly or slowly equilibrium will be reached.

Worked examples

Example 1

When the following reactions come to equilibrium, does the equilibrium mixture contain mostly reactants or mostly products?

- (a) $\text{H}_2(\text{g}) + \text{S}(\text{s}) \rightleftharpoons \text{H}_2\text{S}$; $K_c = 7.8 \times 10^5$
(b) $\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{N}_2\text{H}_4(\text{g})$; $K_c = 7.4 \times 10^{-26}$

Solution

- (a) Contain mostly products ($K_c > 10^3$)
(b) Contain mostly reactants ($K_c < 10^{-3}$)

Example 2

Which of the following reactions yield appreciable equilibrium concentration of both reactants and products?

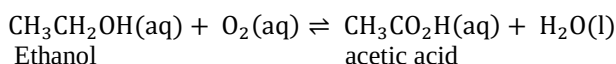
- (a) $2\text{Cu}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CuO}(\text{s})$; $K_c = 4 \times 10^{45}$
(b) $\text{H}_3\text{PO}_4(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq})$; $K_c = 7.5 \times 10^{-3}$
(c) $2\text{HBr}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{Br}_2(\text{g})$; $K_c = 2 \times 10^{-19}$

Solution

(b) Its K_c value is between of 10^{-3} and 10^3

Example 3

When wine spoils, ethanol is oxidised to acetic acid as O_2 from the air reacts with the wine;



The value of K_c for this reaction at $25^\circ C$ is 1.2×10^{82} . Will much ethanol remain when the reaction has reached equilibrium? Explain.

Solution

No. There is almost no ethanol at all when the reaction is at equilibrium.

Explanation

K_c for the reaction very large suggesting that the reaction reach almost to completion. So ethanol being at reactant side will almost be completely consumed when the reaction has reached equilibrium.

Homogeneous and heterogeneous equilibrium constants

Equilibrium constant obtained in homogeneous chemical equilibrium is known as **homogeneous equilibrium constant** while equilibrium constant obtained in heterogeneous chemical equilibrium is known as **heterogeneous equilibrium constant**.

For homogeneous chemical equilibrium, the equilibrium constant expression involves all reagents involved in the system while for heterogeneous equilibrium constant the following order of preference must be considered in selecting terms which should appear in the equilibrium constant expression.

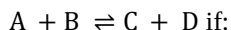
Gas > Solution > Liquid > Solid

As a general rule, **the concentration of pure solids and pure liquids are not included when writing equilibrium constant equation.**

We include only the concentrations of gases and the concentrations of solute in solutions because only those concentrations can be varied. Concentrations of pure solids and liquids depend only on their densities which are independent of their quantities taken and hence they are taken as unity (1) or constant.

Worked examples in writing equilibrium constant expression**Example 4**

Writing an expression for equilibrium constant (K_c) for the reaction,



- (i) A, B, C and D are gases.
- (ii) A, B, C and D are solutions
- (iii) A and C are solid while B and D are gases.
- (iv) C is solid and A, B and D are solutions.

Solution

$$(i) K_c = \frac{[C][D]}{[A][B]}$$

This is the homogeneous equilibrium constant, so all terms must appear in the equilibrium constant expression.

$$(ii) K_c = \frac{[C][D]}{[A][B]}$$

This is also homogeneous equilibrium constant, so all terms must appear in the equilibrium constant expression.

$$(iii) K_c = \frac{[D]}{[B]}$$

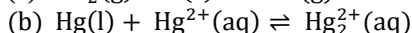
This is the heterogeneous equilibrium constant, so as gaseous phase dominates solid phase in the order of selection of terms, A and C which are solids do not appear in the expression.

$$(iv) K_c = \frac{[D]}{[A][B]}$$

This is the heterogeneous equilibrium constant, so as liquid phase (solution) outweighs solid phase in the order of selection of terms, C which is solid does not appear in the

Example 5

Write the equilibrium constant expression (K_c) for each of the following reactions:



Solution

$$(a) K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]}$$

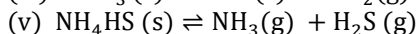
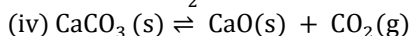
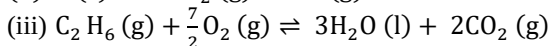
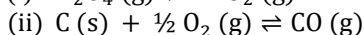
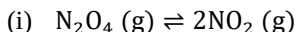
Here C(s) is omitted because it is pure solid.

$$(b) K_c = \frac{[\text{Hg}_2^{2+}]}{[\text{Hg}^{2+}]}$$

Here Hg (l) is omitted because it is pure liquid.

Example 6

Write the equilibrium constant (K_c) for the following reversible reactions.



Solution

$$(i) K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

$$(ii) K_c = \frac{[\text{CO}]}{[\text{O}_2]^{1/2}}$$

$$(iii) K_c = \frac{[\text{CO}_2]^2}{[\text{C}_2\text{H}_6][\text{O}_2]^{7/2}}$$

$$(iv) K_c = [\text{CO}_2]$$

$$(v) K_c = [\text{NH}_3][\text{H}_2\text{S}]$$

Example 7

Write the chemical equation that has the following homogeneous equilibrium constant expression;

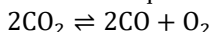
$$K_c = \frac{[\text{CO}]^2[\text{O}_2]}{[\text{CO}_2]^2}$$

Solution

Reagent on the numerator of K_c expression appears as product in the equation while reagents in the denominator of the expression appear as reactant. That is $\text{CO}_2 \rightleftharpoons \text{CO} + \text{O}_2$

Powers in the concentration of each reagent are stoichiometric coefficients of the respective reagents in the equation: That is $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$

Hence the chemical equation corresponding to the given equilibrium constant expression is;



Example 8

Given that: $\text{A} + \text{B} \rightleftharpoons \text{C}$; $K_c = 10\text{dm}^3\text{mol}^{-1}$ at 25°C

Find the equilibrium constant, K_c , for the following reaction at 25°C ;



Solution

With the equation, $\text{C} \rightleftharpoons \text{A} + \text{B}$

$$K_c = \frac{[\text{A}][\text{B}]}{[\text{C}]} = \frac{1}{\frac{[\text{C}]}{[\text{A}][\text{B}]}}$$

But $\frac{[\text{C}]}{[\text{A}][\text{B}]} = K_c$ for $\text{A} + \text{B} \rightleftharpoons \text{C}$ which is $10\text{dm}^3\text{mol}^{-1}$

It follows that; $K_c = \frac{1}{10\text{dm}^3\text{mol}^{-1}} = 0.1\text{mol dm}^{-3}$

Hence the K_c value for the given reaction is 0.1mol dm^{-3}

The reader should notice that:

In the above example, the second equation, $\text{C} \rightleftharpoons \text{A} + \text{B}$, is the reverse of the first equation

$(\text{A} + \text{B} \rightleftharpoons \text{C})$ and therefore the result obtained can be generalised into the following rule;

If the equation is reversed, the equilibrium constant is reciprocated.

Example 9

Given that: $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$; $K_c = 10$ at 25°C

Find the equilibrium constant, K_c for the following reaction at 25°C ; $2\text{A} + 2\text{B} \rightleftharpoons 2\text{C} + 2\text{D}$

Solution

With equation, $2\text{A} + 2\text{B} \rightleftharpoons 2\text{C} + 2\text{D}$

$$K_c = \frac{[\text{C}]^2[\text{D}]^2}{[\text{A}]^2[\text{B}]^2} = \left(\frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} \right)^2$$

But $\frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} = K_c$ for $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$ which is 10

It follows that; $K_c = 10^2 = 100$

Hence the K_c value for the given reaction is 100

Again, you should notice that:

In this example, the second equation ($2\text{A} + 2\text{B} \rightleftharpoons 2\text{C} + 2\text{D}$) can be obtained by multiplying the first equation ($\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$) by 2. So the obtained result can also be generalised to the following rule:

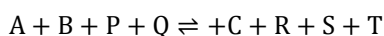
If the equation is multiplied by a factor, the equilibrium constant is raised to the same factor.

Example 10

Given that: $\text{A} + \text{B} \rightleftharpoons \text{C}$; $K_c = 10\text{dm}^3\text{mol}^{-1}$

$\text{P} + \text{Q} \rightleftharpoons \text{R} + \text{S} + \text{T}$; $K_c = 100\text{mol dm}^{-3}$

Find the equilibrium constant, K_c , for the following reaction:



Solution

With the equation, $A + B + P + Q \rightleftharpoons C + R + S + T$

$$K_c = \frac{[C][R][S][T]}{[A][B][P][Q]} = \left(\frac{[C]}{[A][B]} \right) \left(\frac{[R][S][T]}{[P][Q]} \right)$$

But $\frac{[C]}{[A][B]} = K_c$ for $A + B \rightleftharpoons C$ which is $10 \text{ dm}^3 \text{ mol}^{-1}$

And $\frac{[R][S][T]}{[P][Q]} = K_c$ for $P + Q \rightleftharpoons R + S + T$ which is 100 mol dm^{-3}

It follows that; $K_c = 10 \text{ dm}^3 \text{ mol}^{-1} \times 100 \text{ mol dm}^{-3} = 1000$

Hence the K_c for the given reaction is 1000

Here there is a final thing to notice!

In this example, the third equation ($A + B + P + Q \rightleftharpoons C + R + S + T$) is the sum of other first two equations ($A + B \rightleftharpoons C$ and $P + Q \rightleftharpoons C + R + S + T$).

So the obtained result can also be generalised to the following rule:

When chemical equations are added, their equilibrium constants are multiplied together to get the overall equilibrium constant.

Putting all three rules together!

The previous last three examples gave us the **rules of manipulating equilibrium constant**, which may be assembled together as follows:

Rule 1:

If the equation is reversed, the equilibrium constant is reciprocated.

Rule2:

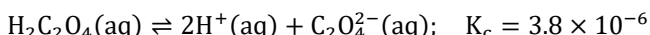
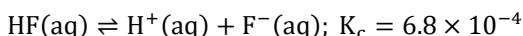
If the equation is multiplied by a factor, the equilibrium constant is raised to the same factor.

Rule 3:

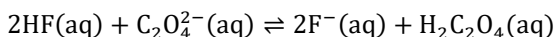
When chemical equations are added, their equilibrium constants are multiplied together to get the overall equilibrium constant.

Example 11

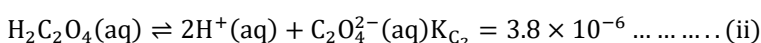
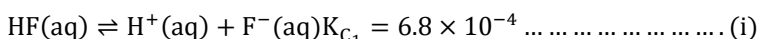
Given the following information:



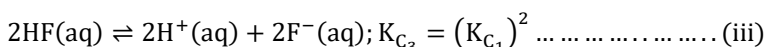
Determine the value of K_c for the reverse reaction?

**Solution**

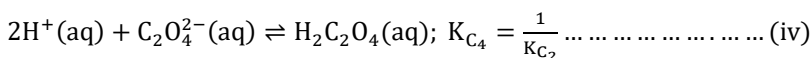
Given that



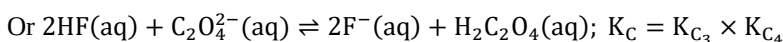
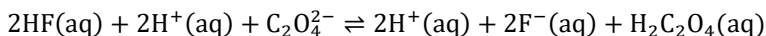
Taking 2(i) gives;



Revering (ii) gives;



Taking (iii) + (iv) gives;



$$\text{Thus the required } K_c = (K_{C_1})^2 \times \frac{1}{K_{C_2}} = (6.8 \times 10^{-4})^2 \times \frac{1}{3.8 \times 10^{-6}} = 0.1217$$

Hence the K_c of the given reaction is 0.1217

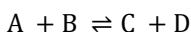
Relationship between equilibrium constant and rate constants

Equilibrium constant, K_c relate to rate constants of forward and backward reaction according to the following equation: $K_c = \frac{K_f}{K_b}$

Where K_f is the **rate constant (or velocity constant)** of forward reaction

And K_b (or K_r) is the **rate constant (velocity constant)** of backward (or reverse) reaction.

To understand this considers the following **single bimolecular step** reversible chemical reaction:



$$\text{From which: } R_f = K_f [\text{A}] [\text{B}]$$

$$R_b = K_b [\text{C}] [\text{D}]$$

Where R_f and R_b are rates of forward and backward reaction respectively

But at equilibrium; $R_f = R_b$

$$\text{Then } K_f [\text{A}] [\text{B}] = K_b [\text{C}] [\text{D}]$$

$$\text{From which: } \frac{K_f}{K_b} = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$$

$$\text{But } \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} = K_c$$

$$\text{Hence } K_c = \frac{K_f}{K_b}$$

Understand this!

Deriving above relationship by using by more general equation; $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$, is beyond the scope of this book. As we know, the rate law of multistep reaction **cannot** be deduced from balanced chemical equation by simply writing $R_f = K_f[\text{A}]^a[\text{B}]^b$ or $R_b = K_b[\text{C}]^c[\text{D}]^d$. That is **not** correct; we can only deduce rate law directly from chemical equation if the reaction follows **single step** mechanism as we have learned in the chemical kinetics.

Calculations involving equilibrium constant

Example 12

Alcohol reacts in reversible reaction with acid to form ester and water:

i.e. Alcohol + Acid $\rightleftharpoons$ Ester + water

When 1 mole of ethanol (ethyl alcohol) reacts with 1 mole ethanoic acid until equilibrium at certain temperature, 0.333 mole of each alcohol and acid and 0.666 mole of each ester and water will be present; calculate the amount of ester when:

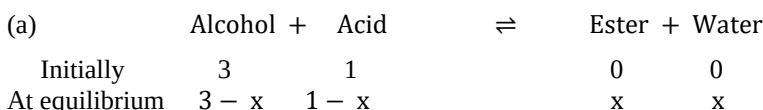
- 3 moles of ethanol are mixed with 1 mole of ethanoic acid
- 92g of ethanol (r. m. m = 46) are mixed with 60g of ethanoic acid (r. m. m = 60)
- 1 mole of ethanol is mixed with 1 mole of acid in presence of 1 mole of water.

Solution

$$K_c = \frac{[\text{Ester}][\text{Water}]}{[\text{Alcohol}][\text{Acid}]}$$

Where $[\quad] = \frac{n}{V}$

$$K_c = \frac{\left(\frac{0.666}{V}\right)\left(\frac{0.666}{V}\right)}{\left(\frac{0.333}{V}\right)\left(\frac{0.333}{V}\right)} = \frac{(0.666)^2}{(0.333)^2} = 4$$



$$K_c = \frac{\frac{x}{V} \times \frac{x}{V}}{\left(\frac{3-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{x^2 - 4x + 3}$$

Since K_c does not depend on original amount of reagents present in the system then;

$$4 = \frac{x^2}{x^2 - 4x + 3};$$

$$4x^2 - 16x + 12 = x^2;$$

$$3x^2 - 16x + 12 = 0$$

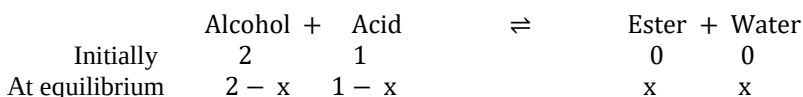
$x = 0.9$ ($x = 4.43$ is not practical answer because it exceeds the initial amount of alcohol and acid)

Hence the amount of ester is 0.9moles.

(b) Using $n = \frac{m}{M_r}$

$$\text{Number of moles of ethanol} = \frac{92\text{g}}{46\text{g mol}^{-1}} = 2\text{mol}$$

$$\text{Number of moles of ethanoic acid} = \frac{60\text{g}}{60\text{g mol}^{-1}} = 1\text{mol}$$



$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{2-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{x^2 - 3x + 2} = 4$$

Then: $3x^2 - 12x + 8 = 0$; $x = 0.8$

Amount of ester present at equilibrium is 0.8moles.

(c)

	Alcohol	+	Acid	$\rightleftharpoons$	Ester	+	Water
Initially	1		1		0		1
At equilibrium	$1 - x$		$1 - x$		x		$1 + x$

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{1+x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2+x}{x^2-2x+1} = 4$$

Then; $4x^2 - 8x + 4 = x^2 + x$

Or $3x^2 - 9x + 4 = 0$; $x = 0.54$

Hence the amount of ester is 0.54moles.

Example 13

1 mole of dinitrogen tetroxide was allowed to dissociate to nitrogen dioxide gas in a flask of certain volume at 500K. At equilibrium 1 mole of nitrogen dioxide was found to be present. If the equilibrium constant for the reaction is 0.4molL^{-1} . Calculate the volume of the flask.

Solution

The reaction equation;

	$\text{N}_2\text{O}_4(\text{g})$	$\rightleftharpoons$	$2\text{NO}_2(\text{g})$
Initially	1		0
At equilibrium	$1 - x$		$2x$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)} = \frac{4x^2}{(1-x)V}$$

But at equilibrium 1mole of nitrogen dioxide was found to be present;

So $2x = 1$ or $x = 0.5$

Then;

$$K_c = 0.4\text{molL}^{-1} = \frac{4 \times 0.5^2\text{mol}^2}{V(1 - 0.5)\text{mol}}$$

From which; $V = 5\text{L}$

The volume of the flask is 5L

Example 14

The value of K_c for the reaction:

$\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$ at 750°C is 0.771. If 1 mole of hydrogen gas and 1 mole of carbon dioxide are mixed in 1 Litre container at 750°C ; what are concentrations of all substances at equilibrium?

Solution

	$\text{H}_2(\text{g})$	+	$\text{CO}_2(\text{g})$	$\rightleftharpoons$	$\text{H}_2\text{O}(\text{g})$	+	$\text{CO}(\text{g})$
Initially	1		1		0		0
At equilibrium	$1 - x$		$1 - x$		x		x

$$K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{x^2 - 2x + 1} = 0.771$$

Then $0.229x^2 + 1.54x - 0.771 = 0$

$x = 0.4675$

Using $[\] = \frac{n}{V}$

$[\text{H}_2\text{O}] = \frac{0.4675}{1} \text{M} = 0.4675 \text{M}$

$[\text{CO}] = \frac{0.4675}{1} \text{M} = 0.4675 \text{M}$

$[\text{H}_2] = \frac{(1-0.4675)}{1} \text{M} = 0.5325 \text{M}$

$[\text{CO}_2] = \frac{(1-0.4675)}{1} \text{M} = 0.5325 \text{M}$

Example 15

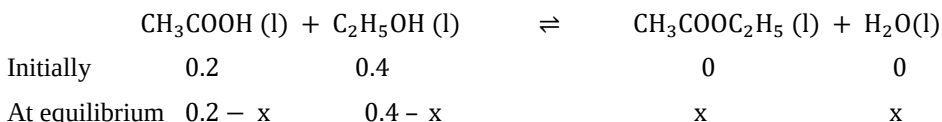
12g of acetic acid is heated with 18.6g of ethanol in 1dm³ flask at 298K. At equilibrium the amount of acetic acid which remains unreacted was found to be 1.8g. Calculate the equilibrium constant.

Solution

Initially: Number of moles of acetic acid = $\frac{12\text{g}}{60\text{g mol}^{-1}} = 0.2\text{mol}$

Number of moles ethanol = $\frac{18.6\text{g}}{46\text{g mol}^{-1}} = 0.4\text{mol}$

At equilibrium: Number of moles acetic acid = $\frac{1.8\text{g}}{60\text{g mol}^{-1}} = 0.03\text{mol}$



$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.2-x}{V}\right)\left(\frac{0.4-x}{V}\right)} = \frac{x^2}{x^2 - 0.6x + 0.08}$$

But at equilibrium, number of moles of CH₃COOH is 0.03mol

Then $0.2 - x = 0.03$ or $x = 0.17$

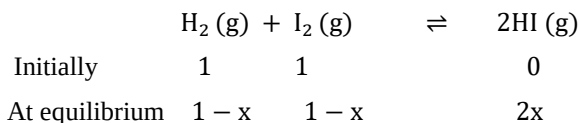
Then $K_c = \frac{0.17^2}{0.17^2 - (0.6 \times 0.17) + 0.08} = 4.1884$

Thus the equilibrium constant is 4.1884

Example 16

1 mole of hydrogen gas and 1 mole of iodine are mixed together in 1dm³ flask and the reaction was allowed to establish the equilibrium at 473K. Calculate the percentage of HI if the equilibrium constant is 4.

Solution



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{4x^2}{x^2 - 2x + 1} = 4$$

$$\text{Then: } 4x^2 = 4x^2 - 8x + 4$$

$$\text{From which; } 8x = 4 \quad \text{or} \quad x = 0.5$$

$$\text{At equilibrium; } n_T = 1 - x + 1 - x + 2x = 2 \quad \text{and} \quad n_{\text{HI}} = 2x = 2 \times 0.5 = 1$$

$$\text{Then } \% \text{HI} = \frac{n_{\text{HI}}}{n_T} \times 100\% = \frac{1}{2} \times 100\% = 50\%$$

Hence the percentage of HI is 50%

Example 17

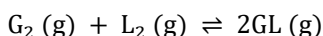
6.22 cm³ of the gas G₂ was mixed with 5.6 cm³ of the L₂ gas in 1 dm³ flask at 25°C. At equilibrium 9.66 cm³ of GL were found in the flask. Calculate the equilibrium constant.

The reaction equation is $\text{G}_2(\text{g}) + \text{L}_2(\text{g}) \rightleftharpoons 2\text{GL}(\text{g})$

Solution

For gases: Mole ratio = volume ratio (This fact is derived from Avogadro's law)

Then the volume of each gas at equilibrium can be deduced as follows:



$$\text{Initially:} \quad \begin{array}{ccc} 6.22 & 5.6 & 0 \end{array}$$

$$\text{At equilibrium:} \quad \begin{array}{ccc} 6.22 - x & 5.6 - x & 2x \end{array}$$

$$\text{Then } K_c = \frac{[\text{GL}]^2}{[\text{G}_2][\text{L}_2]} = \frac{\left(\frac{n_{\text{GL}}}{V}\right)^2}{\left(\frac{n_{\text{G}_2}}{V}\right)\left(\frac{n_{\text{L}_2}}{V}\right)} \quad \text{where } V \text{ is the volume of the flask}$$

$$\text{Then } K_c = \frac{(n_{\text{GL}})^2}{n_{\text{G}_2} \times n_{\text{L}_2}} = \frac{n_{\text{GL}}}{n_{\text{G}_2}} \times \frac{n_{\text{GL}}}{n_{\text{L}_2}}$$

$$\text{But } \frac{n_{\text{GL}}}{n_{\text{G}_2}} = \frac{V_{\text{GL}}}{V_{\text{G}_2}} \quad \text{and} \quad \frac{n_{\text{GL}}}{n_{\text{L}_2}} = \frac{V_{\text{GL}}}{V_{\text{L}_2}} \quad (\text{From Avogadro's law})$$

$$\text{Thus } K_c = \frac{V_{\text{GL}}}{V_{\text{G}_2}} \times \frac{V_{\text{GL}}}{V_{\text{L}_2}} = \frac{(2x)^2}{(6.22-x)(5.6-x)} = \frac{4x^2}{(6.22-x)(5.6-x)}$$

But at equilibrium, 9.66 cm³ of GL were found to be present in the flask.

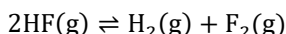
$$\text{Thus; } 2x = 9.66 \quad \text{or} \quad x = 4.83$$

$$\text{Then } K_c = \frac{4 \times 4.83^2}{(6.22-4.83)(5.6-4.83)} = 87.2$$

Hence the equilibrium constant is 87.2

Example 18

At certain temperature, $K_c = 4$ for the following reaction:

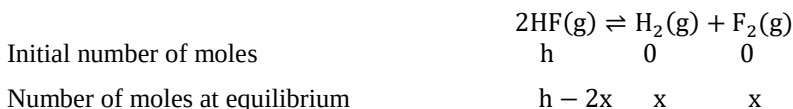


The maximum amount of F₂(g) that was formed in the course of the above reaction in a 1.0L closed reaction vessel was found to be 0.045mol. What was initial amount of HF in the reaction vessel? (Assume initially there were HF only in the vessel).

Solution

The maximum amount of F₂(g) is formed when the reaction is at equilibrium. Thus 0.045mol is an equilibrium amount of F₂(g).

Reaction equation;



Then;

$$K_c = \frac{[\text{H}_2][\text{F}_2]}{[\text{HF}]^2} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{h-x}{V}\right)^2} = \frac{x^2}{(h-2x)^2}$$

Substituting;

$$4 = \frac{(0.045)^2}{(h - 2 \times 0.045)^2}$$

Then;

$$\sqrt{4} = \sqrt{\frac{(0.045)^2}{(h - 2 \times 0.045)^2}}; 2 = \frac{0.045}{h - 0.09}$$

From which; $h = 0.1125\text{mol}$

The initial amount of HF was 0.1125mol

Equilibrium constant in terms of partial pressures, K_p

Partial pressure of gas varies direct proportional to its molar concentration (concentration in mol/dm^3); this can be clearly understood by considering the ideal gas equation which is;

$$PV = nRT.$$

$$\text{From which: } P = \left(\frac{n}{V}\right)RT$$

$$\text{But } \frac{n}{V} = \text{Molar concentration, []}$$

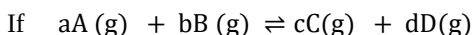
$$\text{Thus } P = []RT$$

For given (constant) temperature: $RT = \text{Constant}$

$$\text{Then } P = \text{Constant} \times []$$

$$\text{Hence } P \propto []$$

So for gases it is possible to write equilibrium constant in terms of partial pressure, that is; for the system of chemical equilibrium whose reagents are in gaseous state, the equilibrium constant (K_p) expression can be written as follows:



$$\text{Then } K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Where P_A , P_B , P_C and P_D are partial pressures of A, B, C and D respectively.

K_p is more commonly given in units of atm raised to certain powers (rather than Nm^{-2} or mmHg), so whenever its units are deliberately omitted (in the examination question), you should assume the units in terms of atm.

Also it is important to keep in mind that, for gases, equilibrium constant is more commonly given in terms of partial pressures (K_p) than concentrations (K_c). So whenever you are asked about just equilibrium constant without specifying whether it is K_c or K_p and the question is about gaseous equilibrium, the implication is K_p .

Example 19

The reaction of the formation of the nitrosyl chloride;

$2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$ was studied at 25°C . The partial pressure at equilibrium

Were found to be: $P_{\text{NOCl}} = 12\text{atm}$

$P_{\text{NO}} = 5 \times 10^{-2}\text{atm}$

$P_{\text{Cl}_2} = 3 \times 10^{-1}\text{atm}$

Calculate the value of K_p for the reaction

Solution

$$K_p = \frac{(P_{\text{NOCl}})^2}{(P_{\text{NO}})^2(P_{\text{Cl}_2})} = \frac{(12\text{atm})^2}{(5 \times 10^{-2}\text{atm})^2(3 \times 10^{-1}\text{atm})} = 192000\text{atm}^{-1}$$

Thus K_p is 192000atm^{-1}

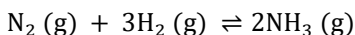
Example 20

For the reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

- (a) Calculate the mole percentage of ammonia in the equilibrium mixture formed at 400°C and $3 \times 10^7\text{Pa}$ pressure when gaseous hydrogen and nitrogen are mixed in 3:1 mole ratio and there is 61% conversion of nitrogen to ammonia.
- (b) Calculate the value of K_p in (a) above.

Solution

For 'a' moles of N_2 there are 3a moles of H_2 , i.e. $n_{\text{H}_2} : n_{\text{N}_2} = 3:1$ (given)



Initially a 3a 0

At equilibrium a - x 3a - 3x 2x

At equilibrium: $n_T = (a - x) + (3a - 3x) + 2x = 4a - 2x$

$$\% \text{NH}_3 = \frac{n_{\text{NH}_3}}{n_T} \times 100\% = \left(\frac{2x}{4a - 2x} \right) \times 100\%$$

$$\text{But } x = \frac{61a}{100} = 0.61a$$

$$\text{Then } \% \text{NH}_3 = \frac{2 \times 0.61a}{4a - (2 \times 0.61a)} \times 100\% = \frac{1.22a}{2.78a} \times 100\% = 43.88\%$$

(a) Percentage of ammonia is 43.88%

$$P_{\text{N}_2} = X_{\text{N}_2} P_T = \left(\frac{a - x}{4a - 2x} \right) P_T$$

$$P_{\text{H}_2} = X_{\text{H}_2} P_T = \left(\frac{3a - 3x}{4a - 2x} \right) P_T$$

$$P_{\text{NH}_3} = X_{\text{NH}_3} P_T = \left(\frac{2x}{4a - 2x} \right) P_T$$

Substituting $x = 0.61a$ in each of the above expression for partial pressure:

$$P_{N_2} = \frac{0.39a}{2.78a} P_T = 0.14P_T$$

$$P_{H_2} = \frac{1.17a}{2.78a} P_T = 0.42P_T$$

$$P_{NH_3} = \frac{1.22a}{2.78a} P_T = 0.4388P_T$$

$$K_p = \frac{(P_{NH_3})^2}{(P_{H_2})^3 (P_{N_2})} = \frac{(0.4388P_T)^2}{(0.42P_T)^3 (0.14P_T)} = \frac{18.56}{P_T^2}$$

But $P_T = 3 \times 10^7 \text{ Pa}$

$$K_p = \frac{18.56}{(3 \times 10^7 \text{ Pa})^2} = 2.062 \times 10^{-14} \text{ Pa}^{-2}$$

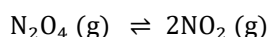
(b) Hence K_p is $2.062 \times 10^{-14} \text{ Pa}^{-2}$

Example 21

1.28 moles of dinitrogen tetraoxide (N_2O_4) was allowed to dissociate into nitrogen dioxide (NO_2) in a 5 litres vessel at 298K. At equilibrium 75% was found to be undissociated and the total pressure was 15 atm. What would be the degree of dissociation of N_2O_4 if the total pressure of the mixture was 10 atm?

Solution

Degree of dissociation is $(100 - 75) \% = 25\%$



Initially 1.28 0

At equilibrium $1.28 - x$ $2x$

$$\text{Then } K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{(X_{NO_2} P_T)^2}{X_{N_2O_4} P_T} = \frac{X_{NO_2}^2 P_T}{X_{N_2O_4}}$$

$$\text{But } n_T = (1.28 - x) + 2x = 1.28 + x$$

$$\text{So } X_{NO_2} = \frac{2x}{1.28+x}$$

$$\text{And } X_{N_2O_4} = \frac{1.28-x}{1.28+x}$$

$$\text{Then } K_p = \frac{\left(\frac{2x}{1.28+x}\right)^2 P_T}{\left(\frac{1.28-x}{1.28+x}\right)} = \frac{4x^2 P_T}{1.28^2 - x^2}$$

$$\text{Thus } K_p = \frac{4x^2 P_T}{1.6384 - x^2}$$

$$\text{But } x = \frac{25}{100} \times 1.28 \text{ moles} = 0.32 \text{ moles}$$

$$\text{And } P_T = 15 \text{ atm}$$

$$\text{Therefore: } K_p = \frac{4 \times 0.32^2 \times 15 \text{ atm}}{1.6384 - 0.32^2} = 4 \text{ atm}$$

If the total pressure, P_T is changed to 10 atm, the value of K_p remains the same (K_p is only temperature dependent like K_c)

$$\text{Thus } K_p = 4 = \frac{10 \times 4x^2}{1.6384 - x^2} \quad \text{Or } 40x^2 = 4 \times 1.6384 - 4x^2$$

$$\text{Or } 44x^2 = 4 \times 1.6384 = 6.5536$$

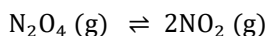
$$x = \sqrt{\frac{6.5536}{44}} = 0.386$$

$$\text{Degree of dissociation, } \alpha = \frac{\text{Number of moles dissociated}}{\text{Number of moles before dissociation}} = \frac{0.386}{1.28} = 0.3 \text{ or } 30\%$$

Alternative solution:

Since the equilibrium constant does depend on initial amount of reagents present in the system, for simplifying the work we may assume 1 mole as initial amount of N_2O_4 instead of the given 1.28 moles.

When the initial amount is 1mole, numerical value of number of moles dissociated is equal to the numerical value for the degree of the dissociation, α



Initially 1 0

At equilibrium $1 - \alpha$ 2α

$$\text{Then } K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{(X_{\text{NO}_2} P_T)^2}{X_{\text{N}_2\text{O}_4} P_T} = \frac{X_{\text{NO}_2}^2 P_T}{X_{\text{N}_2\text{O}_4}} = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2 P_T}{\left(\frac{1-\alpha}{1+\alpha}\right)} = \frac{4\alpha^2 P_T}{1-\alpha^2}$$

$$\text{But } \alpha = \frac{25}{100} = 0.25 \text{ and } P_T = 15\text{atm}$$

$$\text{Then } K_p = \frac{4 \times 0.25^2 \times 15}{1 - 0.25^2} \text{atm} = 4\text{atm}$$

When $P_T = 10\text{atm}$

$$4 = \frac{4\alpha^2 P_T}{1-\alpha^2} = \frac{10 \times 4\alpha^2}{1-\alpha^2} = \frac{40\alpha^2}{1-\alpha^2} \quad \text{or } 44\alpha^2 = 4 \quad \text{or } \alpha = 0.3$$

Hence the degree of dissociation is 0.3 or 30%.

It can be recognised that the second method is easier one and is more useful when the question is concerned with the degree of dissociation.

Example 22

0.8 moles of PCl_5 was allowed to dissociate to PCl_3 and Cl_2 in 5dm^3 vessels at 250°C . At equilibrium 60% of PCl_5 was found to dissociate completely and the total pressure was measured to be 30mmHg. Calculate:

- Equilibrium constant, K_p
- What would be the total pressure if the degree of dissociation of PCl_5 was 35%?

Solution

Since the equilibrium constant does not depend on the initial amount of reagents present in the system, for simplifying the work we may assume the initial amount to be 1 mole instead of the given 0.8 moles.

Equilibrium for the reaction is:



Initially 1 0 0

At equilibrium $1 - \alpha$ α α

$$n_T = (1 - \alpha) + 2\alpha = 1 + \alpha.$$

$$K_p = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{(X_{\text{PCl}_3} P_T)(X_{\text{Cl}_2} P_T)}{(X_{\text{PCl}_5} P_T)} = \frac{\left(\frac{\alpha}{1+\alpha}\right) P_T \left(\frac{\alpha}{1+\alpha}\right) P_T}{\left(\frac{1-\alpha}{1+\alpha}\right) P_T} = \frac{\alpha^2 P_T}{1 - \alpha^2}$$

(a) When $\alpha = \frac{60}{100} = 0.6$

$$K_p = \frac{0.6^2 \times 30 \text{ mmHg}}{1 - 0.6^2} = 16.875 \text{ mmHg}$$

(b) When $\alpha = \frac{35}{100} = 0.35$

Substituting the value of α to the above K_p expression $16.875 = \frac{0.35^2 P_T}{1 - 0.35^2}$

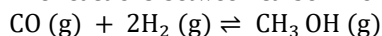
From which $P_T = 120.88 \text{ mmHg}$

Thus the total pressure would be 120.88 mmHg.

On your own attempt to solve the question by using the given initial amount of 0.8 moles

Example 23

The reactions between carbon monoxide and hydrogen proceed according to the following equation:



A dm^3 flask maintained at 700K, contain 0.1mole of carbon monoxide and suitable catalyst. When hydrogen is introduced into the flask until the equilibrium, the total pressure reaches 7atm and 0.06 moles of methanol is formed. Calculate the equilibrium constant, K_p .

Solution

	CO (g)	$+ 2\text{H}_2 \text{ (g)}$	$\rightleftharpoons$	$\text{CH}_3\text{OH (g)}$
Initially	0.1	a		0
At equilibrium	$0.1 - x$	$a - 2x$		x

$$n_T = (0.1 - x) + (a - 2x) + x = 0.1 - 2x + a$$

By Dalton's law of partial pressure; $P_T = P_{\text{CO}} + P_{\text{H}_2} + P_{\text{CH}_3\text{OH}}$

$$= (n_{\text{CO}} + n_{\text{H}_2} + n_{\text{CH}_3\text{OH}}) \frac{RT}{V}$$

$$\text{Then } \frac{P_T V}{RT} = (n_{\text{CO}} + n_{\text{H}_2} + n_{\text{CH}_3\text{OH}}) = n_T$$

$$\text{So } \frac{7 \times 1}{0.082 \times 700} = 0.1 - 2x + a$$

$$\text{But } x = 0.06$$

$$\text{Then } 0.122 = 0.1 - (2 \times 0.06) + a = n_T \text{ or } a = 0.142$$

Thus the initial amount of H_2 was 0.142 moles.

$$K_p = \frac{P_{\text{CH}_3\text{OH}}}{(P_{\text{CO}})(P_{\text{H}_2})^2} = \frac{X_{\text{CH}_3\text{OH}} P_T}{(X_{\text{CO}} P_T)(X_{\text{H}_2} P_T)^2} = \frac{\frac{n_{\text{CH}_3\text{OH}}}{n_T} P_T}{\left(\frac{n_{\text{CO}}}{n_T} P_T\right) \left(\frac{n_{\text{H}_2}}{n_T} P_T\right)^2} = \frac{n_{\text{CH}_3\text{OH}} \times n_T^2}{n_{\text{CO}} \times n_{\text{H}_2}^2 \times P_T^2}$$

$$\text{But } n_{\text{CH}_3\text{OH}} = x = 0.06 \text{ moles}$$

$$n_{\text{CO}} = 0.1 - x = 0.1 - 0.06 = 0.04 \text{ moles}$$

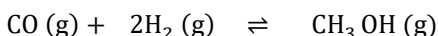
$$n_{\text{H}_2} = a - 2x = 0.142 - (2 \times 0.06) = 0.022 \text{ mole}$$

$$n_T = 0.122 \text{ moles}$$

And $n_T = 7\text{atm}$

$$\text{Substituting } K_p = \frac{0.06 \times 0.122^2}{0.04 \times 0.022^2 \times (7\text{atm})^2} = 0.94\text{atm}^{-2}$$

Alternative solution:



Initially 0.1 0

At equilibrium $0.1 - x$ x

But $x = 0.06\text{moles}$

Then:

$$n_{\text{CO}} = 0.1 - x = (0.1 - 0.06)\text{moles} = 0.04\text{moles}$$

$$P_{\text{CO}} = \frac{n_{\text{CO}}RT}{V} = \frac{0.04 \times 0.082 \times 700\text{atm}}{1} = 2.296\text{atm}$$

$$P_{\text{CH}_3\text{OH}} = \frac{n_{\text{CH}_3\text{OH}}RT}{V} = \frac{0.06 \times 0.082 \times 700}{1} = 3.444\text{atm}$$

At equilibrium: $P_T = P_{\text{CO}} + P_{\text{H}_2} + P_{\text{CH}_3\text{OH}}$ (From Dalton's law of partial pressure)

$$7\text{atm} = 2.296\text{atm} + P_{\text{H}_2} + 3.444\text{atm}$$

$$P_{\text{H}_2} = 1.26\text{atm}$$

$$K_p = \frac{P_{\text{CH}_3\text{OH}}}{(P_{\text{CO}})(P_{\text{H}_2})^2} = \frac{3.444\text{atm}}{(2.296\text{atm})(1.26\text{atm})^2} = 0.94\text{atm}^{-2}$$

Hence the equilibrium constant, K_p is 0.94atm^{-2}

Example 24

Ammonium hydrogen sulphide is allowed to dissociate into ammonia and hydrogen sulphide at 500K. At equilibrium the total pressure was measured to be 0.6atm. Calculate:

- The partial pressure of each.
- The equilibrium constant, K_p .

Solution



Initially a 0 0

At equilibrium $a - x$ x x

That is at equilibrium $n_{\text{NH}_3} = n_{\text{H}_2\text{S}}$ and hence $P_{\text{H}_2\text{S}} = P_{\text{NH}_3} = P$

$$\left(\begin{array}{l} \text{As } P_{\text{H}_2\text{S}} = \frac{n_{\text{H}_2\text{S}}RT}{V} \text{ and } P_{\text{NH}_3} = \frac{n_{\text{NH}_3}RT}{V}; \\ \text{so if } n_{\text{H}_2\text{S}} = n_{\text{NH}_3} \text{ then their respective partial pressures must be equal} \end{array} \right)$$

$$P_T = P_{\text{NH}_3} + P_{\text{H}_2\text{S}} = P + P = 2P; \text{ thus } P = \frac{P_T}{2} = \frac{0.6\text{atm}}{2} = 0.3\text{atm}$$

- Hence the partial pressure of NH_3 is 0.3atm and the partial pressure of H_2S is 0.3atm.
- $K_p = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}} = 0.3\text{atm} \times 0.3\text{atm} = 0.09\text{atm}^2$

Hence the equilibrium constant, K_p is 0.09atm^2

Example 25

Given that $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$ and equilibrium constant is 0.108 atm^2 . A sample of NH_4HS is introduced into evacuated flask where it dissociated and establishes the equilibrium. Calculate the total pressure exerted by the gases in the flask.

Solution

$$K_p = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}}$$

$$\text{But } P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = P$$

$$\text{Then } K_p = P \times P = P^2$$

$$P = \sqrt{K_p} = \sqrt{0.108 \text{ atm}^2} = 0.33 \text{ atm}$$

By Dalton's law of partial pressure;

$$P_T = P_{\text{NH}_3} + P_{\text{H}_2\text{S}} = 0.33 \text{ atm} + 0.33 \text{ atm} = 0.66 \text{ atm}$$

Hence the total pressure exerted by gases in the flask is 0.66 atm

Example 26

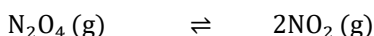
In the equilibrium: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

3.2 g of dinitrogen tetraoxide occupy a volume of 1 dm^3 at $1 \times 10^5 \text{ Pa}$, and 25°C . Calculate:

- The degree of dissociation,
- The equilibrium constant, K_p .

Solution

$$\text{Number of moles of } \text{N}_2\text{O}_4 = \frac{m}{M_r} = \frac{3.2}{92} = 0.035 \text{ moles}$$



$$\text{Initially} \quad 0.035 \quad 0$$

$$\text{At equilibrium} \quad 0.035 - x \quad 2x$$

$$n_T = 0.035 - x + 2x = 0.035 + x$$

By Dalton's law of partial pressure:

$$P_T = P_{\text{N}_2\text{O}_4} + P_{\text{NO}_2} = \frac{n_{\text{N}_2\text{O}_4}RT}{V} + \frac{n_{\text{NO}_2}RT}{V} = (n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2}) \frac{RT}{V}$$

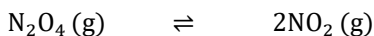
$$\text{But } n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2} = n_T$$

$$\text{Then } P_T = \frac{n_T RT}{V} \text{ or } n_T = \frac{P_T V}{RT} = \frac{10^5 \times 10^{-3}}{8.314 \times 298} = 0.04 = 0.035 + x$$

$$\text{From which; } x = (0.04 - 0.035) \text{ moles} = 0.005 \text{ moles}$$

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Original number of moles before dissociation}} = \frac{0.005}{0.035} = 0.14 \text{ or } 14\%$$

- Hence the degree of dissociation is 0.14 or 14%



$$\text{Initially} \quad 1 \quad 0 \quad (\text{Assuming initial amount of } \text{N}_2\text{O}_4 \text{ is } 1 \text{ mole})$$

$$\text{At equilibrium} \quad 1 - \alpha \quad 2\alpha$$

$$n_T = 1 - \alpha + 2\alpha = 1 + \alpha; K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})} = \frac{(X_{\text{NO}_2} P_T)^2}{(X_{\text{N}_2\text{O}_4} P_T)} = \frac{X_{\text{NO}_2}^2 P_T}{X_{\text{N}_2\text{O}_4}}$$

Substituting values for mole fractions of NO_2 and N_2O_4 to above K_p expression gives:

$$K_p = \frac{4\alpha^2 P_T}{1 - \alpha^2} = \frac{4 \times 0.14^2 \times 10^5}{1 - 0.14^2} \text{ Pa} = 7.9967 \times 10^3 \text{ Pa}$$

(b) Hence the equilibrium constant, K_p is $7.9967 \times 10^3 \text{ Pa}$

Example 27

Consider the reaction: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}); K_p = 0.131 \text{ atm}$

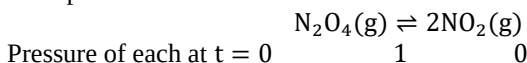
A flask initially contains $\text{N}_2\text{O}_4(\text{g})$ at 1.00 atm pressure. Calculate the pressures of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ at equilibrium.

Solution

Since partial pressures of gases, varies directly proportional to the number of moles,

mole ratio = pressure ratio

Thus pressures can be treated like moles as follows;



Pressure of each at equilibrium $1 - x \qquad 2x$

$$\text{Then } K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})} = \frac{(2x)^2}{1-x} = \frac{4x^2}{1-x} = 0.131$$

$$\text{From which } 4x^2 + 0.131x - 0.131 = 0$$

Solving above equation gives practical value of $x = 0.165$ ($x = -0.198$ is ignored because pressure value cannot be negative)

Hence at equilibrium

$$\text{Pressure of } \text{N}_2\text{O}_4 = 1 - x = 1 - 0.165 \text{ atm} = 0.835 \text{ atm}$$

$$\text{Pressure of } \text{NO}_2 = 2x = 2 \times 0.165 \text{ atm} = 0.33 \text{ atm}$$

Example 28

A sample of $\text{CaCO}_3(\text{s})$ is introduced into a sealed container of volume 0.82 L and heated to 1000 K until equilibrium is reached. The equilibrium constant for the reaction

$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ is $4 \times 10^{-2} \text{ atm}$ at this temperature. Calculate the mass of CaO present at equilibrium.

Solution

Given that; $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

From which; $K_p = P_{\text{CO}_2}$

Thus P_{CO_2} at 1000 K was $4 \times 10^{-2} \text{ atm} = K_p$

From ideal gas equilibrium; $n = \frac{PV}{RT}$

Thus number of moles of CO_2 at equilibrium will be given by;

$$n_{\text{CO}_2} = \frac{P_{\text{CO}_2} V}{RT} = \frac{4 \times 10^{-2} \times 0.82}{0.082 \times 1000} \text{ or } 4 \times 10^{-4} \text{ mol}$$

Since initially there were no CO_2 in the container, number of moles of CO_2 produced in the reaction will be equal to the number of moles of the CO_2 at the equilibrium.

Thus n_{CO_2} produced in the reaction, $= 4 \times 10^{-4} \text{ mol}$

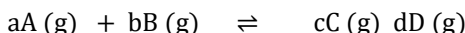
From the stoichiometric of the reaction, mole ratio of CO_2 to CaO is 1:1

Thus $n_{\text{CO}_2} \text{ produced} = n_{\text{CaO}} \text{ produced} = 4 \times 10^{-4} \text{ mol}$

Using $m = nM_r$; mass of $\text{CaO} = 4 \times 10^{-4} \times 56$ or 0.0224 g

Relationship between K_p and K_c

Consider the following system of homogeneous chemical equilibrium where by all reagents are in gaseous phase.



From which; $K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$

But from ideal gas equation: $PV = nRT$ or $P = \frac{nRT}{V}$; but $\frac{n}{V} = []$

So $P = []RT$

Substituting $P = []RT$ in above K_p expression:

$$K_p = \frac{([C]RT)^c ([D]RT)^d}{([A]RT)^a ([B]RT)^b} = \frac{[C]^c [D]^d (RT)^{c+d}}{[A]^a [B]^b (RT)^{a+b}}$$

But: $\frac{[C]^c [D]^d}{[A]^a [B]^b} = K_c$

$c + d =$ Total number of molecules at products side for forward reaction

$a + b =$ Total number of molecules at reactants side for forward reaction

Let $c + d = n$

$a + b = m$

Then $K_p = K_c \frac{(RT)^n}{(RT)^m}$

Hence $K_p = K_c (RT)^{n-m}$ or $K_c = K_p (RT)^{m-n}$

Example 29

0.04 moles of SO_3 was allowed to dissociate in 3 Litres vessel at 900K. At equilibrium the amount of SO_3 present is found to be 0.0284 moles

(i) Derive the relationship between K_c and K_p

(ii) Calculate K_c and K_p

Solution

Equation for the reaction is: $2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g)$

$$K_p = \frac{(P_{\text{SO}_2})^2 (P_{\text{O}_2})}{(P_{\text{SO}_3})^2}$$

But from ideal gas equation: $PV = nRT$; $P = \left(\frac{n}{V}\right)RT$

But $\frac{n}{V} = []$; so $P = []RT$

$$\text{Then } K_p = \frac{([\text{SO}_2]\text{RT})^2([\text{O}_2]\text{RT})}{([\text{SO}_3]\text{RT})^2} = \frac{[\text{SO}_2]^2[\text{O}_2]\text{RT}}{[\text{SO}_3]^2}$$

$$\text{But } \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = K_c$$

$$\text{Hence } K_p = K_c \text{ RT.}$$



$$\text{Initially} \quad 0.04 \quad 0 \quad 0$$

$$\text{At equilibrium} \quad 0.04 - 2x \quad 2x \quad x$$

$$K_c = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{\left(\frac{2x}{V}\right)^2 \left(\frac{x}{V}\right)}{\frac{(0.04-2x)^2}{V}}$$

$$\text{But } 0.04 - 2x = 0.0284 \text{ (Amount of SO}_3 \text{ remained at equilibrium)} = 0.0058$$

$$\text{Thus } K_c = \frac{4 \times 0.0058^3}{(0.04 - (2 \times 0.0058))^2 \times 3} = 3.225 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{But from (i); } K_p = K_c \text{ RT}$$

$$\text{Where } R = 0.082 \text{ and } 900\text{K.}$$

$$\text{Then } K_p = 3.225 \times 10^{-4} \times 0.082 \times 900 \text{ atm} = 0.0238 \text{ atm}$$

$$\text{Hence } K_p = 0.0238 \text{ atm}$$

Example 30

0.196g of nitrogen gas was reacted with 0.14g of hydrogen in 1 litre flask at 500K. At equilibrium the total pressure was found to be 10% less than the original pressure. Calculate:

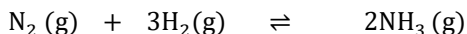
- K_p for the reaction.
- Percentage volume of each gas.

Solution

$$\text{Using } n = \frac{m}{M_r}$$

$$\text{Number of moles of nitrogen gas} = \frac{0.196}{28} \text{ moles} = 0.007 \text{ moles}$$

$$\text{Number of moles hydrogen gas} = \frac{0.14 \text{ moles}}{2} = 0.07 \text{ moles}$$



$$\text{Initially} \quad 0.007 \quad 0.07 \quad 0$$

$$\text{At equilibrium} \quad 0.007 - x \quad 0.07 - 3x \quad 2x$$

$$n_T = (0.007 - x) + (0.07 - 3x) + 2x = 0.077 - 2x \text{ (At equilibrium)}$$

$$n_T \text{ before the reaction} = (0.007 + 0.07) = 0.077 \text{ moles}$$

$$\text{From ideals gas equation } P = \frac{nRT}{V}$$

$$\text{So before the reaction: } P_o = \frac{0.077RT}{V}$$

$$\text{At equilibrium} \quad P_{eq} = \frac{(0.077-2x)RT}{V}$$

$$\text{But } P_{eq} = \frac{90}{100} P_o = 0.9 P_o$$

$$\text{Then } \frac{0.9P_0}{P_0} = \frac{(0.077-2x)RT}{V} \div \frac{0.077RT}{V} = \frac{0.077-2x}{0.077} = 0.9$$

$$0.077 - 2x = 0.077 \times 0.9$$

$$2x = 0.0077; x = 0.00385.$$

From the equation for the reaction:

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{0.007-x}{V}\right)\left(\frac{0.07-3x}{V}\right)^3} = \frac{V^2 \times 4x^2}{(0.007-x)(0.07-3x)^3}$$

$$= \frac{1 \times 4 \times 0.00385^2}{(0.007 - 0.00385)(0.07 - (3 \times 0.00385))^3} = 94.26 \text{ dm}^6 \text{ mol}^{-2}$$

$$\text{Using } K_p = K_c (RT)^{n-m}$$

Where: n is the number of molecules in the products side = 2

m is the number of molecules in the reactants side = 4

$$K_p = K_c (RT)^{2-4} = K_c (RT)^{-2}$$

$$\text{But } K_c = 94.26 \text{ dm}^6 \text{ mol}^{-2}, R = 0.082, T = 500\text{K}$$

$$\text{Thus } K_p = 94.26 \times (0.082 \times 500)^{-2} \text{ atm}^{-2} = 0.056 \text{ atm}^{-2}$$

Hence the K_p for the reaction is 0.056 atm^{-2}

$$\text{At equilibrium: } n_T = 0.077 - 2x = 0.077 - (2 \times 0.00385) = 0.0693 \text{ moles}$$

Since volume ratio = mole ratio (The relationship is true only for gases according to Avogadro's law)

$$\text{Then: } \% \text{NH}_3 = \frac{n_{\text{NH}_3}}{n_T} \times 100\% = \frac{2 \times 0.00385}{0.0693} \times 100\% = 11.11\%$$

Thus the percentage of ammonia by volume is 11.11%

$$\% \text{N}_2 = \frac{n_{\text{N}_2}}{n_T} \times 100\% = \frac{(0.007 - x)}{n_T} \times 100\% = \frac{(0.007 - 0.00385)}{0.0693} \times 100\% = 4.5\%$$

Hence the percentage by volume of N_2 is 4.5%

$$\% \text{H}_2 = \frac{n_{\text{H}_2}}{n_T} \times 100\% = \frac{(0.07 - 3x)}{n_T} \times 100\% = \frac{(0.07 - (3 \times 0.00385))}{0.0693} \times 100 = 84.34\%$$

Hence the percentage by volume of H_2 is 84.34%

Example 31

At 400°C the value of K_c for the reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is $0.509 \text{ dm}^6 \text{ mol}^{-2}$.

If 2.5 moles of N_2 , 7.5 moles of H_2 were introduced into 2.5 Litres flask and in the pressure of catalyst allowed coming to equilibrium at 400°C . What would be the equilibrium concentration of each gas? What is the value of K_p for the reaction?

Solution

	$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$		
Initially	2.5	7.5	0
At equilibrium	$2.5 - x$	$7.5 - 3x$	$2x$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{2.5-x}{V}\right)\left(\frac{7.5-3x}{V}\right)^3} = \frac{V^2 \times 4x^2}{(2.5-x)(3(2.5-x))^3}$$

$$\text{Thus } K_c = \frac{V^2 \times 4x^2}{27(2.5-x)^4} = 0.509$$

$$\text{Then } \sqrt{\frac{V^2 \times 4x^2}{27(2.5-x)^4}} = \sqrt{0.509}; \quad \frac{V \times 2x}{5.196(2.5-x)^2} = 0.713$$

Substituting $V = 2.5\text{L}$ and simplifying above equation gives;

$$3.7x^2 - 23.52x + 23.155 = 0; \quad x = 1.22$$

$$\text{Using } \left[\right] = \frac{n}{V}$$

Thus at equilibrium:

$$[\text{N}_2] = \frac{2.5-x}{V} = \frac{2.5-1.22}{2.5} = 0.512\text{M}$$

$$[\text{H}_2] = \frac{7.5-3x}{V} = \frac{7.5-(3 \times 1.22)}{2.5} = 1.536\text{M}$$

$$[\text{NH}_3] = \frac{2x}{V} = \frac{2 \times 1.22}{2.5} = 0.976\text{M}$$

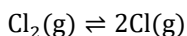
$$K_p = K_c(RT)^{n-m} \text{ where } n = 2 \text{ and } m = 4$$

$$\text{Then } K_p = 0.509 \times (0.082 \times 673)^{-2} \text{atm}^{-2} = 1.67 \times 10^{-4} \text{atm}^{-2}$$

The K_p for the reaction is $1.67 \times 10^{-4} \text{atm}^{-2}$

Example 32

At 1200°C , the following equilibrium is established between chlorine atoms and molecules;



The composition of the equilibrium mixture may be determined by measuring the rate of effusion of the mixture through a pin hole. It is found that at 1200°C and 1atm pressure; the mixture effuses 1.16 times as fast as krypton effuses under the same condition. Calculate the equilibrium constant, K_c

Solution

If M_m and M_{Kr} represents molar mass of the mixture and krypton respectively,

And R_m and R_{Kr} represents rate of diffusion of the mixture and krypton respectively

$$\text{Then } \frac{R_{\text{Kr}}}{R_m} = \sqrt{\frac{M_m}{M_{\text{Kr}}}}$$

$$\text{Or } M_m = M_{\text{Kr}} \left(\frac{R_{\text{Kr}}}{R_m} \right)^2$$

$$\text{But } \frac{R_m}{R_{\text{Kr}}} = 1.16 \quad \text{or} \quad \frac{R_{\text{Kr}}}{R_m} = \frac{1}{1.16}$$

$$\text{Then } M_m = 84 \times \left(\frac{1}{1.16} \right)^2 = 62.4257\text{g/mol}$$

Considering the dissociation of Cl_2 ;

$$\text{Van't Hoff's factor, } i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{71}{62.4257} = 1.1374$$

And degree of dissociation, $\alpha = \frac{i-1}{N-1} = \frac{1.1374-1}{2-1} = 0.1374$

It follows that: $\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Cl}(\text{g})$

At equilibrium; $1 - \alpha \quad 2\alpha$

$$K_p = \frac{(P_{\text{Cl}})^2}{P_{\text{Cl}_2}} = \frac{(X_{\text{Cl}}P_T)^2}{X_{\text{Cl}_2}P_T} = \frac{(X_{\text{Cl}})^2 P_T}{X_{\text{Cl}_2}}$$

$$\text{But } X_{\text{Cl}} = \frac{n_{\text{Cl}}}{n_T} = \frac{2\alpha}{1+\alpha} = \frac{2 \times 0.1374}{1+0.1374} = 0.2416$$

$$\text{And } X_{\text{Cl}_2} = \frac{n_{\text{Cl}_2}}{n_T} = \frac{1-\alpha}{1+\alpha} = \frac{1-0.1374}{1+0.1374} = 0.7584$$

$$\text{Substituting } K_p = \frac{(0.2416)^2 \times 1 \text{ atm}}{0.7584} = 0.077 \text{ atm}$$

$$\text{Using } K_c = K_p(RT)^{m-n} = 0.077 \times (0.82 \times 1473)^{-1} \text{ mol dm}^{-3} = 6.37 \times 10^{-4} \text{ mol dm}^{-3}$$

Hence the equilibrium constant, $K_c = 6.37 \times 10^{-4} \text{ mol dm}^{-3}$

Reaction quotient (Q)

The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient**. The reaction quotient, *is the ratio of product of concentration of products to that of reactants raised to power equal to their stoichiometric coefficients obtained in the course of the chemical reaction.*

The quotient is useful in determination of the **position of the chemical equilibrium** (*the direction to which the reaction proceeds more so as to establish the equilibrium*) by comparing its value with that of the equilibrium constant at given temperature. Like equilibrium constant, the reaction quotient is derived directly from the stoichiometry of the balanced equation and for gases, it can be written in terms of partial pressures as well.



$$\text{Then, } Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \left(\text{or } Q_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \right)$$

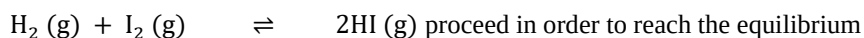
- When $Q_c < K_c$, the position of the chemical equilibrium shifts to the right (product side), that is; more product will be formed to establish equilibrium.
- When $Q_c > K_c$, the position of the chemical equilibrium shifts to the left (reactant side), that is; more reactant will be formed to establish equilibrium.
- When $Q_c = K_c$, the reaction is at equilibrium.

The reader should recognise the difference in the meaning of '[]' as used in equilibrium constant expression and in reaction quotient expression:

- In equilibrium constant, K_c expression, '[]' stands for molar equilibrium concentration i.e. the concentration of reagent (s) when the system is at equilibrium.
- In reaction quotient, Q_c expression '[]' stands for molar concentration at any time in the course of the chemical reaction, i.e. the system not necessary to be at equilibrium.

Example 33

At 450°C, Q_c for hydrogen iodide synthesis is 50.5. You place 1×10^{-2} moles of hydrogen, 3×10^{-2} moles of iodine and 2×10^{-2} moles of hydrogen iodide in a 2 litres container at 450°C. In which direction the reaction.



Solution

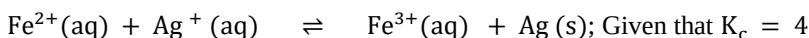
$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2 \times 10^{-2}}{V}\right)^2}{\left(\frac{1 \times 10^{-2}}{V}\right)\left(\frac{3 \times 10^{-2}}{V}\right)} = 1.33$$

But $K_c = 50.5$; thus $Q_c < K_c$

Hence the reaction will proceed to the right hand side to reach the equilibrium.

Example 34

The solution containing 0.2M of Fe^{2+} , 0.1M of Ag^+ and 0.5M of Fe^{3+} were mixed together with silver and the reaction was left to establish the equilibrium. Calculate the percentage of each reagent in the solution at equilibrium if the equilibrium reaction is formed as follows:

**Solution**

Calculating Q_c so as to determine the position of chemical equilibrium,

$$Q_c = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^+]} = \frac{0.5}{0.2 \times 0.1} = 25$$

But $K_c = 4$

Thus $Q_c > K_c$ and hence the position of the chemical equilibrium shift to the left so as to establish the equilibrium (backward reaction is more favoured)

$$\begin{array}{rcccl}
 & Fe^{2+}(aq) & + & Ag^+(aq) & \rightleftharpoons & Fe^{3+}(aq) & + & Ag(s) \\
 \text{Initially} & 0.2 & & 0.1 & & 0.5 & & \\
 \text{At equilibrium} & 0.2 + x & & 0.1 + x & & 0.5 - x & & \\
 K_c = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^+]} = \frac{0.5 - x}{(0.2 + x)(0.1 + x)} = \frac{0.5 - x}{x^2 + 0.3x + 0.02} = 4
 \end{array}$$

(Here there is no need of dividing by the volume because we have already given with number of moles in one litre of the solution for each reagent i.e. molarity of each reagent)

$$4x^2 + 1.2x + 0.08 = 0.5 - x \text{ or } 4x^2 + 2.2x - 0.42 = 0; x = 0.15$$

$$n_{Fe^{2+}} = 0.2 + x = (0.2 + 0.15) \text{ moles} = 0.35 \text{ moles}$$

$$n_{Ag^+} = 0.1 + x = (0.1 + 0.15) \text{ moles} = 0.25 \text{ moles}$$

$$n_{Fe^{3+}} = 0.5 - x = (0.5 - 0.15) \text{ moles} = 0.35 \text{ moles}$$

$$n_T = (0.35 + 0.25 + 0.35) \text{ moles} = 0.95 \text{ moles}$$

$$\%Fe^{2+} = \frac{n_{Fe^{2+}}}{n_T} \times 100\% = \frac{0.35}{0.95} \times 100\% = 36.842\%$$

$$\%Ag^+ = \frac{n_{Ag^+}}{n_T} \times 100\% = \frac{0.25}{0.95} \times 100\% = 26.316\%$$

$$\%Fe^{3+} = \frac{n_{Fe^{3+}}}{n_T} \times 100\% = \frac{0.35}{0.95} \times 100\% = 36.842\%$$

Hence: Percentage of Fe^{2+} is 36.842%

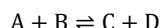
Percentage of Ag^+ is 26.316%

Percentage of Fe^{3+} is 36.842%

DIGGING DEEPER EXERCISE 13

EXERCISE 13A: BINDER QUESTIONS

Question 1

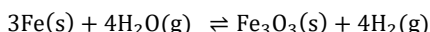


Sketch the graph of concentration of reactants and products against time for the above hypothetical reversible reaction which attain chemical equilibrium with:

- (a) $K_c > 1$
- (b) $K_c < 1$
- (c) $K_c = 1$

Question 2

When added to $\text{Fe}_3\text{O}_4(\text{s})$ in a closed container, which one of the following substances; $\text{H}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$ or $\text{O}_2(\text{g})$ will allow equilibrium to be established in the following reaction:

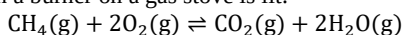


Question 3

For the reaction $\text{A}_2 + 2\text{B} \rightleftharpoons 2\text{AB}$, the rate of the forward reaction is 18M/s and the rate of the reverse reaction is 12M/s. The reaction is not at equilibrium. Will the reaction proceed in the forward or reverse direction to attain equilibrium?

Question 4

The following reaction occurs when a burner on a gas stove is lit:



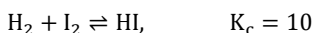
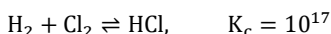
Is an equilibrium among CH_4 , O_2 , CO_2 , and H_2O established under these conditions? Explain your answer.

Question 5

List down at least five defining traits of chemical equilibrium.

Question 6

The equilibrium constant for synthesis of hydrogen chloride, hydrogen bromide and hydrogen iodide are given below:



- (i) What do the values of K_c tell you about the extent of each reaction?
- (ii) Which of these reactions you would regard as complete conversion?

Question 7

Give reasons argue for or against the statement that, "reactions with large equilibrium constants are very fast."

Question 8

Why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

Question 9

Write the equilibrium constant expression for K_c for each of the following reactions;

- (a) $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$
- (b) $\text{SnO}_2(\text{s}) + 2\text{CO}(\text{g}) \rightleftharpoons \text{Sn}(\text{s}) + 2\text{CO}_2(\text{g})$
- (c) $\text{Cr}(\text{s}) + 3\text{Ag}^+(\text{aq}) \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + 3\text{Ag}(\text{s})$
- (d) $3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2(\text{g})$

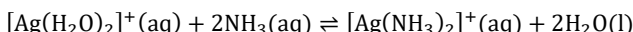
Question 10

Write the equilibrium constant expression for the following reactions:

- (i) $\text{N}_2\text{H}_4(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
- (ii) $3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g})$
- (iii) $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$
- (iv) $\text{Cr}(\text{s}) + 3\text{Ag}^+(\text{aq}) \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + 3\text{Ag}(\text{s})$

Question 11

Most metal ions combine with other ions in solution for example in aqueous ammonia; silver (I) ions are in equilibrium with different complex ions.



A room temperature, K_c for this reaction is 1×10^7 . Which of the two silver complex ions is the more stable? Give a reason for your choice.

Question 12

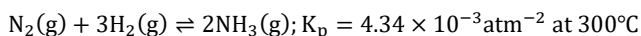
Each of the following mixture was placed in a closed container and allowed to stand. Which is capable of attaining the equilibrium? $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$.

In each case, provide an explanation for your answer.

- (i) Pure CaCO_3
- (ii) CaO and a CO_2 pressure greater than the value of K_p
- (iii) Some CaCO_3 and a CO_2 pressure greater than the value of K_p
- (iv) CaCO_3 and CaO

Question 13

For the formation of NH_3 from N_2 and H_2 :



What is the value of K_p for the reverse reaction?

Question 14

The equilibrium constant for the reaction of N_2 with O_2 to form NO equals $K_c = 1 \times 10^{-30}$ at 25°C . $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}); K_c = 1 \times 10^{-30}$

Using this information, write the equilibrium constant expression and calculate the equilibrium constant for the following reaction: $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$

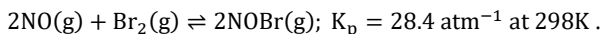
Question 15

Identify each reaction as essentially going to completion or not taking place

- (a) $\text{N}_2(\text{g}) + 3\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NCl}_3(\text{g})$ $K_c = 3.0 \times 10^{11}$
- (b) $2\text{CH}_4(\text{g}) \rightleftharpoons \text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g})$ $K_c = 9.5 \times 10^{-13}$
- (c) $2\text{NO}(\text{g}) + 2\text{CO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 2\text{CO}_2(\text{g})$ $K_c = 2.2 \times 10^{59}$

Question 16

Consider the following reaction equation:



In the reaction mixture at equilibrium, the partial pressure of NO is 108 torr and that of Br_2 is 126 torr. What is the partial pressure of NOBr in this mixture?

Question 17

The equilibrium constant (K_c) for the reaction: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ is 4.63×10^{-3} at 25°C .

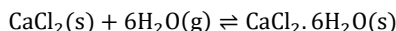
What is the value of K_p for this reaction at this temperature?

Question 18

For the reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$; $K_p = 4.3 \times 10^{-4}(-375^\circ\text{C})$. Calculate K_c for this reaction.

Question 19

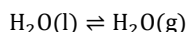
Anhydrous calcium chloride often used as a desiccant. In the presence of excess of CaCl_2 , the amount of the water taken up is governed by $K_p = 6.4 \times 10^{85} \text{atm}^{-6}$ for the following reaction at room temperature:



What is the equilibrium vapour pressure of water in a vessel that contains $\text{CaCl}_2(\text{s})$?

Question 20

The vapour pressure of water at 25°C is 0.0313atm . Calculate the value of K_p and K_c at 25°C for the following equilibrium:

**EXERCISE 13B: REAL QUESTIONS****Question 21**

With a help of an equation in each case, give two examples of chemical equilibrium in the real daily life.

Question 22

Inside the sealed Pepsi soda, not all carbon dioxide molecules are dissolved in the water; some molecules escape from the solution in the gaseous form. So there is carbon dioxide gas residing between the liquid solution and the cap. However, if we look at the bottle, these undissolved gas molecules are not observed; explain why?

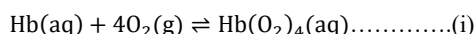
Question 23

The concept of equilibrium is not only applicable for chemical changes, physical changes, such as phase transitions, are also reversible and may establish equilibria too. Evaporation of water of in a closed container is a good example of this we are witnessing in a daily life.

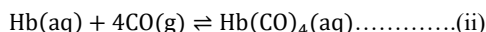
- Explain clearly how the physical equilibrium is achieved during the evaporation of water.
- Which is the physical quantity that is resulted from the evaporation is equivalent to equilibrium constant? Give reason(s) to justify your answer.
- Compare and contrast the physical equilibrium and chemical equilibrium.

Question 24

Haemoglobin (Hb) carries oxygen inside the human body according to the following equation:



The haemoglobin may also carry carbon monoxide inside the human body according to the following equation:



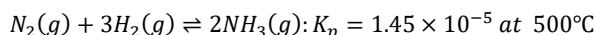
It is known that equilibrium constant for the second reaction is much higher than that of the first reaction.

- Between haemoglobin-oxygen bond and haemoglobin-carbon monoxide bond, which one is stronger? Give reason.
- If one is subjected to equal concentration of both oxygen gas and carbon monoxide gas, which gas will be consumed more?

Question 25

Your friend **Kipute**, was asked to solve the following problem:

Consider the following reaction:



In equilibrium mixture of the three gases at 500°C , the partial pressure of H_2 is 0.928atm and that of N_2 is 0.432atm . What is the partial pressure of NH_3 in the equilibrium mixture.

After solving, she found $P_{\text{NH}_3} = 2.24 \times 10^{-2} \text{atm}$. How could you help your friend to recognise that the answer is wrong without re-working the problem?

Question 26

Kipute was asked to calculate the least amount of acetic acid and she found the mass of 1.8g. Without re-working the problem, how could you show that the answer she got was correct? The problem was:

12g of acetic acid is heated with 18.6g of ethanol in 1dm³ flask at 298K. Calculate the least amount of acetic acid which may be present in the flask under these conditions if the equilibrium constant is 4.2.

Question 27

Mr. Akilikubwa aimed to design a chemical reaction that he would use to prepare at least 5g of lime from limestone. He wanted to achieve this by heating 20g of limestone in a sealed container of volume 5L to 800°C. The equilibrium constant for the thermal decomposition of limestone at this temperature is 1.16atm.

- Was **Mr. Akilikubwa** successful in his design?
- Would the amount of lime increase by adding more limestone? Give a reason based on your calculation.
- Would the amount of lime increase or decrease or remain the same by using a sealed container of larger volume? Give a reason based on your calculation.

Question 28

Mr. Akilikubwa aimed to design a chemical reaction that he would use to prepare a sample of lime from limestone. He wanted to achieve this by heating a sample of limestone in a closed vessel of volume 10L to 800°C. However, he is bothered by the fact that the decomposition of limestone is reversible, so he would have extra work of separating lime from limestone after completing the preparation. The equilibrium constant for the thermal decomposition of limestone at this temperature is 1.16atm.

- What maximum amount of limestone would **Mr. Akilikubwa** put in the vessel without a worry of having the extra duty of separation?
- What mass of lime will be obtained as the only solid substance in the vessel?

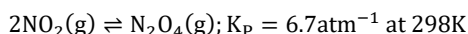
EXERCISE 13C: HOT QUESTIONS**Question 29**

Consider the following reaction: $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{S(g)}$

At certain temperature, $K_c = 8.5 \times 10^{-3}$. A reaction mixture at this temperature containing solid NH_4HS has $[\text{NH}_3] = 0.166\text{M}$ and $[\text{H}_2\text{S}] = 0.166\text{M}$. Will more of the solid form or will some of the existing solid decompose as equilibrium is reached?

Question 30

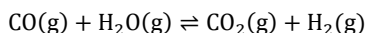
Nitrogen dioxide dimerises according to the following equation;



A 2.25L container contains 0.55mol of NO_2 and 0.082mol of N_2O_4 at 298K. Is the reaction at equilibrium? If not, in what direction will the reaction proceed?

Question 31

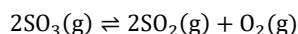
A 700k, carbon monoxide reacts with water to form carbon dioxide and hydrogen:



The equilibrium constant for this reaction at 700K is 5.1 considers an experiment in which 1.00mol of CO(g) and 1.00mol of $\text{H}_2\text{O(g)}$ are mixed together in a 1.00L flask at 700K. Calculate the concentrations of all species at equilibrium.

Question 32

Sulphur trioxide decomposes at high temperature in a sealed container;



Initially, the vessel is charged at 1000K with $\text{SO}_3\text{(g)}$ at a partial pressure of 0.500atm. At equilibrium, the SO_3 partial pressure is 0.200atm. Calculate the value of K_p at 1000K.

Question 33

At temperature near 800°C, steam is passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H₂. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

The mixture of gases that results is an important industrial fuel called **water gas**

- (a) At 880°C, the equilibrium constant for this reaction is $K_p = 14.1$. What are the equilibrium partial pressures of H₂O, CO and H₂ in the equilibrium mixture at this temperature if we start with solid carbon and 0.100mol of H₂O in a 1L vessel?
- (b) What is the minimum amount of carbon required to achieve equilibrium under these conditions?
- (c) What is the total pressure in the vessel at equilibrium?

Question 34

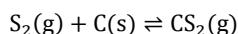
20g Of CaCO₃(s) were placed in a closed vessel, heated and maintained at 727°C under equilibrium:



And it is found that 75% of CaCO₃ was decomposed if the volume of the container was 15L, calculate the value of K_p .

Question 35

The equilibrium constant for the reaction is 9.40 at 900°C



When 1.42atm of S₂ and excess of C(s) come to equilibrium; partial pressure of which component changes to the maximum and of which one changes to the minimum and hence calculate their values.

Question 36

An analysis of the gaseous phase (S₂(g) and CS₂(g)) present at equilibrium at 1000°C in the reaction;

$C(s) + S_2(g) \rightleftharpoons CS_2(g)$; shows it to be 13.71% C and 86.29% S, by mass. What is K_c for this reaction?

Question 37

The reaction: $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$, is at equilibrium at temperature in which the equilibrium constant, K_c , is 375 mol⁻¹dm³. The equilibrium amount of oxygen found in a 0.755litre containing this equilibrium mixture is 0.148 mol. What is the ratio of [NO] to [NO₂] in this equilibrium mixture.

Question 38

At temperature close to 400°C, hydrogen iodide has a degree of dissociation of 20%. Calculate the composition of the equilibrium mixture produced if 1mole of hydrogen and 2.1mole of iodine react to equilibrium at this temperature.

Question 39

At a certain temperature, the equilibrium pressures of steam and hydrogen in contact with iron and its black oxide Fe₃O₄ were found to be 1533Nm⁻² (11.5mmHg) and 32190Nm⁻²(241.5 mmHg) respectively. Calculate:

- (a) The pressure of hydrogen in equilibrium with 1066 Nm⁻² (8 mmHg) of steam pressure.
 - (b) The pressure of hydrogen and steam at a total pressure of 101300 Nm⁻²(760mmHg) at this temperature.
- Equation for the reaction is $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

Question 40

The equilibrium constant of the reaction: $CO_2 + H_2 \rightleftharpoons CO + H_2O$ at 1000°C is 1.6. What is the percentage by volume of each gas in the equilibrium mixture at 1000°C produced from:

- (a) A mixture of 50cm³ hydrogen and 50cm³ carbon dioxide.
- (b) 25cm³ each of carbon dioxide and monoxide and 50cm³ of hydrogen.

Question 41

0.5 moles of hydrogen gas and 0.5 moles of iodine gas react in a 10L evacuated vessel at 440°C, hydrogen iodide is formed. The equilibrium constant, K_c for the reaction at 440°C is 50.

- (i) Calculate the value of K_p
- (ii) Calculate number of moles of I₂ remain unreacted at equilibrium

Question 42

1 mole of H_2 , 2moles of I_2 and 3moles of HI are injected in 1L vessel. What will be the concentration of H_2 , I_2 and HI at equilibrium at 490 °C? (The equilibrium constant for the reaction at 490°C is 45.9).

Question 43

5g of PCl_5 were completely vapourised at 250°C in a vessel of 1.9L capacity. The equilibrium mixture exerted a pressure of 1atm. Calculate:

- (i) The degree of dissociation.
- (ii) K_c and K_p for the reaction.

Question 44

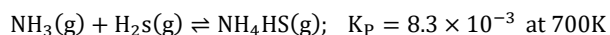
What will be percentage of dissociation when 1 mole of H_2S gas is introduced in a vessel of 1.1L at 1000K? The value of K_c for the reaction is 10^{-6} .

Question 45

Calculate the value of K_p at 700K for each of the reaction represented below;

- (i) $NH_4HS(g) \rightleftharpoons NH_3(g) + H_2S(g)$
- (ii) $2H_2S(g) + N_2(g) + 3H_2(g) \rightleftharpoons 2NH_4HS(g)$

Given that:



Chapter 14

FACTORS AFFECTING POSITION OF CHEMICAL EQUILIBRIUM**LE CHATELIER'S PRINCIPLE**

Equilibrium plays a very important role in the study of chemical reactions as it tells us about the direction of chemical reactions. The equilibrium helps us to control the reaction conditions to favour formation of desired products. In order to have that control, it is important to understand factors which affect equilibrium position.

There are three common factors which affect position of chemical equilibrium, namely;

- Concentration
- Pressure
- Temperature

The effect of mentioned factors on position of chemical equilibrium is generally explained by **Le Chatelier's principle** which states that, *"If a chemical system is in equilibrium and one of the factors involved in the equilibrium is altered, the equilibrium will shift so as to tend to annul the effect of the change"*

CONCENTRATION AND POSITION OF CHEMICAL EQUILIBRIUM**General rule derived from Le Chatelier's principle:**

Change in concentration of reagent(s) involved in system of chemical equilibrium, shifts the position of chemical equilibrium to the side of lower concentration.

The effect of change in concentration on position of chemical equilibrium can also well explained by the concept of **reaction quotient, Q_c** as done below:

Consider the following chemical system of reversible reaction: $aA + bB \rightleftharpoons cC + dD$

If the chemical system is at equilibrium; $Q_c = K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

If concentration of A or B is lowered, denominator in the above expression is decreased thus making, $Q_c > K_c$ and hence the position of chemical equilibrium shifts to the left i.e. reverse reaction become more favoured.

If concentration of C or D is increased, numerator in the above expression is increased thus making, $Q_c > K_c$ and hence the position of chemical equilibrium shifts to the left i.e. reverse reaction become more favoured.

If concentration of C or D is lowered, numerator in the above expression is decreased thus making $Q_c < K_c$ and hence position of chemical equilibrium shifts to the right.

If concentration of A or B increased, denominator in the above expression is increased thus making $Q_c < K_c$ and hence position of chemical equilibrium shifts to the right.

The reader should remember that: change in concentration has no effect on the value of equilibrium constant (K_c), it is only alters the reaction quotient (Q_c).

PRESSURE AND POSITION OF CHEMICAL EQUILIBRIUM

When chemical system is at equilibrium and the pressure of the system is increased or decreased, Le Chatelier's principle requires the position of chemical equilibrium to shift so as to decrease the added pressure or to increase the pressure respectively in order to re-store the equilibrium.

General rule

If the chemical system is in equilibrium and the pressure of the system is increased the position of chemical equilibrium shifts to the side of lower volume i.e. to the side with fewer gaseous molecules

while decreasing pressure of the system shifts position of chemical equilibrium to the side of greater volume i.e. to the side with greater number of gaseous molecules.

To understand the concept, consider the following case of formation of ammonia from its constituent gaseous elements according to the following equation: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

From the above equation:

- **Four** gaseous molecules (**one** molecule of nitrogen molecule and **three** hydrogen molecules) react to give **two** gaseous molecules of ammonia.
- Thus the forward reaction is accompanied by decrease in number of gaseous molecules from **four** to **two**. *In other words, we can say that the forward reaction is accompanied by decrease in volume because according to Avogadro's law, volume of gases varies directly proportional to their number of molecules.*
- Since pressure exerted by the gas at given temperature increase with an increase of number of gas molecules; from the above fact we can conclude that the *forward reaction is accompanied by decrease in pressure and the reverse reaction is accompanied with increase in pressure.*
- Thus if the chemical system is at equilibrium and the pressure of the system is increased, to lower the added pressure the reaction must proceed in forward direction i.e. equilibrium shifts to the side of lower volume while if the pressure is decreased, to increase the pressure the reaction must proceed in backward direction i.e. equilibrium shifts to the side of greater volume.

For better understanding on the concept of effect of pressure on position of chemical equilibrium, you should understand the following facts in addition to the above explained facts:

- The greater the volume difference (difference in number of gaseous molecules between products side and reactants side), the greater effect the pressure has on position of chemical equilibrium.
- Pressure has no effect on position of chemical equilibrium in systems which do not involve gaseous reagents because liquid state is less compressible while solids are incompressible.
- Changing pressure has no effect on position of chemical equilibrium of reaction with gaseous reagents without involving the change in volume i.e. reactions which do not involve the change in number of gaseous molecules from reactants side to products side.
- Pressure has effect on position of chemical equilibrium which involves gaseous reagent(s) accompanied with change in volume from the reactants to products side.
- Effect of pressure is the special case of effect of concentration in chemical system which involves gaseous reagents as for gases; the pressure varies directly proportional to their concentration. So like concentration, effect of pressure can be explained by using reaction quotient, R_Q and then comparing the quotient with K_p
- Like concentration, changing in the pressure has no effect on the value of equilibrium constant, K_p

TEMPERATURE AND POSITION OF CHEMICAL EQUILIBRIUM

The effect of temperature is well explained by **Vant Hoff's law of mobile** which states that, "*Increase in temperature and decrease in temperature favours forward reaction for endothermic reaction and exothermic reaction respectively and vice versa*"

The simpler way to understand this!

- For endothermic reaction, heat must be supplied to the system for the reaction to occur. Thus the heat may be regarded as the reactant for the reaction.

That is: $\text{reactants} + \text{heat} \rightleftharpoons \text{products}$

- So if heat is added by raising temperature, the equilibrium will shift to the right to eliminate the added heat and if it is decreased, the equilibrium will shift to the left to compensate the reduced heat.

- For exothermic reaction, heat is evolved after the reaction. Thus the heat may be regarded as the product for the reaction.

That is: $\text{reactants} \rightleftharpoons \text{products} + \text{heat}$

- So if the heat is added by raising temperature, the equilibrium will shift to the left to eliminate the added heat and if it is decreased the equilibrium will shift to the right to compensate the reduced heat.

So the most useful ability in understanding the effect of temperature on position of chemical equilibrium is the ability to identify **endothermic** and **exothermic reaction**.

Identification of endothermic and exothermic chemical reactions

This can be done by studying:

- Thermo-chemical equation
- Energy profile diagram

By studying thermo-chemical equation

This can simply be done by considering the sign of heat of reaction:

- If the heat of reaction is **positive**, then the reaction is **endothermic**.
- If the heat of reaction is **negative**, then the reaction is **exothermic**.

By studying energy profile diagram

There is a limit of potential energy below which no reaction will take place and the energy barrier is known as **activation energy**. So at initial stages of reaction the potential energy must increase until the activation energy is attained.

Once the activation energy has been attained, there is a formation of an intermediate product which is known as **activated complex**, e.g. for the reaction; $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$, the activated complex is H_2Cl_2 .

So if the energy is sufficient the new product (HCl in the above example) is formed but if it is insufficient the activated complex disintegrates to the original reactants (H_2 and Cl_2) and no reaction will occur.

If the energy is sufficient, the final product is formed by the activated complex starting to releasing energy to the surroundings so as to get new stability of new compound. The final potential energy of final product is what determines whether the reaction is endothermic or exothermic. **If the potential energy of the product is greater than that of reactants (which was assumed to be zero) then the reaction is endothermic and if it is less, the reaction become exothermic.**

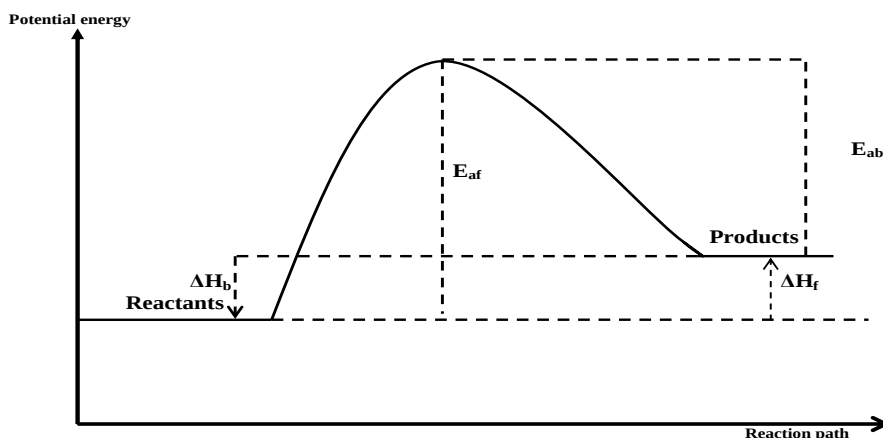


Figure 14.1 Energy profile diagram for endothermic chemical reaction

Where:

E_{af} and E_{ab} are activation energies for forward and backward reaction respectively (for endothermic reaction, $E_{af} > E_{ab}$)

ΔH_f and ΔH_b are heats of reactions for forward and backward reactions respectively

It should be noted that (as seen from the figure above), heat of reaction for forward and backward reaction are equal in magnitude but opposite in sign. If the forward reaction is endothermic then the backward reaction is exothermic and vice-versa.

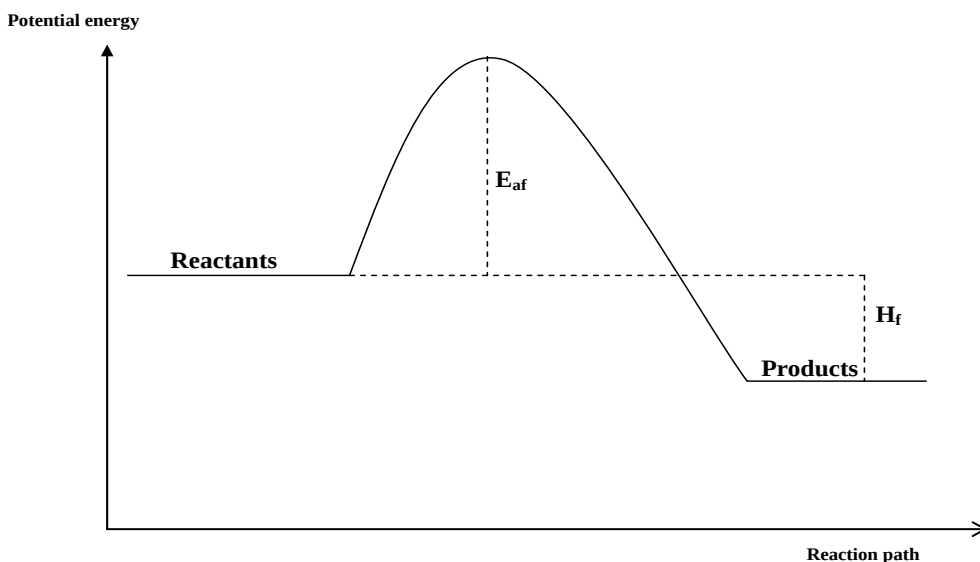


Figure 14.2 Energy profile diagram for exothermic chemical reaction

Note: in this case of exothermic reaction, $E_{af} < E_{ab}$ in contrast to endothermic reaction where $E_{af} > E_{ab}$

The reader should understand that:

Temperature is the only factor which can change the position of chemical equilibrium by changing the value of equilibrium constant.

Position of chemical equilibrium of reactions with greater magnitude of heat of reaction is more affected by change in temperature than those with smaller value of the magnitude.

Change in temperature has negligible effect on the position of the chemical equilibrium in reaction whose magnitude of heat of reaction is close to zero.

Kinetics of effect of temperature on the position of chemical equilibrium

Recall: $K_c = \frac{k_f}{k_b}$

If K'_c is the equilibrium constant at T_1 where corresponding rate constants are k'_f and k'_b for forward and backward reaction respectively;

And K''_c is the equilibrium constant at T_2 where corresponding rate constants are k''_f and k''_b for forward and backward reaction respectively;

That is $K'_c = \frac{k'_f}{k'_b}$ and $K''_c = \frac{k''_f}{k''_b}$

Then from the Arrhenius equation: $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

Or $k_2 = k_1 \ln^{-1}\left(\frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right)$

Therefore:

$$k''_f = k'_f \ln^{-1}\left(\frac{E_{af}}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right)$$

$$k''_b = k'_b \ln^{-1}\left(\frac{E_{ab}}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right)$$

Where E_{af} and E_{ab} are activate energies for forward and backward reaction respectively. Now to make things look simpler, let:

$$\ln^{-1}\left(\frac{E_{af}}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right) = n_1$$

And $\ln^{-1}\left(\frac{E_{ab}}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right) = n_2$

Then $K''_c = \frac{k'_f \times n_1}{k'_b \times n_2}$; but $\frac{k'_f}{k'_b} = K'_c$

And therefore $K''_c = \frac{n_1}{n_2} K'_c$

Now consider the following two cases;

First case: The temperature is increased from T_1 to T_2

For endothermic reaction, $E_{af} > E_{ab}$

That means that $n_1 > n_2$ and $\frac{n_1}{n_2} > 1$

Hence $K''_c > K'_c$ for endothermic reaction.

To conclude; increase in temperature increases K_c value for endothermic reaction and thus shifts the position of chemical equilibrium to the right. This result agrees with the result from Le-Chatelier's principle as explained earlier.

For exothermic reaction, $E_{af} < E_{ab}$

That means that $n_1 < n_2$ and therefore $\frac{n_1}{n_2} < 1$

Hence $K''_c < K'_c$ for exothermic reaction.

To conclude; increase in temperature decreases K_c value of exothermic reaction and thus shifts the position of chemical equilibrium to the left. Again this result agrees with Le-Chatelier's principle.

Second case: The temperature is decreased from T_1 to T_2

For exothermic reaction, $E_{af} > E_{ab}$

Since now $T_1 - T_2$ is negative number, $n_1 < n_2$ and therefore $\frac{n_1}{n_2} < 1$

Hence $K_c'' < K_c'$ indicating that the new equilibrium has shifted to the left as result of decrease in temperature in the endothermic reaction.

For exothermic reaction, $E_{af} < E_{ab}$

Again as $T_2 - T_1$ is negative number, $n_1 > n_2$ and therefore $\frac{n_1}{n_2} > 1$

Hence $K_c'' > K_c'$ indicating that the new equilibrium has shifted to the right as result of decreasing temperature in the exothermic reaction.

CATALYST AND CHEMICAL EQUILIBRIUM

Catalyst affects how fast equilibrium is achieved (with catalyst, the equilibrium is achieved sooner) but does not affect equilibrium position, why? This is because the forward and backward (reverse) reactions pass through the same transition state, the catalyst lowers the activation energy barrier for the forward and backward reaction by the same amount. The catalyst therefore increases the rate of forward and backward reaction by the same factor, and the composition of the equilibrium mixture is unchanged.

- Because a catalyst has no effect on the equilibrium concentration, it does not appear in the balanced equation or in the equilibrium constant expression.

Catalysts decrease the activation energy of both forward and backward reaction by equal amount as illustrated in the figure below.

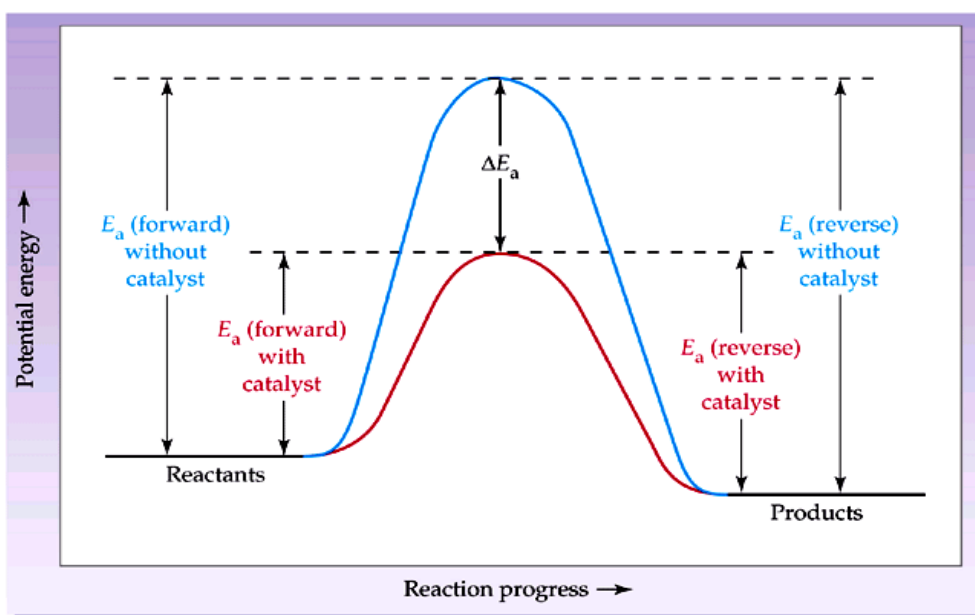


Figure 14.3 Effect of catalyst on reversible reaction

Kinetics of effect of catalyst in the position of chemical equilibrium

Let:

E_{afu} be activation energy for forward uncatalysed reaction

E_{abu} be activation energy for backward uncatalysed reaction

K_{cu} be equilibrium constant for uncatalysed reaction

K_{cc} be equilibrium constant for catalysed reaction

k_{fu} and k_{bu} be the rate constants for uncatalysed forward and backward reaction respectively

K_{fc} and K_{bc} be the rate constant for catalysed forward and backward reaction respectively

Then using: $K_c = \frac{k_f}{k_b}$

For uncatalysed reaction:

$$K_{cu} = \frac{k_{fu}}{k_{bu}}$$

But from Arrhenius equation ($k = Ae^{-E_a/RT}$)

$$k_{fu} = Ae^{-E_{afu}/RT} \text{ and } k_{bu} = Ae^{-E_{abu}/RT}$$

$$\text{Then } K_{cu} = \frac{Ae^{-E_{afu}/RT}}{Ae^{-E_{abu}/RT}} = e^{\frac{E_{abu}}{RT} - \frac{E_{afu}}{RT}} \quad (\text{Apply division exponent rule})$$

$$\text{Therefore } K_{cu} = e^{\frac{(E_{abu} - E_{afu})}{RT}}$$

But $E_{afu} - E_{abu} = -(E_{afu} - E_{abu}) = -H_u$ (where H_u is the heat of uncatalysed reaction)

$$\text{Hence } K_{cu} = e^{\frac{-H_u}{RT}}$$

(Generally equilibrium constant (K_c) at temperature (T) is related to heat of reaction (H_r) by the following equation; $K_c = e^{\frac{-H_r}{RT}}$).

For catalysed reaction:

$$\text{Similarly } K_{cc} = e^{\frac{-H_c}{RT}}$$

Then finding the ratio of K_c values for catalysed and uncatalysed reaction

$$\frac{K_{cu}}{K_{cc}} = \frac{e^{\frac{-H_u}{RT}}}{e^{\frac{-H_c}{RT}}} = e^{\left(\frac{H_c - H_u}{RT}\right)}$$

But $H_c = H_u$ and therefore; $H_c - H_u = 0$

$$\text{Thus } \frac{K_{cu}}{K_{cc}} = e^0 = 1$$

$$\text{Hence } K_{cu} = K_{cc}$$

Conclusion

The catalyst does not change the value of equilibrium constant. It has no effect on the equilibrium constant value and the position of equilibrium as well.

Example 1

Sulphuric acid is manufactured by the contact process which makes use of the equilibrium reaction:
 $\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$

Heat is given out in the formation of sulphur trioxide. State what effect there would be on the equilibrium concentration of sulphur trioxide if (i) the pressure were increased (ii) the temperature were raised.

Solution

- (i) Concentration of sulphur trioxide will be increased (the forward reaction proceed with reduction of volume, thus increasing pressure will shift the position of equilibrium to the right and hence the production of SO_3 will be increased).
- (ii) Concentration of sulphur trioxide will be decreased (since heat is given out; the forward reaction is exothermic so increase in temperature shifts position of equilibrium to the left and hence the production of SO_3 will be decreased).

Example 2

The equation for the reaction by which ammonia is manufactured is $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

- (a) What would be the effect on the equilibrium concentration of ammonia of
 - (i) Increasing the pressure
 - (ii) Increasing the nitrogen concentration
- (b) The equilibrium concentration of ammonia increases as the temperature is lowered. Is heat evolved or absorbed when ammonia is formed?
- (c) Why is a catalyst used in this reaction?

Solution

- (a) (i) Concentration of ammonia will be increased
 - (ii) Concentration of ammonia will be increased
- (b) Heat is evolved (low temperature favours forward reaction of exothermic reaction)
- (c) High percentage yield of ammonia is ensured by employing low temperature; but at low temperature the rate of the production of the gas is very slow and hence catalyst must be employed to increase the rate of production of the ammonia gas by enabling the equilibrium to be reached earlier.

Example 3

At 400°C, the three gases, hydrogen, iodine and hydrogen iodide exist together in equilibrium. The equation for the reaction is $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$

What effect will an increase in pressure have on the position of equilibrium?

Solution

Increase in pressure has no effect on position of chemical equilibrium because the reaction does not accompany with change in volume of the reagents.

Example 4

The reaction $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$ is reversible and (from left to right) endothermic, all reagents being gaseous. If the system is in equilibrium which (at temperature which allows quite rapid reaction), what if any, will be the effect on the equilibrium of

- (a) Doubling the total pressure
- (b) Doubling the pressure of nitrogen
- (c) Lowering temperature slightly
- (d) Explain briefly why this reaction (when used industrially) was not catalysed? What alternative was available?

Solution

- (a) Has no effect
 (b) *Position of chemical equilibrium will shift to right* because doubling the pressure of nitrogen gas, doubles its concentration so to lower the added concentration the equilibrium must shift to the right by producing more NO
 (c) Position of equilibrium will shift to the left
 (d) Since the forward reaction is endothermic, the production of NO (forward reaction) is favoured by high temperature which also increases the rate of production of NO at the same time. So industrially, they employ high temperature.

Example 5

Two solid allotropes A and B of densities 2.07 and 1.97gcm^{-3} respectively are in equilibrium according to $A(s) \rightleftharpoons 2B(s)$ $\Delta H = +0.4\text{kJmol}^{-1}$

What is the effect of pressure in above equilibrium?

Solution

Has no effect because pressure has no effect in reaction whose reagents are in solid phase which are always incompressible

Example 6

Consider the reaction: $X_2(g) + 3Y_2(g) \rightleftharpoons 2XY_3(g)$ $\Delta H = -92\text{kJ/mol}$

Is the production of XY_3 favoured by low or large volume of the flask? Explain.

Solution

The production of the given gas is favoured by low volume of the flask: The reaction is accompanied with decrease of volume from the left to the right so the forward reaction (production of XY_3) is favoured by high pressure and from Boyle's law whereby pressure varies inversely proportional to the volume; high pressure is obtained when the volume of flask is low.

APPLICATION OF LE CHATELIER'S PRINCIPLE**Haber process**

Haber process is the industrial manufacture of ammonia.

It uses the following reaction:



The reaction (from left to right) is exothermic.

Effect of pressure

Ammonia is produced from its elements with significant reduction of volume of gases. Therefore, if the system is in equilibrium and the pressure is then raised, the equilibrium must shift so as to tend to lower the pressure (Le – Chatelier's principle). To do this, the volume must be reduced by production of more ammonia. That is **high pressure favours the production of ammonia**.

Effect of Temperature

The formation of ammonia from its elements is exothermic. If the system is in equilibrium and the temperature is then lowered, the equilibrium must shift so as to tend to raise the temperature again. That is, heat must be liberated by the production of more ammonia. That is **low temperature favour the production of ammonia**. However, by lowering the temperature the rate of the reaction is reduced, that is larger amount of ammonia would be produced over very long time. So it is necessary to introduce a catalyst which give sufficient reaction rate in spite of a relatively low temperature.

Effect of Concentration

If the system is in equilibrium and more nitrogen or hydrogen is then added to increase their concentration, Le Chatelier's principle requires the equilibrium to shift so as to tend to reduce the added concentration and this is done by the production of more ammonia. *However, this is not an economic, so does not applied in practice and there is no particular advantage in using excess of either material.*

The gases are used in the theoretical proportion of nitrogen to hydrogen, 1:3 by volume.

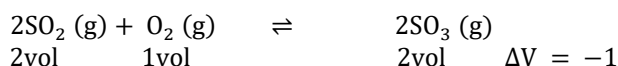
Conclusion

The conditions chosen in Haber process in accordance with the above discussion are:

- Very high pressure (200 – 500atm).
- Temperature of about 450°C.
- Catalyst: Finely divided reduced iron, usually 'promoted' by alumina (aluminium oxide).

Contact process

Contact process is the industrial manufacture of sulphuric acid. The first step in the contact process is the conversion of sulphur dioxide to sulphur trioxide according to the following reaction:



The reaction (from left to right) is exothermic.

Effect of pressure

Sulphur trioxide is produced from its elements with small reduction of volume of gases. Therefore increasing in pressure of the system favours the production of SO_3 in smaller extent (compared to effect of pressure in production of ammonia where there is greater reduction of volume). *So as the construction of equipment for production of high pressure is very expensive, the application of high pressure in production of SO_3 is not an economic.*

Effect of temperature

The formation of SO_3 according to above reaction is exothermic. If the system is in equilibrium and the temperature is then lowered, the equilibrium must shift so as to tend to raise the temperature again. That is, heat must be liberated by production of more sulphur trioxide. Thus **low temperature favours the production of sulphur trioxide**. *However, by lowering temperature, the rate of the reaction is reduced, that is greater amount of sulphur trioxide would be produced but over very long time which is not an economic. So it is necessary to introduce a catalyst which will give sufficient reaction rate in spite of relatively low temperature.*

Effect of concentration

Suppose that in the contact process reaction, equilibrium has been reached in certain conditions and then the concentration of oxygen relative to sulphur dioxide is raised. Le Chatelier's principle requires the system to react to oppose this change and this is done by combining it with sulphur dioxide to form sulphur trioxide. So **increase in concentration of oxygen (from air) favours the production of sulphur trioxide**. In practice, the sulphur dioxide and air mixture used contains about three times as much oxygen as is theoretically required for the sulphur dioxide content. Use of more air renders the product too dilute in sulphur dioxide. Also the use of high concentration sulphur dioxide relative to oxygen is not an economic (oxygen from air is cheaper than SO_2)

Conclusion

The conditions chosen in contact process in accordance with the above discussion are:

- Relatively low temperature of about 450°C
- High concentration of oxygen (relative to SO_2)
- Catalyst: Vanadium (v) oxide (V_2O_5)

DIGGING EXERCISE 14

EXERCISE 14A: BINDER QUESTIONS

Question 1

Given the hypothetical chemical reaction:



Suggest the direction of equilibrium if:

- (i) Pressure is decreased
- (ii) Temperature is raised
- (iii) K_2 is introduced in the system
- (iv) N_2 is removed from the system
- (v) KN is introduced in the system

Question 2

Consider the equilibrium: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ $\Delta H^\circ = +58\text{kJ/mol}$

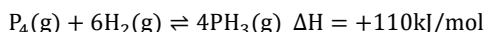
In which direction will equilibrium shift when?

- (a) N_2O_4 is added
- (b) NO_2 is removed
- (c) The total pressure is increased by addition of $\text{N}_2(\text{g})$
- (d) The volume is increased.
- (e) The temperature is decreased.

In each case give clear reason to support your answer.

Question 3

Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:



Question 4

Equilibrium constant is the ratio of rate constant of forward reaction to that of backward reaction $\left(K_c = \frac{k_f}{k_b}\right)$.

It is known that the magnitude of both rate constants are affected by catalyst. However, the catalyst is said to have no effect on the equilibrium constant; explain why.

Question 5

In which scenarios the following factors do not affect position of chemical equilibrium?

- (i) Temperature
- (ii) Concentration
- (iii) Pressure
- (iv) Catalyst

EXERCISE 14B: REAL QUESTIONS**Question 6**

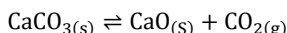
Explain why do we hear a hissing sound when we uncap a Coca Cola bottle?

Question 7

Explain conditions applied to increase the yield of ammonia in the Haber process indicating numerical values of pressure, temperature applied and also the kind of catalyst to be used.

Question 8

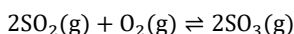
Quick lime is manufactured industrially by heating calcium carbonate in a lime kiln to a particular temperature that is not less than 800°C. Inside the lime kiln, the carbonate undergoes thermal dissociation to produce the quick lime according to the following equation:



Explain why there is a constant pressure of carbon dioxide at the particular temperature and why a current air is blown through the lime kiln during production of quick lime.

Question 9

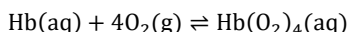
The manufacture of sulphuric acid is carried out on a large scale in most industrialised countries because it is needed by many other industries. In most countries the raw material is sulphur. The process consists of three main stages: the burning of sulphur in air, the conversion of sulphur dioxide to sulphur trioxide and the formation of sulphuric acid. The equation for the conversion to sulphur trioxide is;



- The conversion to sulphur trioxide is favoured by low temperature. Is the reaction exothermic or endothermic? Explain.
- Give the name of the catalyst used in this reaction. State the effect of the catalyst on the percentage yield at equilibrium of sulphur trioxide and on the rates of both forward and reverse reactions.
- A typical operating temperature is 450 °C. State **one** advantage and **one** disadvantage of operating the process at a temperature 50°C lower.

Question 10

Haemoglobin (Hb) is the material in red blood cells responsible for transporting oxygen to the cells of human body. Each haemoglobin molecule carries four oxygen molecules in oxyhaemoglobin ($\text{Hb}(\text{O}_2)_4$), and the equilibrium conditions of the haemoglobin-oxygen interaction can be expressed as follows:



For human to be healthy, sufficient oxygen in the air is needed so as to maintain healthy equilibrium.

- What does sufficient oxygen mean to the position of equilibrium of the above haemoglobin-oxygen interaction?
- At very high altitude, a person tends to feel light-headed. Support this fact by using Le-Chatelier's principle.
- For people born and raised at high altitudes their body produce more haemoglobin. Explain in terms of Le-Chatelier's principle, why this is important.

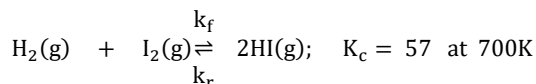
EXAMINATION QUESTIONS FOR PART FOUR

Question 1

- (a) Equilibrium constant is the ratio of rate constant of forward reaction to that of backward reaction ($K_c = \frac{k_f}{k_b}$). It is undeniable fact that the magnitude of both rate constants increases with an increase in temperature. However, for some reactions, magnitude of the equilibrium constant is found to decrease as the temperature increases; explain how is this possible?
- (b) 2.00g of phosphorous pentachloride are allowed to reach equilibrium at 200°C in a vessel of 1dm³ capacity. If the equilibrium constant of the reaction: $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ is 0.008 mol dm⁻³ at this temperature and in the conditions stated, calculate the percentage dissociation of the phosphorous pentachloride at equilibrium.

Question 2

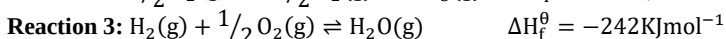
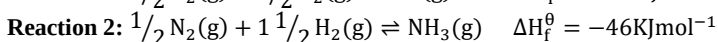
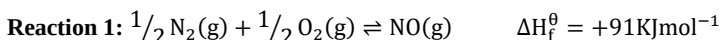
The equilibrium constant, K_c , for the reaction of hydrogen with iodine is 57 at 700K and the reaction is endothermic.



- (a) Is the rate constant, K_f for the formation of HI larger or smaller than the rate constant, K_r for the decomposition of HI?
- (b) The value of K_r at 700 is $1.16 \times 10^{-3} \text{M}^{-1}\text{s}^{-1}$. What is the value k_f at the same temperature?
- (c) How are the values of k_f , k_r and K_c affected by the addition of a catalyst?
- (d) How are the values of k_f , k_r and K_c affected by an increase in temperature?

Question 3

Nitrogen, hydrogen and oxygen undergo the reaction shown below:

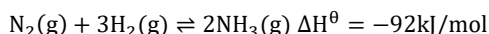


Use this information in answering the question below:

- (a) In which, if any, of the reaction above would the percentage yield of products at equilibrium increase if the temperature were to be raised? Explain your answer.
- (b) In which, if any, of the reactions above would the percentage yield of products at equilibrium not increase if the pressure were to be raised? Explain your answer.
- (c)
- In which direction, if any would any equilibrium reaction move if $\Delta H = 0$ and the temperature were to be decreased?
 - Predict for which of the reactions above the percentage yield of products at equilibrium would be most affected by a change in temperature. Explain your answer.

Question 4

In the Haber process for manufacture of ammonia, nitrogen and hydrogen react as shown in the equation:



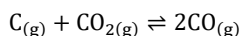
The table shows the percentage yield of ammonia, under different conditions of pressure and temperature when the reaction has reached dynamic equilibrium.

Temperature/ K	600	800	1000
% yield of ammonia at 10MPa	50	10	2
% yield of ammonia at 20MPa	60	16	4
%yield of ammonia at 50MPa	75	25	7

- Explain the meaning of the term **dynamic equilibrium**.
- Use Le-Chatelier's principle to explain why, at given temperature, the percentage yield of ammonia increases with an increase in overall pressure.
- Give reason why a high pressure of 50MPa is not normally used in the Haber process although it gives better yield?
- Many industrial ammonia plants operate at a **compromise temperature** of about 800K.
 - State and explain, by using Le-Chatelier's principle one advantage of using temperature lower than 800K
 - State the major advantage of using a temperature higher than 800K
 - Hence (from (i) and (ii) above) explain why 800K is referred as a **compromise temperature**.

Question 5

- On what factors, does the value of the equilibrium constant of reaction depend?
- At 1127K and 1atm pressure, a gaseous mixture of CO and CO₂ in equilibrium with solid carbon is 90.55% CO by mass:



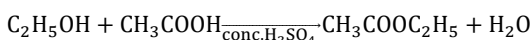
Calculate K_c for this reaction at the above temperature.

Question 6

- What is meant by:
 - A chemical equilibrium
 - The position of chemical equilibrium
- A 1:3 mixture by volume of nitrogen and hydrogen gases was made up and left to equilibrium at $1.01 \times 10^6 \text{ N/m}^2$ at 327°C. Calculate equilibrium constant, K_p given that the equilibrium partial pressure of ammonia is 15%

Question 7

- In the preparation of ethylethanoate shown in the equation below, concentrated H₂SO₄ is often added to the mixture:



- State two (2) functions of concentrated H₂SO₄ in the production of the compound.
 - What will be the effect of adding NaOH(aq) instead of conc. H₂SO₄ in the production of the compound?
- When 1.00 mol/dm^3 of CH₃COOH were heated with 0.18mol of C₂H₅OH in a 1 dm^3 closed vessel, 0.829mol of CH₃COOH remained at equilibrium. Calculate the value of K_c
 - What mass of ethylethanoate should be present in the equilibrium mixture formed under the same experimental conditions as 9(b)(i) above if 0.30moles of ethanol were heated with 0.20moles of ethanoic acid in 1.0 dm^3 closed vessel?

Question 8

- Explain the meaning and significance of equilibrium constant.
- When the solution containing $[\text{Ag}^+] = 0.2 \text{ M}$ was added to the flask containing ferrous solution of 0.100M, Ferric of 0.3M and solid silver; ferrous convert silver ions to solid and itself it undergo oxidation. What are ions concentrations when the equilibrium is established? Given that; equilibrium constant for the reaction is 2.98.

Question 9

- Ammonia is manufactured by passing hot nitrogen at high pressure over on iron catalyst .The equation of the reaction for this process is given as: $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

The equilibrium constant for the reaction is expressed as:

$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$$

Name and state the law applied to get the expression K_c

- If at 402°C, the reaction in (a) above has a K_p value of 2×10^{-14} Pa. calculate the pressure at which ammonia is 95% dissociated into its elements.
- What will happen to the value of K_p if 0.5 mole of NH₃ is added to the equilibrium mixture at 402°C

Question 10

- (a) What does Van't Hoff's law of mobile say about the effect of temperature in the equilibrium position?
(b) At a certain high temperature, the equilibrium constant of the reaction:



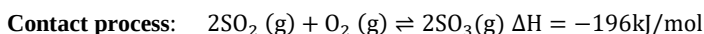
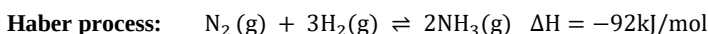
Assuming air to be a mixture of four volumes of nitrogen with one volume of oxygen, calculate the percentage of nitrogen monoxide by volume in the gas produced by allowing air to reach equilibrium at this temperature.

Question 11

- (a) How does reaction quotient relate to equilibrium constant?
(b) At 817°C, K_p for the reaction between CO_2 and excess hot graphite to form CO(g) is 10atm.
(i) What is the mole fraction of each gas at equilibrium at 817°C and the total pressure of 4atm?
(ii) At what total pressure, will the gas mixture contain 6% CO_2 by volume?

Question 12

- (a) Consider the following reaction equations representing Haber process and contact process:



- (i) Which reaction whose equilibrium position is more affected by temperature? Give reason(s) for your answer.
(ii) Which reaction whose equilibrium position is more affected by pressure? Give reason(s) for your answer.
(b) For the reaction: $\text{A} + \text{B} \rightleftharpoons 2\text{C}$; 2 moles of A and 3 moles of B reacts. If the equilibrium constant for the reaction, $K_c = 4$ at 900°C. What will be the equilibrium amount of C?

Question 13

- (a) High pressure increases product yield of both Haber process and contact process. However unlike Haber process, contact process is carried out at just almost atmospheric pressure. Explain.
(b) At 250°C, K_p for the reaction: $\text{N}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{NO}_{(\text{g})}$ is 8×10^{-4} . Nitrogen and oxygen gas are mixed in a volume ration of 4:1 respectively; calculate the percentage of nitric oxide by volume in the gas produced by allowing air to reach equilibrium at 250°C.

Question 14

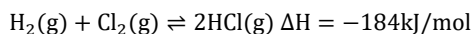
- (a) Write down two advantages of employing high pressure in the Haber process.
(b) At 25°C and 1atm pressure, the partial pressures in the equilibrium pressures of N_2O_4 and NO_2 gases are 0.7atm and 0.3atm respectively. Calculate the partial pressure of these gases when they are in the equilibrium at 25°C and at a total pressure of 10atm.

Question 15

- (a) Which physical factor(s) affect the magnitude of equilibrium constant?
(b) How the factor(s) mentioned in (a) above, affect the magnitude of equilibrium constant?
(c) An equilibrium mixture at 300K contains N_2O_4 and NO_2 gases at 0.28atm and 1.1atm respectively; if the volume of the container is doubled, calculate the new equilibrium pressure of the two gases.

Question 16

- (a) Hydrogen chloride may be prepared by direct combination of hydrogen and chlorine as per the following reaction equation:

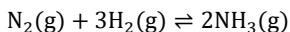


What will be the effect on the percentage yield of HCl when:

- (i) The volume of reaction flask is halved.
(ii) Temperature for the reaction is lowered.
(iii) Concentration of both hydrogen and chlorine gas is doubled.
(b) At 250°C and 1atm of sulphur trioxide gas is 50% dissociated, calculate K_p and K_c for the reaction at 250°C

Question 17

- (a) Ammonia is manufactured by the Haber process in which the following equilibrium is established.



- (i) Why catalyst has no effect on position of this equilibrium?
(ii) At equilibrium, with a pressure of 35MPa and a temperature of 600K, the yield of ammonia is 65%.

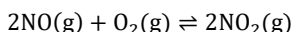
A: State why industry uses a temperature higher than 600K.

B: State why industry uses a pressure lower than 35MPa

- (b) Calculate the numerical value of K_p for the decomposition of SO_2Cl_2 , if its degree of dissociation under atmospheric pressure is 90%.

Question 18

- (a) *Catalyst has no effect on chemical equilibrium.* What is wrong about this argument? Explain clearly.
(b) CO_2 dissociates according to; $2\text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g}) + \text{O}_2(\text{g})$. If under atmospheric pressure, 40% of CO_2 was dissociated; calculate the dissociation constant i.e K_p

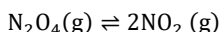
Question 19

For the reaction above the rate constant at 380°C for the forward reaction is $2.6 \times 10^3 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ and this reaction is first order in O_2 and second order in NO . The rate constant for the reverse reaction at 380°C is $4.1 \text{ L mol}^{-1} \text{ s}^{-1}$ and this reaction is second order in NO_2 .

- (a) Write the equilibrium expression for the reaction as indicated by the equation above and calculate the numerical value for the equilibrium constant at 380°C.
(b) What is the rate of the production of NO_2 at 380°C if the concentration of NO is 0.006mol/L and the concentration of O_2 is 0.29mol/L?
(c) The system above is studied at another temperature. A 0.2 mole sample of NO_2 is placed in a 5L container and allowed to come to equilibrium. When equilibrium is reached, 15% of the original NO_2 has decomposed to NO and O_2 . Calculate the value for the equilibrium constant at the second temperature.

Question 20

- (a) What is each of the following principle/law doing?
(i) Le-Chatelier's principle
(ii) Law of mass action
(b) Dinitrogen tetraoxide in its liquid state was used as one of fuels on the Lunar lander expeditions for the NASA space vessels. In the gas phase it decomposes to gaseous nitrogen dioxide as shown in the following equation:



N_2O_4 was allowed to reach at equilibrium at 400°C where the value of $K_p = 0.133 \text{ atm}$. At equilibrium, the pressure of N_2O_4 was found to be 2.71atm.

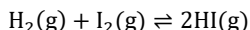
- (i) Write the equilibrium expression in terms of concentration.
(ii) Write the equilibrium expression in terms of partial pressures.
(iii) Calculate the equilibrium pressure of NO_2 .

Question 21

- (a) What do the following term represent?
(i) Reaction quotient
(ii) Equilibrium constant
(b) When 20.85g of PCl_5 was heated in a sealed tube of 4 dm^3 volume, the pressure in the vessel was found to be 1.5 atm. At this pressure it was found that PCl_5 dissociated to 80%. Calculate the partial pressure of each gas.

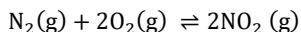
Question 22

- (a) Consider the production of HI by direct combination between I_2 and H_2 as per question;



Can you alter the yield of HI at equation by adding hydrogen gas or decreasing the volume of the container? Explain.

- (b) Nitrogen and oxygen combine endothermically at elevated temperature according to the equation:



If the equilibrium constant for the reaction is 4.3×10^{-3} at 3000°C and 1atm, calculate the composition of each in the equilibrium if 2 moles of each nitrogen and oxygen were heated.

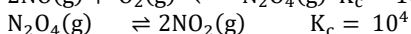
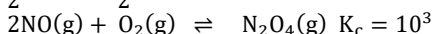
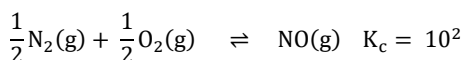
Question 23

- (a) Concentrated sulphuric acid reacts with sodium chloride as follows: $H_2SO_4 + Cl^- \rightleftharpoons HCl + HSO_4^-$

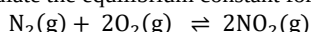
(i) What would be observable result of this reaction?

(ii) Explain why this reaction goes almost completely to the right despite the hydrochloric and sulphuric acids are strong.

- (b) Given with the equilibrium for the following reactions:

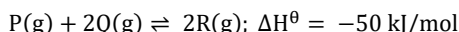


Calculate the equilibrium constant for the following reaction

**Question 24**

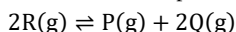
- (a) What does the equilibrium law say and provide the corresponding equation.

- (b) The following dynamic equilibrium was established at temperature T in a closed container.

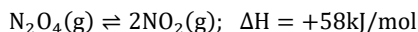


The value of K_c for the reaction was $68.0 \text{ mol}^{-1} \text{ dm}^3$ when the equilibrium mixture contained 3.82mol of P and 5.24mol of R.

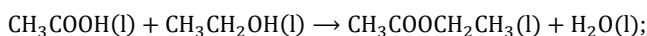
- Write an expression of K_c for this reaction.
- The volume of container was 10 dm^3 . Calculate the concentration in mol dm^{-3} , of Q in the equilibrium mixture.
- State the effect, if any, on the equilibrium amount of P, and on the value of K_c of increasing the temperature.
- State the effect, if any, on the equilibrium amount of P, and on the value of K_c of using a container of larger volume.
- Deduce the value of the equilibrium constant, at temperature T, for the reaction;

**Question 25**

- (a) The following equilibrium is established between colourless dinitrogen tetraoxide gas (N_2O_4) and dark brown nitrogen dioxide gas (NO_2).

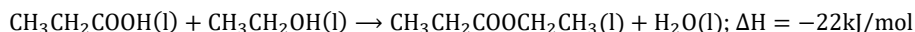


- Give two main features of reaction at equilibrium.
 - Use Le Chatelier's principle to explain why the mixture of gases becomes darker in colour when the mixture is heated at constant pressure.
 - Use Le Chatelier's principle to explain why the amount of NO_2 decreases when the pressure is increased at constant temperature.
- (b) 24.4g of ethanoic acid and 24.3g of ethanol were mixed in stoppered bottle and left for several days to reach equilibrium at room temperature. At the end of that time, the mixture was poured into pure water and made up to a total volume of 250 cm^3 . A 25.0 cm^3 sample of this needed 26.5 cm^3 of 0.400 M NaOH to neutralise the remaining ethanoic acid. Calculate a value of K_c for the reaction:



Question 26

- (a) By referring to Le-Chatelier's principle and behaviour of particles; explain clearly two advantages of using high pressure in Haber process.
- (b) A mixture was prepared using 1.00mol of propanoic acid, 2.00mol of ethanol and 5.00mol of water. At a given temperature, the mixture was left to reach equilibrium according to the following equation:



The equilibrium mixture contained 0.54mol of the ester, ethyl propanoate.

- Write an expression for the equilibrium constant, K_c , for this equilibrium.
- Calculate the number of moles of water in the equilibrium mixture.
- Calculate a value for K_c for this equilibrium at this temperature. Why this K_c value has no units.
- For this equilibrium, predict the effect of an increase in temperature on each of the following:

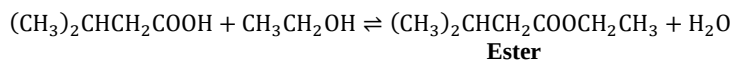
A: The amount of ester at equilibrium.

B: The time taken to reach equilibrium.

C: The value of K_c

Question 27

- (a) When 3-methylbutanoic acid reacts with ethanol in the presence of an acid catalyst, an **equilibrium** is established. The organic product is a pleasant-smelling ester.



The carboxylic acid is very expensive and ethanol is inexpensive. In the manufacture of this ester, the mole ratio of carboxylic acid to ethanol used is 1 to 10 rather than theoretical ratio of 1 to 1.

- By referring to the reaction between the 3-methylbutanoic acid and ethanol above; explain clearly the meaning of the term **equilibrium**.
 - Explain why 1 to 10 mole ratio is used and not the theoretical one. (You should **not** refer to cost).
 - Explain the effect of catalyst in the equilibrium.
- (b) The equilibrium constant for the reaction;

$\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$ at 986°C is 0.63. A mixture of 1.0 mole of water vapour and 3.0 mole of CO is allowed to come to equilibrium. The equilibrium pressure is 2.0atm.

- Calculate the number of moles of H_2 present at equilibrium.
- Calculate the partial pressure of gases at equilibrium mixture.

Question 28

- (a) For the reaction:

$\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$, $K_p = 794$ at 298K and $K_p = 54$ at 700K . Is the formation of HI favoured more at the higher or lower temperature? Give a reason for your answer.

- (b) When a 0.218mol of hydrogen iodide was heated in a flask of volume Vdm^3 , the following equilibrium was established at 700K . $2\text{HI(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$

The equilibrium mixture was found to contain 0.023mol of hydrogen.

- Write an expression for K_c for the equilibrium
- State why the volume of the flask need not be known when calculating a value of K_c
- Calculate the value of K_c at 700K
- Calculate the value of K_c for the equilibrium $\text{H}_2\text{(g)} + \text{I}_2 \rightleftharpoons 2\text{HI(g)}$

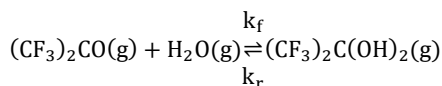
Question 29

- (a) Three reactions, and their equilibrium constants, are gives below.

- $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO(g)}$ $K_c = 4.7 \times 10^{-31}$
- $2\text{NO(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$ $K_c = 1.8 \times 10^{-6}$
- $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$ $K_c = 0.025$

Arrange above equations in order of their tendency to form products.

- (b) Consider the gas-phase hydration of hexafluoroacetone, $(\text{CF}_3)_2\text{CO}$;



At 76°C , the forward and reverse rate constant are $K_f = 0.13\text{M}^{-1}\text{s}^{-1}$ and $K_r = 6.02 \times 10^{-4}\text{s}^{-1}$.

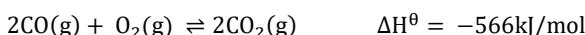
What is the value of the equilibrium constant, K_c ?

- (c) Consider the following heterogeneous equilibrium reaction: $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

At 800°C , the pressure of CO_2 gas is 0.236 atm. Calculate: (i) K_p and (ii) K_c for the reaction at this temperature.

Question 30

- (a) A platinum catalyst is used in automobile catalytic converter to hasten the oxidation of carbon monoxide:

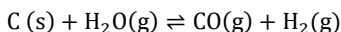


Suppose that you have a reaction vessel containing an equilibrium mixture of $\text{CO}(\text{g})$, $\text{O}_2(\text{g})$ and $\text{CO}_2(\text{g})$. Under the following conditions, will the amount of CO increase, decrease, or remain the same?

- A platinum is added
 - The temperature is increased
 - The pressure is increased by decreasing the volume
 - The pressure is increased by adding argon gas
 - The pressure is increased by adding O_2 gas.
- (b) For the equilibrium: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$; the equilibrium constant, K_p , has the value of 0.497 at 500K. A gas cylinder at 500K is charged with $\text{PCl}_5(\text{g})$ at initial pressure of 1.66atm. What are equilibrium pressures of PCl_5 , PCl_3 and Cl_2 at this temperature?

Question 31

At temperature near 800°C , steam is passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H_2 .



The mixture of gases that results is an important industrial fuel called **water gas**.

- At 880°C , the equilibrium constant for this reaction is $K_p = 14.1$. What are the equilibrium partial pressures of H_2O , CO and H_2 in the equilibrium mixture at this temperature if we start with solid carbon and 0.100mol of H_2O in a 1L vessel?
- What is the minimum amount of carbon required to achieve equilibrium under these conditions?

Question 32

- (a) Listed in the table are forward and reverse rate constant for the reaction: $\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$

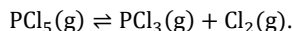
Temperature (K)	$K_f(\text{M}^{-1}\text{s}^{-1})$	$K_r(\text{M}^{-1}\text{s}^{-1})$
1400	0.29	1.1×10^{-6}
1500	1.3	1.4×10^{-5}

Is the reaction endothermic or exothermic? Explain in the terms of kinetics.

- (b) The equilibrium mixture, $\text{SO}_2 + \text{NO}_2 \rightleftharpoons \text{SO}_3 + \text{NO}$ was found to contain 0.6mol SO_3 , 0.4mol of NO , 0.8mol of SO_2 and 0.1mol of NO_2 in a 1L vessel. One mole of NO was then forced into the reaction vessel with volume and temperature being constant. Calculate the amounts of each gas in the new equilibrium mixture.

Question 33

- (a) When 1mol of PCl_5 is introduced into a 5L container at 500K, 78.5% of the PCl_5 dissociates to give an equilibrium mixture of PCl_5 , PCl_3 and Cl_2 .

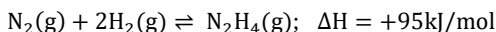


Calculate the value of K_p and K_c

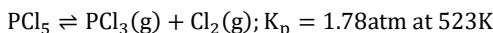
- (b) If the initial concentrations in a particular mixture of reactants and products (in (a) above) are $[PCl_5] = 0.5M$, $[PCl_3] = 0.15M$ and $[Cl_2] = 0.6M$;
- In which direction does the reaction proceed to reach equilibrium?
 - What are the concentrations when the mixture reaches equilibrium?

Question 34

- (a) Suggest four ways in which concentration of hydrazine N_2H_4 could be increased in an equilibrium described by the equation:



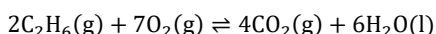
- (b) PCl_5 dissociates according to the reaction;



Find the density of the equilibrium mixture at a total pressure of 1atm.

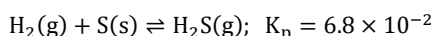
Question 35

- (a) Consider the following reversible equilibrium:



Derive the relationship between K_c and K_p .

- (b) At $90^\circ C$, the following equilibrium is established:



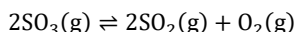
If 0.2mol of hydrogen and 1.0mol of sulphur are heated to $90^\circ C$, in a litre vessel; what will be partial pressure of H_2S at equilibrium?

Question 36

- (a) Equilibrium constant is the ratio of rate constant of forward reaction to that of backward reaction ($K_c = \frac{K_f}{K_b}$).

It is known that the magnitude of both rate constants increases with an increase in temperature. Explain why the K_c value changes as the result of the increase in temperature despite the fact that both K_f and K_b values are increased by the temperature rise.

- (b) A 16g sample of sulphur trioxide was placed in an empty container where it decomposed at 800K according to the following chemical reaction:



At equilibrium, the total pressure and the density of the gaseous mixture were 3.6atm and $3.2gdm^{-3}$ respectively. Calculate K_p for this reaction.

Question 37

- (a) At a given temperature, the reaction quotient for a system at equilibrium is constant. Is this correct? Rationalise your answer.
- (b) When 2.98 moles of I_2 and 8.10 moles of H_2 are heated at constant volume at $444^\circ C$ until equilibrium, 5.64moles of HI are formed. If we start with 5.3 moles of I_2 and 7.94 moles of H_2 , how much HI is present at equilibrium at the same temperature?

Question 38

- (a) The expression for an equilibrium constant, K_c , for a homogeneous equilibrium reaction is given below.

$$K_c = \frac{[A]^3[B]^2}{[C]^4[D]^3}$$

- Write an equation for the forward reaction.
- Deduce the units of K_c
- State what can be deduced from the fact that the value of K_c is larger when the equilibrium is established at a lower temperature.

(b) Consider the following reaction: $2\text{NOBr(g)} \rightleftharpoons 2\text{NO(g)} + \text{Br}_2\text{(g)}$.

If nitrosyl bromine (NOBr) is 33.33% dissociated at 25°C and a total pressure is 0.28atm. Calculate K_p for the dissociation at this temperature.

Question 39

(a) The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[\text{NH}_3]^4[\text{O}_2]^5}{[\text{NO}]^4[\text{H}_2\text{O}]^6}$$

Write the balanced chemical equation corresponding to this expression.

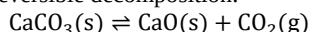
(b) Study the gases equilibrium: $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$ $\Delta H^\theta\text{(g)} = \text{kJ/mol}$

(i) Write an expression for the equilibrium constant, K_p , in terms of partial pressure.

(ii) At 60°C, 1.00dm³ of the gas weighed 2.585g under a pressure of $1.01 \times 10^5\text{N/m}^2$. Find the degree of dissociation of N_2O_4 and the value of K_p .

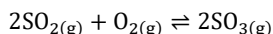
Question 40

(a) The following equation represents a reversible decomposition:



Under what condition(s) will decomposition in a closed container proceed to completion so that no CaCO_3 remains?

(b) At 311K Sulphur dioxide and oxygen combine in equilibrium reaction according to the equation:



0.1mole of oxygen and 0.2 mole of sulphur dioxide are introduced into a 0.2L flask and were allowed to react. If the equilibrium amount of oxygen and sulphur dioxide is 10% of the equilibrium mixtures, calculate:

(i) The equilibrium amount of oxygen, sulphur dioxide and sulphur trioxide

(ii) Calculate the total pressure of the system at equilibrium

Question 41

(a) For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Comment on the magnitude of equilibrium constant(K_c) for this reaction?

(b) 23.8g of sulphur thiochloride (SOCl_2) were mixed with 19.2g of SO and 142g of Cl_2 in 1 dm³ vessel at once and the reaction was allowed to establish equilibrium. Calculate the equilibrium composition of each gas if the equilibrium constant K_c for the reaction: $\text{SOCl}_{2\text{(g)}} \rightleftharpoons \text{SO}_{\text{(g)}} + \text{Cl}_{2\text{(g)}}$ is 1.2M.

Question 42

(a) What is the chemical equilibrium?

(b) What are necessary conditions for chemical equilibrium to be established?

(c) When one mole ethanoic acid (acetic acid) is maintained at 25°C with one mole of ethanol, one third of the ethanoic acid remains when equilibrium is attained. How much would have remained if three quarters of one mole of ethanol had been used instead of one mole at the same temperature?

Question 43

(a) Consider the following equilibrium: $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{CrO}_4^{2-} + 2\text{H}^+$
orange yellow

What would you expect to see if:

(i) Dilute sodium hydroxide is added to the equilibrium mixture?

(ii) Dilute hydrochloric acid is added to the equilibrium mixture?

(iii) Calcium chloride is added to the equilibrium mixture?

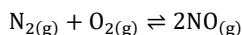
(b) At 1 atmosphere, and 55°C N_2O_4 is 50% dissociated. Calculate the equilibrium constant for this reaction in terms of pressure. Hence calculate the degree of dissociation of the gas at 55°C and 10 atmosphere pressure.

Question 44

- (a)
- Briefly explain the dynamic nature of equilibrium reaction.
 - Use hydrogen (H_2) and iodine (I_2) gases which produce hydrogen iodide (HI) gas to illustrate the point mentioned in (a)(i)
- (b) At certain temperature, and a pressure of 1 atmosphere, iodine vapour contains 40% by volume of iodine atoms. $I_2 \rightleftharpoons I + I$. At what total pressure (without temperature change) would this pressure reduced to 20?

Question 45

- (a) For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Comment on the value of equilibrium constant for the titration reaction.
- (b) Nitrogen and oxygen combine at high temperatures with absorption of heat according to the equation:



The equilibrium constant for this reaction at 2680K and 1atm is 3.6×10^{-3} when equal volumes of nitrogen and oxygen are mixed at 2680K and 1atm and allowed to react until equilibrium is reached. Calculate the fraction

- Of the original nitrogen which is used in the reaction.
- By volume of nitric oxide in the mixture.

Question 46

- (a) Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal? Rationalise your answer.
- (b) Pure phosphorous pentachloride gas is introduced into an evacuated vessel and comes to equilibrium at 250°C, the reaction being $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.

The total pressure is 202kPa and the mole fraction of the chlorine gas is 0.407.

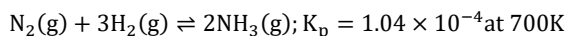
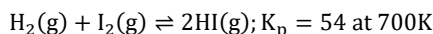
- What are the partial pressure of phosphorous trichloride and phosphorous pentachloride gases?
- Calculate K_p for the reaction at 250°C.

Question 47

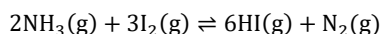
- (a) In the course of a chemical reaction, when does a reaction quotient:
- Is zero?
 - Is infinitely large?
- (b) At 700K, CO_2 and H_2 react to form CO and H_2O . For this process, K_c value is 0.11. If a mixture of 0.45 mole of CO_2 and 0.45 mole of H_2 is heated;
- Calculate the amount of each at equilibrium.
 - After equilibrium is reached another 0.34moles of CO_2 and 0.34 moles of H_2 are added to the reaction mixture. Find out the composition of the mixture of the new equilibrium state.

Question 48

- (a) Given the following information:



Determine the value of K_p of the following reaction at 700K.



- (b) In a mixture of nitrogen gas and hydrogen gas at molar ratio of 1:3, the molar percent of NH_3 at equilibrium was found to be 1.2 at 500°C and 10atm
- Calculate K_p .
 - Find the pressure at which the equilibrium mixture at this temperature contain 10.4 molar percent?

Question 49

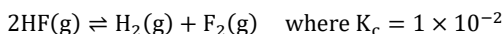
- (a) Is a system at equilibrium if the concentrations of reactants and products are equal? Rationalise your answer.
- (b) At 450°C, K_c for the equilibrium: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is 1.8. How many moles of NH_3 must be placed in 1litre container in order to yield an equilibrium concentration of hydrogen gas of 6 moles per litre?

Question 50

- (a) Why the equilibrium of decomposition of calcium carbonate to calcium oxide is not be achieved in the open container?
- (b) A mixture of SO_3 , SO_2 gas and O_2 gas is maintained in 10litre flask at 500°C for which K_c for the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ is 100.
- (i) If the moles of SO_2 and SO_3 are equal in the flask how many moles of O_2 are present?
- (ii) If the number of moles of SO_3 is twice the number of moles of SO_2 , how many moles of O_2 present?

Question 51

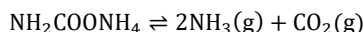
- (a) Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.
- (b) Consider the reaction:



In an experiment, 5mol of $HF(g)$, 0.5mol of $H_2(g)$, and 0.75mol of $F_2(g)$ are mixed in a 5L flask and allowed to react to equilibrium, calculate concentrations of all species at equilibrium.

Question 52

- (a) Equilibrium concentration depends on equilibrium constant. Explain whether you agree or disagree with this statement.
- (b) Solid ammonium carbamate(NH_2COONH_4) dissociates as;



In a closed vessel, solid ammonium carbamate is in equilibrium with dissociation products. At equilibrium, ammonia is added such that the partial pressure of NH_3 at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at equilibrium to that of original total pressure.

PART FIVE

IONIC EQUILIBRIA

The equilibrium established between the unionised molecules and the ions in the solution of weak electrolytes is known as ionic equilibrium (plural: ionic equilibria).

Acids, bases and salts
&
Solubility and solubility product

Chapter 15

ACIDS AND BASES

In our daily lives we use several acidic and basic chemicals. Some of the acidic chemicals are naturally derived like citric acid in fruits and some are synthetically derived like sulphuric acid. Acids and bases are very important for modern society. They exist everywhere in our body and in our surroundings; for example, vinegar (contains acetic acid), soft drinks (contains carbonic acid), buttermilk (contains lactic acid), soap (contains base).

CONCEPTS OF ACIDS AND BASES

The concept of acids and bases have been defined many times in different ways. Several scientists put various definitions to characterize the acids and bases in which some of the concepts are quite narrow and some are comprehensive. The earliest definitions were made on the basis of their taste and their effect on other substances.

Three important theories of the concept of acids and bases which we are going to discuss in this book are:

- Arrhenius theory
- Bronsted – Lowry theory
- Lewis theory

Arrhenius theory of acids and bases

Arrhenius proposed the concept of acid and base based on the theory of ionisation. It was the first modern approach to acid-base concept. This theory explains many phenomena like strength of acids and bases, salt hydrolysis and neutralisation.

According to **Arrhenius theory of acids and bases**:

Acids are substances which produce hydrogen ions when dissolved in water.

- Example of **Arrhenius acids** include compounds like HCl, H₂SO₄, HCN and CH₃COOH which give hydrogen ions (H⁺) when dissolved in water (aqueous solution).

Bases are substances which produce hydroxide ions when dissolved in water.

- **Arrhenius bases** include compounds like NaOH and KOH which give hydroxide ions (OH⁻) in aqueous solution.

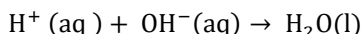
Interpretation of Arrhenius theory

The following pieces of information can be deduced from the Arrhenius theory:

Information 1: For a substance to act as an acid, it must contain ionisable hydrogen.

Information 2: For a substance to act as a base, it must contain ionisable hydroxyl group.

Thus by combining the first two pieces, Arrhenius theory suggests that neutralisation happens because hydrogen ions and hydroxide ions react to produce water.



Information 3: For a substance to act as an acid or a base, water must be present.

The necessity of water as a solvent medium for acid-base reaction, makes the Arrhenius theory of acids and bases to be also known as **water theory** of acids and bases.

Information 4: For a substance to act as an acid or a base, it must be soluble in water.

Advantages of the Arrhenius theory

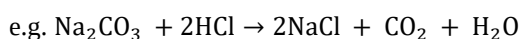
Despite of its flaws, Arrhenius theory is still important in the following ways:

- It explains the properties of acids and bases in aqueous medium.
- It explains acid-base neutralisation of acid by reaction with base.
- It explains salt hydrolysis.
- It introduces the concept of acidity and basicity.

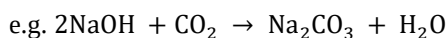
Disadvantages of the Arrhenius theory

The Arrhenius theory has the following drawbacks:

- It is only applicable to the acid – base behaviour in the aqueous medium (water) only.
- It does not provide any explanation to the acid – base behaviour in absence of water.
- It failed to explain why some compounds with hydrogen of oxidation state of +1 such as HCl dissolve in water to give acidic solution while others such as CH₄ do not.
- It failed to explain why some compounds such as NH₃ and Na₂CO₃ have basic characteristics although they have no hydroxyl (OH⁻) group.



- It failed to explain why some compounds such as CO₂ have got acidic characteristics although they have no hydrogen (H) atom in their molecules.



- It does not explain acid-base characters for substances which are insoluble in water like aluminium hydroxide.

Acidity and basicity

Acidity of a base is the number of moles of hydrogen protons (H⁺) required by one mole of the base for its complete neutralisation.

Examples:

- 1) One mole of NaOH needs one mole of H⁺ to form water in neutralisation reaction and hence it is said to have acidity of 1, i.e. it is **monoacid**.
- 2) One mole of Ca(OH)₂ needs two moles and hence it has acidity of 2.
- 3) One mole Al(OH)₃ needs three moles and hence it has acidity of 3.

Basicity of an acid is the number of hydroxyl ions required by one mole of the acid for its complete neutralisation.

Examples:

- 1) One mole of HCl(aq) needs one mole of OH⁻ for its complete neutralisation and hence it is said to have basicity of 1, i.e. it is **monobasic**.
- 2) One mole of H₂SO₄ needs two moles and hence it has basicity of 2, i.e. it is **dibasic**.
- 3) One mole of H₃PO₃ needs three moles and hence it is **tribasic**.

Monoprotic and polyprotic acids

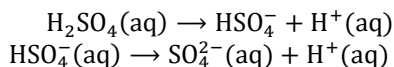
Depending on a number of ionisable hydrogen ions (protons) present in one molecule of an acid; acids can be classified into:

- Monoprotic and
- Polyprotic

Monoprotic acid is an acid whose one molecule contains one ionisable hydrogen only like HCl.

Polyprotic acid is an acid whose one molecule contains more than one ionisable hydrogen.

When one molecule of acid like H_2SO_4 contains two ionisable hydrogen, the acid is known as **diprotic**. Diprotic acids undergo ionisation process in two steps. They may undergo one or two dissociation (ionisation) depending on the acidity of solution. For example, H_2SO_4 ionises in two steps according to the following equations:



Then;

Bronsted – Lowry concept of acid and base

We have been previously learned an Arrhenius acid-base theory which provided a good start towards the acid-base chemistry but it has certain limitations. After this theory, Bronsted and Lowry proposed a different definition of acid-base that based on the abilities of compound to either donate or accept the protons. This theory is known as Bronsted-Lowry theory. This theory gives a more general and useful acid-base definition and applies to wide range of chemical reactions.

According to Bronsted – Lowry theory of acids and bases:

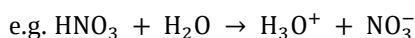
An **acid** is any hydrogen containing specie which is capable of donating one or more hydrogen protons (H^+) to a base.

- Thus the acid is a **proton donor**.

A **base** is any specie which is capable of accepting one or more hydrogen protons (H^+) from an acid

- Thus the base is a **proton acceptor**.

Acids and bases which are classified on the basis of Bronsted – Lowry theory are termed as **Bronsted acids and bases**.



Interpretation of Bronsted-Lowry theory

The following pieces of information can be deduced from the Bronsted-Lowry theory:

Information 1: An acid must contain positively polarized hydrogen.

Information 2: For a substance to act as an acid there should be another substance to act as a base and vice versa. (You cannot have donor without acceptor and vice versa).

In other words, acids and bases are interdependent.

Information 3: Acid-base reactions involve transfer of hydrogen protons from acid to base.

The presence of hydrogen proton as a necessary component of acid-base reaction, makes the Bronsted-Lowry theory of acids and bases to be also known as **proton theory** of acids and bases.

Information 4: The extent of an acid – base reaction is governed not only by the proton donating ability of the acid, but also by the proton accepting ability of the base.

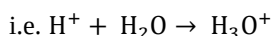
The relationship between the Bronsted – Lowry theory and the Arrhenius theory

The Bronsted – Lowry theory does not go against the Arrhenius theory in any way – it just adds to it as the following points explains:

- Hydroxide ions are still bases because they accept hydrogen ions (H^+) from acid and form water.
 $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$
- An Acid produces hydrogen ions in solution because it reacts with the water molecules by giving proton to them. $\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+$

Thus all Arrhenius acids and bases are Bronsted acids and bases but not all Bronsted acids and bases are Arrhenius acids and bases.

It is important to realize that: Whenever you talk about hydrogen ions in solution, H^+ (aq), what you are actually talking about are hydronium (sometime spelled hydroxonium) ions, H_3O^+ .



The free hydrogen ions do not exist in aqueous solution.

Advantages of Bronsted – Lowry theory over Arrhenius theory

- It expands the list of potential acids and bases to include positive and negative ions as well as neutral molecules or ions with at least one pair of non-bonding electrons (lone pair).
- It explains the role of water in acid – base reaction (water accepts H^+ from acid to form H_3O^+).
- It expands to include solvent other than water and reactions which occur in the gas or solid phase e.g. $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
- It explains the difference in relative strength of a pair of acid and a pair of base.
- It can explain the **levelling effect of water**. *The fact that strong acids and bases will all have the same strength when dissolved in water.*
- It links acid and base into conjugate acid – base pair (This will be discussed later in this chapter).

Disadvantages of Bronsted – Lowry Concept

- It failed to explain why some compounds such as CO_2 , SO_2 and AlCl_3 have acidic characters although they have not hydrogen atoms in their structures.
- It failed to explain the basic nature of oxides (basic oxides) like CaO and Na_2O .
- According to Bronsted-Lowry theory, same compound is act as acid in one reaction and act as base in other reaction. So, sometimes it is very difficult to predict the exact acid or base in a reaction.

Strong and Weak acids and bases

Bronsted – Lowry concept of acids and bases enable us to classify acids and bases into strong and weak. The classification is done due to their ability of donating or accepting hydrogen proton (H^+) which in turn affects degree of ionisation of the compounds in water.

A strong acid is an acid that has high ability donating hydrogen proton to the base so that it undergoes essentially complete ionisation in water.

Examples of strong acids are HCl , HNO_3 and H_2SO_4 . The ionisation of these strong acids in water is a typical acid – base reaction. For better understanding of the concept considers HCl which ionises in water according to the following equation: $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$

In the above reaction (ionisation): the acid (HCl) loses a proton to the base. The equilibrium lies far towards the right (complete ionisation of HCl) because H_2O is stronger base (better proton acceptor) than Cl^- and HCl is stronger acid (better electron donor) than H_3O^+ and hence the reaction become irreversible.

A weak acid is an acid which has low ability of donating hydrogen proton to the base so that only a small proportion of its molecules undergo ionisation in water.

Carbonic acid (H_2CO_3) is a typical weak acid which ionises in water according to the following equation: $\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_3^-$

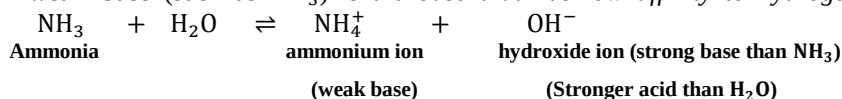
In the above reaction (ionisation): the equilibrium lies towards the non ionised side of the equation because H_3O^+ is the stronger acid than H_2CO_3 and HCO_3^- is stronger base than H_2O and hence large part of carbonic acid molecules remains unionised.

Another example of weak acid is CH_3COOH (Generally most of organic acids are weak).

Bases are classified as strong or weak depending on their affinity for hydrogen ions.

A strong base (such as OH^-) is the base that has high affinity to hydrogen proton of an acid.

A weak base (such as NH_3) is the base that has low affinity to hydrogen proton of an acid.



The student should note that:

The compound NH_4OH does not exist. We commonly write NH_4OH instead of solution of ammonia $\text{NH}_3(\text{aq})$ just for simplicity of understanding some concept and not in actual sense.

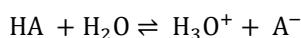
Conjugate acids and bases

The concept of conjugate acids and bases is useful for comparison of acidity and basicity.

The **conjugate base of an acid** is the ion or molecule that is formed when an acid loses its hydrogen ion. For example, the chloride ion, Cl^- , is the conjugate base of HCl .

The **conjugate acid of a base** is the product of the reaction of the base and a hydrogen ion. We say the base has been protonated. Thus, the conjugate acid of NH_3 is NH_4^+ .

In order to have better understanding of the concept of conjugate acid and base, consider an acid HA , and think of the reaction (ionisation of HA in water) as being reversible.

**Thinking about forward reaction:**

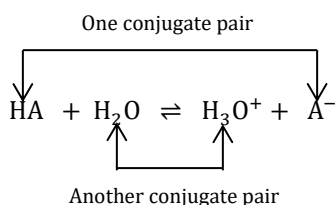
- The HA is an acid because it is donating proton (hydrogen ion) to the water.
- The water is base because it is accepting proton from the HA .

But there is also back (reverse) reaction between hydronium and A^- ion.

Thinking about backward reaction:

- The H_3O^+ is an acid because it is donating a hydrogen proton to the A^- ion.
- The A^- ion is a base because it is accepting a proton from the H_3O^+ .

The reversible reaction contains two acids and two bases. We think them in pairs, called **conjugate pairs**.



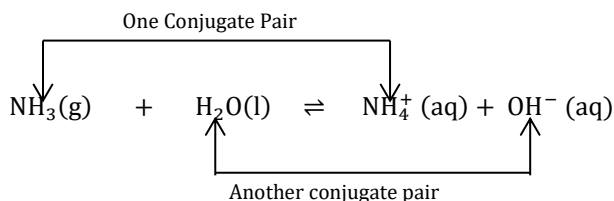
When the acid, HA , loses proton it forms a base, A^- . When the base, A^- accepts a proton back again, it obviously reforms the acid HA . These two are conjugate pair. Thus:

- If you are thinking about HA as an acid, then A^- is its conjugate base.
- If you are thinking about A^- as the base, then HA is its conjugate acid.

The water and hydronium ion is also a conjugate pair.

- Thinking of water as a base, the hydronium ion is its conjugate acid because it has the extra hydrogen ion which it can give away again.
- Thinking about the hydronium ion as an acid, then water is its conjugate base as the water can accept a hydrogen ion back again to reform the hydroxonium ion.

The reaction between ammonia and water is another example which may give conjugate pairs.



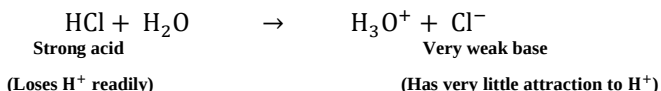
Definition of conjugate pair

These are two species which differ from each other by the presence or absence of transferable hydrogen ion.

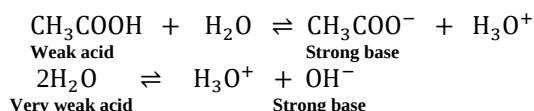
Relative strengths of conjugate acid-base pairs

Acidic or basic strengths of conjugate acid or base can be derived from known basic or acidic strengths of base or acid respectively as follows:

- If an acid is a strong acid, its conjugate base is a weak base.



- If an acid is weak, its conjugate base is a strong base.

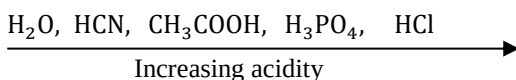


Similarly:

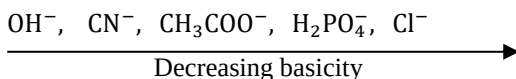
- If the base is strong, its conjugate acid is weak.
- If the base is weak, its conjugate acid is strong.

Thus, as the acid strengths of a series of compounds increase, the base strength of their conjugate bases decrease.

e.g. If acidic strengths of some conjugate acids follows the following trend:



Then the basic strengths of corresponding conjugate bases must follow the following order:



Lewis concept of acids and bases

The Bronsted-Lowry theory which we have been previously studied was a good startup for acid-base chemistry. The Bronsted-Lowry concept was based on the transfer of proton from one chemical species called acid to another called base. But this theory has its flaws too as we have seen. After Bronsted-Lowry theory, Lewis proposed a new acid-base theory which is based on their transfer of electrons (hence it is also known as electronic theory of acids and bases). This theory is more advanced and flexible than Bronsted-Lowry because it explains the acid-base behavior in that molecules which do not contain hydrogen or in non-aqueous medium.

According to Lewis theory of acids and bases:

- An **acid** is any specie (charged or uncharged) that can accept a pair of electrons. E.g. H^+ , BF_3 , AlCl_3 and Ag^+ . Thus Lewis acid is an **electron pair acceptor**.
- A **base** is any specie (charged or uncharged) that can donate a pair of electrons. E.g. OH^- , NH_3 , F^- and CH_3COO^- . Thus Lewis base is an **electron pair donor**.

So the Lewis acid-base reaction leads to the formation of dative bond whereby all shared electrons come from the Lewis base. In other words, the acid-base reaction involves transfer electrons from base to acid.

Examples:

- 1) $\text{H}_3\text{N} + \text{BF}_3 \rightarrow \text{H}_3\text{N} - \text{BF}_3$
- 2) $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$

The reader should understand that:

The Lewis definition is the most general theory, having no requirements for solubility or protons. It expands the list of acids and bases by including the following:

- 1) All cations (like Na^+ , Cu^{2+} and Fe^{3+}) which are regarded as Lewis acids.
- 2) All anions (like SO_4^{2-} and O^{2-}) which are regarded as Lewis bases.
- 3) The ion, molecule or an atom which has incomplete octet of electrons (for example, BF_3) are regarded as Lewis acids.
- 4) All molecules or atoms with lone pair like H_2O and NH_3 are regarded as Lewis bases.
- 5) The electron-rich pi (π) system like in benzene, ethene and ethyne are also considered as Lewis bases.
- 6) Molecules with multiple bonds between atoms of different electronegativities like NO_2 and CO_2 are regarded as Lewis acids.
- 7) All molecules with expanded octet like SF_4 and PCl_5 are regarded as Lewis acids.

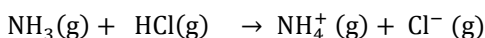
Relationship between the Lewis theory and Bronsted – Lowry theory

All Bronsted Lowry acids and bases are also Lewis acids and bases but reverse is not true.

For bases: The Bronsted – Lowry theory says that some species are bases because they are combining with hydrogen ions. The reason they are combining with hydrogen ions is that they have lone pair of electrons (non-bonding electrons)-which is what the Lewis theory says. The two are entirely consistent. Thus all Bronsted bases are also Lewis bases.

For acids: Lewis acids are electron pair acceptors. Compounds like BF_3 are Lewis acids because they can accept lone pair from Lewis bases although on the Bronsted – Lowry theory, the BF_3 has nothing remotely acidic about it. This is an extension of the term acid well beyond any common use.

What about more obviously acid – base reactions – like for example, the reaction between ammonia and hydrogen chloride gas?



What exactly accepting the lone pair of electron on the nitrogen? Most of students (even some textbooks) often misleads by writing as if the ammonia is donating its lone pair to hydrogen ion – a simple proton with no electrons around it. You don't usually get free hydrogen ions in chemical systems. They are so reactive that they are always attached to something else. They are not any uncombined hydrogen ions in HCl.

There is not any empty orbital anywhere on the HCl which can accept a pair of electrons. Why is then the HCl a Lewis acid?

Chlorine is more electronegative than hydrogen thus making the hydrogen chloride to be polar molecules with partial positive charge on hydrogen atom. ($\delta^+\text{H} - \text{Cl}^{\delta-}$). The lone pair on nitrogen is attracted to the slightly positive hydrogen atom. As it approaches it, the electrons in the H – Cl bond are more repelled towards the chlorine. Eventually, a coordinate bond is formed between the nitrogen and hydrogen and the chlorine breaks away as a chloride ion as shown below:



Thus the whole HCl molecule is acting as a Lewis acid. It is accepting a pair of electrons from the ammonia and in the process it breaks up. **Lewis acids do not necessarily have an existing empty orbital.**

Disadvantages of Lewis theory

- It fails to account for the relative strength of acids and bases because it is not based on ionisation.
- An acid – base reaction being an electron – transfer reaction, should be quite fast. However, many Lewis acid – base reactions are slow.
- It cannot explain the concept of relative strength of acids and bases.

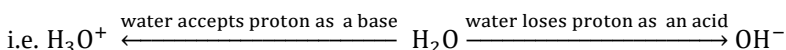
Note: The main advantage of the Lewis theory is that it is much more general than other definitions.

Amphoteric and amphiprotic substances

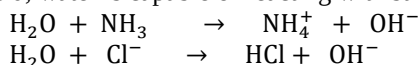
Amphoteric substance is the substance which can act as either an acid or a base.

- Thus amphoteric substance can react with both acid and base depending on relative strength of the two; with stronger acid, amphoteric substance acts as a base while with stronger base, the substance acts as an acid.

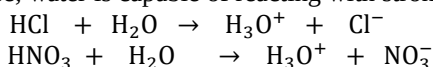
A good example of amphoteric substance is water which is capable of accepting hydrogen proton to form H_3O^+ (hydronium ion) thus acting as the base and it is also capable of losing hydrogen proton to form OH^- (hydroxide ion) thus acting as the acid.



As an acid, water is capable of reacting with stronger base (than itself) like NH_3 and Cl^- .



As a base, water is capable of reacting with stronger acid (than itself) like HCl and HNO_3 .



Some metal oxides like aluminium oxides (Al_2O_3) are also amphoteric – they react with both acids and bases.

Amphiprotic substance is one which can both donate hydrogen protons and also accept them.

- Again water is a good example of amphiprotic substance as explained earlier in the case of amphoteric substance.
- Another example is hydrogen sulphate ions (HSO_4^-) which can lose a hydrogen ion to form sulphate ions (SO_4^{2-}) or accept one to form sulphuric acid (H_2SO_4).

But as well as being amphiprotic, these compounds are also amphoteric as amphoteric means that they have reactions as both acids and bases. **So what is the difference between the two terms?**

All amphiprotic substances are also amphoteric – but the reverse is not true. There are amphoteric substances which do not either donate or accept hydrogen ions when they act as acids or bases. According to Lewis theory, the acid – base reaction does not necessarily involve hydrogen ion. Some metal oxides like aluminium oxides are amphoteric. For example, they react as bases because the oxide ions accept hydrogen ions (protons) to make water. That is not a problem as far as the definition of amphiprotic is concerned – but the reaction as an acid is. The aluminium oxide does not contain any hydrogen to donate! But aluminium oxide is capable of accepting lone pair of hydroxide ions in empty orbital of aluminium ion of the oxide thus acting as Lewis acid.

WORKED EXAMPLES**Example 1**

In each of the following indicate the acid / base conjugate pairs:

- (i) $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightleftharpoons \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$
 (ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}_3\text{O}^+$
 (iii) $\text{NH}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{OH}^-$
 (iv) $\text{H}_2\text{O} + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$
 (v) $\text{HSO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3 + \text{OH}^-$

Solution

- (i) $\text{H}_2\text{SO}_4 / \text{HSO}_4^-$ and $\text{H}_2\text{NO}_3^+ / \text{HNO}_3$
 (ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} / [\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ and $\text{H}_3\text{O}^+ / \text{H}_2\text{O}$
 (iii) $\text{H}_2\text{O} / \text{OH}^-$ and $\text{NH}_3 / \text{NH}_2^-$
 (iv) $\text{H}_2\text{O} / \text{OH}^-$ and $\text{HCO}_3^- / \text{CO}_3^{2-}$
 (v) $\text{H}_2\text{O} / \text{OH}^-$ and $\text{H}_2\text{SO}_3 / \text{HSO}_3^-$

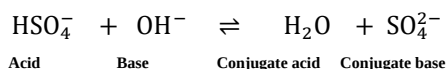
Example 2

In each of the following pairs of substances, write an equation to show how the pair reacts to form a conjugate acid – base pair.

- (i) Hydrogen sulphate ion and hydroxide ion
 (ii) Bicarbonate ion and water
 (iii) Carbonic acid and water
 (iv) Carbonate ion and water
 (v) Hydrogen sulphate ion and water

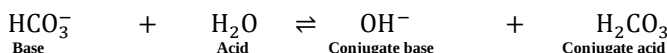
Solution

- (i) Hydroxide ion (which is conjugate base of weak acid, H_2O) is stronger base than hydrogen sulphate ion which is conjugate base of stronger acid, H_2SO_4 . Thus OH^- is better proton acceptor in the reaction.



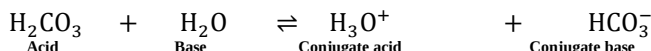
Where conjugate acid – base pairs are $\text{HSO}_4^- / \text{SO}_4^{2-}$ and $\text{H}_2\text{O} / \text{OH}^-$

- (ii) Bicarbonate ion being stronger base (than water) as it's conjugate acid, carbonic acid, is weaker acid than H_3O^+ (conjugate acid of H_2O), it must be proton acceptor in the reaction.



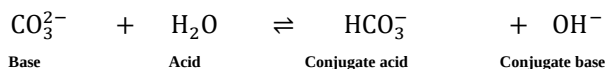
Where conjugate acid – base are $\text{H}_2\text{O} / \text{OH}^-$ and $\text{H}_2\text{CO}_3 / \text{HCO}_3^-$

- (iii) Carbonic acid being stronger acid compared to water which is conjugate acid of very strong base, OH^- , it must be proton donor in the reaction.



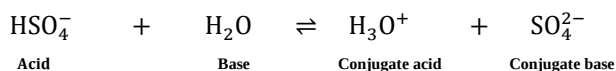
Where conjugate acid – base pairs are $\text{H}_2\text{CO}_3 / \text{HCO}_3^-$ and $\text{H}_3\text{O}^+ / \text{H}_2\text{O}$.

- (iv) Carbonate ion having no hydrogen at all, it must be proton acceptor in the reaction.



Where conjugate acid – base pairs are $\text{HCO}_3^- / \text{CO}_3^{2-}$ and $\text{H}_2\text{O} / \text{OH}^-$

- (v) H_2O is stronger base than HSO_4^- whose conjugate acid, H_2SO_4 is stronger acid than H_3O^+ (conjugate acid of H_2O) and hence water is proton acceptor in the reaction.



Where conjugate acid – base pairs are $\text{HSO}_4^-/\text{SO}_4^{2-}$ and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$

Be careful: In writing chemical equation to show the formation of acid-base conjugate pairs, the reversibility sign ($\rightleftharpoons$ and not $\rightarrow$) must be used.

ACID – BASE TITRATION

An **acid-base titration** is the determination of the concentration of an acid or base by exactly neutralising the acid/base with an acid or base of known concentration.

It makes use of **neutralisation reaction** that occurs between acids and bases and the knowledge of how acids and bases will react if their formulas are known.

The method of quantitative analysis which involves the experimental determination of volumes of solutions which react together completely is known as **titrimetric analysis**.

Some important definitions related to acid-base titration

Standard solution is the solution of known concentration in the titration. It is also known as **titrant** or **titrator**. An aqueous sodium carbonate is a good example of titrant which is commonly used in the experiment.

Analyte or **titrand** is the solution of unknown concentration in the titration.

Alkalimetry, (sometimes spelled **alkimetry**), is the specialized analytic use of acid – base titration to determine the concentration of a basic substance. Thus in alkalimetry, the analyte is the basic substance.

Acidimetry, (sometimes spelled **acidometry**), is the specialized analytic use of acid – base titration to determine the concentration of an acidic substance. Thus in acidimetry, the analyte is the acidic substance.

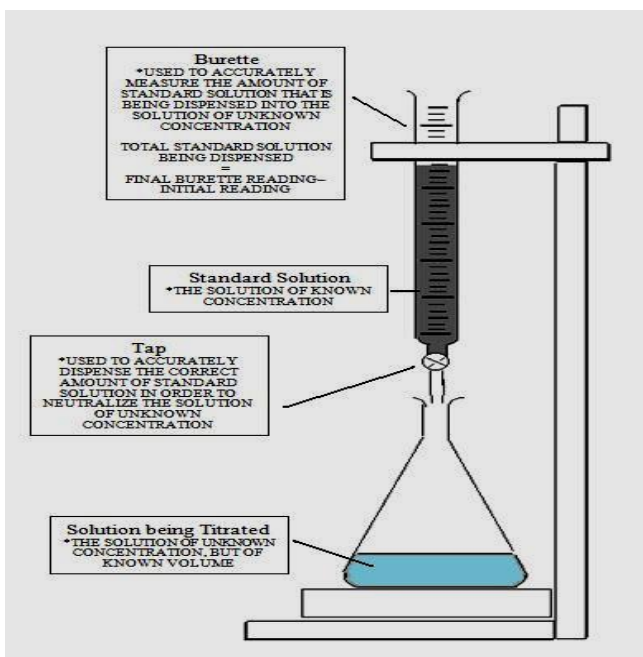


Figure 15.1 Titration diagram

Uses of acid – base titration

Acid – base titration is useful in:

- Determination of unknown concentration of acid or base
- Determination of percentage purity of chemicals

Acid – base indicators (pH indicator)

Acid-base indicators are used to detect pH of a solution. In theory, any substance that undergoes a reversible chemical change when pH changes can be used as an acid-base indicator. But in practice, a sharp change in some easily detectable property of the substance is required. Usually, the property is colour; but other properties such as odour can also change with pH. Almost any flower, fruit, or plant part that is red, blue, or purple can change color with pH. Carrots, rose petals, blue and red grapes, strawberries and red cabbage are good examples of common materials that can be used as acid-base indicators.

By definition:

An acid-base indicator is an organic compound that changes colour with a change in pH.

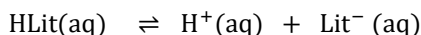
Working of acid-base indicators

Usually acid-base indicators operate as weak acid. To have better understanding of this, we are going to discuss three simple indicators, namely:

- Litmus
- Methyl orange (MO indicator)
- Phenolphthalein (POP indicator)

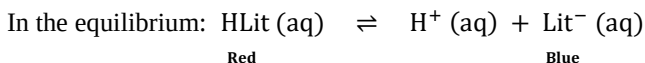
Litmus

Litmus is a weak acid. It has a seriously complicated molecule which we will simplify to HLit where the “H” is the hydrogen proton which can be given away to something else and the “Lit” is the rest of the weak acid molecule. Thus when the litmus (acid) is dissolved in water, the litmus being weak acid ionises according to the following equation:



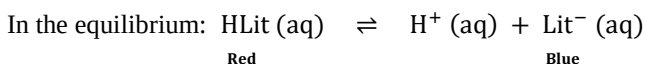
The un-ionised litmus (HLit) is **red**, whereas the ion (Lit^-) is **blue**. *Now, what would happen if hydroxide ions or some more hydrogen ions were added to the solution?*

Adding hydroxide ions:



Addition of hydroxide ions (OH^-) is equivalent to removal of $\text{H}^+(\text{aq})$ because OH^- and H^+ react together to form H_2O . So according to be Le Chatelier's principle, the equilibrium will shift to the right and more $\text{Lit}^-(\text{aq})$ are formed making the solution blue and hence **the litmus turns blue in basic solution**.

Adding hydrogen ions:



Addition of hydrogen ions (H^+) increases its concentration. Thus according to Le Chatelier's principle, the equilibrium will shift to the left by forming more HLit (aq) - the unionised litmus. Hence the litmus turns **red in acidic solution**.

If the concentration of H₂Li⁺ and Li⁺ are equal:

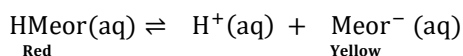
At some point during the movement of the position of equilibrium, the concentrations of the two colours will become equal. Thus the colour of the solution will be a mixture of the two (blue and red colourations) which is purple.

The reader should understand that:

The concentration of un-ionised indicator and that of ionised indicator not necessarily to be equal at pH of 7; among the common acid-base indicators, litmus is the only indicator which the 50/50 colour does occur at close to pH of 7 and this explains why the litmus is commonly used as test for acids and alkalis while other indicators do not. The pH at which the 50/50 colour occurs is determined by an equilibrium constant for the dissociation of the indicator which is known as **dissociation constant** for the indicator (and not by the neutrality of the solution).

Methyl Orange

Methyl orange is one of the indicators commonly used in titration. Again we will simplify its structure to HMeor where the “H” is the hydrogen proton which can be given away to something else and the “Meor” is the rest of the weak acid molecule. Thus the methyl orange ionises in solution according to the following equation:

**Adding hydroxide ions:**

Addition of hydroxide ions (OH⁻) is equivalent to removal of H⁺(aq) because they react together to form H₂O. So according to Le Chatelier's principle, the equilibrium will shift to the right and more Meor⁻(aq) are formed making the solution yellow and hence **the methyl orange is yellow in alkaline solution.**

Adding hydrogen ions:

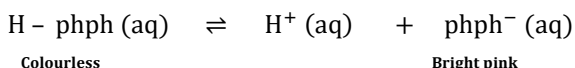
Addition of hydrogen ions (H⁺) increase its concentration, thus according to Le Chatelier's principle, the equilibrium will shift to the left by forming more unionised HMeor. Hence **the methyl orange is red in acidic solution.**

It should be noted that:

In methyl orange case, the half – way stage where the mixture of red and yellow produces an orange colour happens at pH of 3.7 – nowhere near neutral!

Phenolphthalein

Phenolphthalein is another commonly used indicator for titrations, and is another weak acid.

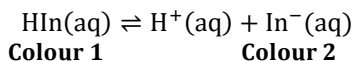


In this case adding hydroxide ions removes the hydrogen ions from the equilibrium which shifts the position of equilibrium to the right to replace them – turning the indicator pink. Adding extra hydrogen ions shifts the position of equilibrium to the left and turns the indicator colourless. Hence **the phenolphthalein is pink in alkaline solution and it is colourless in acidic solution.** The half – way stage happens at pH of 9.3. Since a mixture of pink and colourless is simply paler pink, this is difficult to detect with any accuracy.

Dissociation constant for pH indicator

So far we have studied that the point at which the pH indicator changes its colour is determined by dissociation constant for the indicator and not necessary for that change to occur at $\text{pH} = 7$.

To have more understanding of this, consider the indicator, HIn (where **H** stands for ionisable hydrogen atom of the indicator and **In** stands for anionic part of the indicator) which ionises according to the following equation:



Where **colour 1** is the colour of un-ionised indicator. It is also known as **acid colour** because it is observed when the concentration of H^+ is relatively high.

And **colour 2** is the colour of ionised indicator. It is also known as **base colour** because it is observed when the concentration of OH^- is relatively high.

Then from this equation of dissociation of the indicator, its equilibrium constant will be;

$$K_c = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

But because this is the equilibrium constant for the dissociation of the indicator, to be more specific, we are going to call it K_{in} (where **in** stands for indicator).

$$\text{That is; } K_{\text{in}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

But it is clearly understood that the intensity of colour 1 will be equal to the intensity of colour 2 when $[\text{HIn}] = [\text{In}^-]$

Then from the equation, $K_{\text{in}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$; when $[\text{In}^-] = [\text{HIn}]$; $K_{\text{in}} = [\text{H}^+]$

Thus the indicator starts to change its colour when the concentration of hydrogen ions is equal to the dissociation constant for the indicator.

When $[\text{H}^+] > K_{\text{in}}$, **colour 1** is observed (position of equilibrium shifts to the left) and when $[\text{H}^+] < K_{\text{in}}$, **colour 2** is observed.

Also from $[\text{H}^+] = K_{\text{in}}$ (when $[\text{HIn}] = [\text{In}^-]$)

$$-\log[\text{H}^+] = -\log K_{\text{in}}$$

$$\text{Or } \text{pH} = \text{p}K_{\text{in}} \quad (-\log[\text{H}^+] = \text{pH} \text{ and likewise } -\log K_{\text{in}} = \text{p}K_{\text{in}})$$

Hence the indicator starts to change its colour when **pH = pK_{in}** and when:

- **pH < pK_{in}**, **colour 1** is observed (By taking negative logarithm to both sides of the above relation, $[\text{H}^+] > K_{\text{in}}$)
- **pH > pK_{in}**, **colour 2** is observed (By taking negative logarithm to both sides of the above relation, $[\text{H}^+] < K_{\text{in}}$)

And of course when **pH = pK_{in}**, **colour mixture of colour 1 and colour 2** will be observed.

pH range of indicators

The end point of an indicator does not occur at a specific pH, rather than there is a range of pH within which the end point will occur. The exact values for the three indicators we have looked are:

Table 16.1 pH of common acid-base indicators

Indicator	pH at a half way of ionisation of the indicator i.e. at 50/50 colour mixture	pH range
Litmus	6.5	5 - 8
Methyl orange	3.7	3.1 – 4.4
Phenolphthalein	9.3	8.3 – 10.0

Choosing indicators for titrations

The point at which the indicator changes colour is called the **end point**.

A suitable indicator should be chosen, preferably one that will experience a change in colour (an end point) as close as possible to the **equivalence point (stoichiometric point)** of the reaction. That varies from titration to titration.

The **equivalence point of the reaction**, the point at which equivalent amount of reactants have reacted in exactly equation proportion will have a pH dependent on the relative strengths of the acid and base used.

The pH of the equivalence point can be estimated using the following rules:

- A strong acid will react with strong base to form a neutral (**pH = 7**) solution.
- A strong acid will react with a weak base to form an acidic (**pH < 7**) solution. Formation of the acidic solution is explained by the **cationic hydrolysis (cationic hydrolysis will be discussed in detail in chapter 19)** of the salt which is formed in the neutralisation reaction
- A weak acid will react with a strong base to form a basic (**pH > 7**) solution. Formation of basic solution is explained by **anionic hydrolysis (anionic hydrolysis will be discussed in detail in chapter 18)** of a salt which is formed in the neutralisation reaction.

When a weak acid reacts with a weak base, the equivalence point solution will be basic if the base is stronger and acidic if the acid is stronger (as result of the hydrolysis). If both are of equal strength, the hydrolysis will not occur and hence the equivalence point of the solution will be neutral. So in few words can say that: **It is difficult to get suitable indicator for titration of weak acids against weak bases because the titration is complicated by hydrolysis.**

However, even under presence of the suitable indicators, **weak acids are not often titrated against weak bases because the colour change shown with the indicator is often quick, and therefore very difficult for the observer to see the change in colour.**

Thus after above discussion, choice of suitable indicator different kinds of titration can be done as follows:

Methyl orange for the titration involving strong acid and weak base.

Reason for the choice: The end point of methyl orange indicator is found when the solution is acidic (pH range of 3.1 – 4.4) while the solution at equivalence point of the reaction between strong acid and weak base is also acidic as the result of cationic hydrolysis of a salt formed in the neutralisation reaction.

Phenolphthalein indicator for the titration involving weak acid and strong base.

Reason for the choice: The end point of phenolphthalein indicator is found when the solution is basic (pH range of 8.3 – 10) while the solution at equivalence point of the reaction between weak acid and strong base is also basic as the result of anionic hydrolysis of a salt formed in the neutralisation reaction.

Any indicator (methyl orange or phenolphthalein) for the titration involving weak acid and strong base.

Reason for the choice: In strong acid – strong base titration, both the hydrogen ions and hydroxyl ions concentrations are very small ($1 \times 10^{-7} \text{M}$) at the equivalence point. Consequently, the addition of single drop (negligible volume) of the base (or the acid) causes a large change in $[\text{OH}^-]$ or $[\text{H}^+]$ in the pH of the solution and hence either of the two indicators may be used although neither of the two has end point at pH of 7.

It should be noted that: The litmus is always not used as indicator in acid–base titration because the litmus colour change happens over an unusually wide pH range (5 – 8). However, it is useful for detecting acids and alkalis in the laboratory because it changes colours around pH of 7.

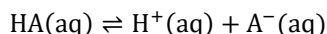
Example 3

A certain acid – base indicator has K_a of 10^{-4} with pH range of 3.4 – 4.7. The colour of ionised indicator is yellow and that of unionised indicator is red. When a half of the indicator has been ionised, the colour of the indicator becomes orange.

- Calculate the pH at which the colour of the indicator is orange.
- Is the indicator suitable test for acid and base? Explain.
- Can the indicator be used to indicate the end point of the titration between strong acid and weak base or weak acid and strong a base? Give reasons for your choice.
- What colour the indicator will show in 10^{-2}M HCl ? Explain.

Solution

- Let HA be the acid –base indicator which is weak acid.



Red

Yellow

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} ; \quad [\text{H}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]}$$

$$\text{Then } -\log[\text{H}^+] = -\log\left(\frac{K_a[\text{HA}]}{[\text{A}^-]}\right) \text{ or } -\log[\text{H}^+] = -\log K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{Thus } \text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

The indicator become orange when a half indicator has been ionised, i.e. $[\text{A}^-] = [\text{HA}]$

$$\text{Then } \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{p}K_a + \log 1 = \text{p}K_a$$

$$\text{So } \text{pH} = \text{p}K_a \text{ when } [\text{A}^-] = [\text{HA}]$$

$$\text{Substituting the given value of } K_a \text{ gives } \text{pH} = -\log 10^{-4} = 4$$

Hence the colour of indicator becomes yellow when pH is 4

- No.** For the given indicator, $[\text{A}^-] = [\text{HA}]$ occurs at pH which is not close 7; so it is possible for two acidic solutions with different pH (say pH of 3 and pH of 5) to give different colour with the indicator or for acidic solution with pH of above 4 to have the same colour as that basic solution (e.g. an acid solution with pH = 5 will give yellow colour like any basic solution which commonly have pH above 7).
- The indicator is suitable for a titration between strong acid and weak base because at the **equivalence point** of the titration, the solution is acidic and the **end –point** (the point at which

indicator changes its colour) of the indicator also occurs when the solution is acidic (pH range of 3.4 – 4.7).

- (iv) **Red colour**; pH of $10^{-2}\text{M HCl} = -\log 10^{-2}\text{M} = 2$; at pH of 2, pH value is less than pK_a value, so the position of equilibrium will lie to the left hand side and hence the indicator will show red colour.

Calculations on acid – base titration

Example 4

1.400g of pure anhydrous sodium carbonate was made up into 250cm^3 of aqueous solution. 25.0cm^3 of this solution required 24.50cm^3 of a certain sample of hydrochloric acid. Calculate the molarity of the acid and its concentration in gdm^{-3} . If the remaining acid occupied 920cm^3 , how would it made exactly decimolar? Is the titration acidimetry or alkalimetry?

Solution

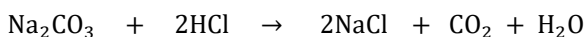
Mass Na_2CO_3 in 250cm^3 of its solution 1.4g

Thus mass of Na_2CO_3 in 25cm^3 of its solution = $\frac{1.4 \times 25}{250}$ g

Using $n = \frac{m}{M_r}$;

Number of moles of Na_2CO_3 reacted in the titration = $\frac{1.4 \times 25}{250 \times 106}$ moles

Na_2CO_3 reacts with HCl according to the following equation:



From which mole ratio of NaCl to HCl is 1: 2

Thus number of moles of HCl reacted = $\frac{1.4 \times 25 \times 2}{250 \times 106}$ moles = number of moles of HCl in 24.5cm^3 of its solution

Using $[] = \frac{n}{v}$;

$$[\text{HCl}] = \frac{1.4 \times 25 \times 2 \times 1000}{250 \times 106 \times 24.5} \text{ M} = 0.1078\text{M}$$

Molarity of the acid is 0.1078M

Mass concentration = Molarity $\times$ Molar mass = $0.1078 \times 36.5\text{gdm}^{-3} = 3.9347\text{gdm}^{-3}$

Thus mass concentration of the acid is 3.9347gdm^{-3}

By dilution principle: $M_c V_c = M_d V_d$

Where: M_c is the molarity of concentrated solution = 0.1078M

M_d is the molarity of diluted solution = 0.1M (decimolar)

V_c is the volume of concentrated solution = 920cm^3

V_d is the volume of diluted solution

$$\text{Then } V_d = \frac{M_c V_c}{M_d} = \frac{0.1078 \times 920}{0.1} \text{ cm}^3 = 991.8\text{cm}^3$$

Volume of distilled water added = $V_d - V_c = (991.8 - 920)\text{cm}^3 = 71.8\text{cm}^3$

Hence 71.8cm^3 of distilled water must be added to 920cm^3 of the acid solution in order to convert it to exactly 0.1M (decimolar).

The titration is **acidimetry**

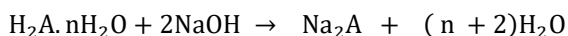
Example 5

5.032g of dibasic organic acid, of anhydrous relative molecular mass 90, were made up to one dm³ of aqueous solution. 25cm³ of this solution required 19.97cm³ of 0.10M Sodium hydroxide for neutralisation with phenolphthalein as indicator. Calculate the number of moles of water of crystallization per mole of the crystalline acid.

Solution

Let the formula of the organic acid be H₂A. nH₂O;

Then the acid will react with NaOH according to the following equation



From which mole ratio of H₂A. nH₂O to NaOH is 1: 2

$$\text{Number of moles of NaOH reacted} = \frac{19.97}{1000} \times 0.1 = 1.997 \times 10^{-3} \text{ mol}$$

Thus from the above mole ratio, number of moles of the acid in 25cm³ of the solution

$$= \frac{1.997 \times 10^{-3}}{2} \text{ moles} = 9.985 \times 10^{-4} \text{ moles}$$

Then number of moles of the acid in 1dm³ (1000cm³)

$$= \frac{9.985 \times 10^{-4} \times 1000}{25} \text{ moles} = 0.03994 \text{ moles}$$

But 5.032g of the organic acid were used;

$$\text{Then using } M_r = \frac{m}{n};$$

$$\text{Molar mass of hydrated organic acid} = \frac{5.032\text{g}}{0.03994\text{mol}} = 126\text{gmol}^{-1}$$

But relative molecular mass of anhydrous acid = 90;

$$\text{Where } 90 + 18n = 126 \text{ or } n = 2;$$

Hence number of moles of water of crystallization per mole of the crystalline acid is 2.

Example 6

1.6g of metallic oxide of type MO was dissolved in 100 cm³ of 1M hydrochloric acid. The resulting liquid was made up to 500cm³ with distilled water. 25cm³ of the solution then required 21.02cm³ of 0.1020M sodium hydroxide for neutralisation. Calculate the mass of oxide reacting with 1 mole of hydrochloric acid and hence the molar mass of the oxide and the relative atomic mass of the metal.

Solution

After the reaction between MO and HCl, the resulting solution was neutralised by NaOH (alkaline solution). This suggests that the solution was acidic and hence HCl was in excess.

Number of moles of NaOH in 21.02cm³ of its solution

$$= \frac{21.02}{1000} \times 0.1020 \text{ moles} = 2.144 \times 10^{-3} \text{ moles}$$

NaOH reacts with HCl according to the following equation: $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

From which mole ratio of NaOH to HCl is 1: 1

Thus number of moles of HCl in 25cm³ of its solution was also

$$2.144 \times 10^{-3} \text{ moles} = 2.144 \times 10^{-3} \text{ moles}$$

Then number of moles of HCl in 500cm³ of its solution

$$= \frac{2.144 \times 10^{-3} \times 500}{25} \text{ moles} = 0.04288$$

0.04288 moles is the amount of unreacted HCl in its reaction with MO

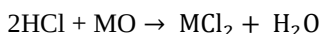
But total number of moles of HCl was $\frac{100}{1000} \times 1 \text{ moles} = 0.1 \text{ moles}$

Thus number of moles of HCl reacted = $(0.1 - 0.04288) \text{ moles} = 0.05712 \text{ mol}$

And therefore, 0.05712 moles of HCl reacted with 1.6g of the oxide.

Whence 1mole of HCl reacted with $\frac{1.6}{0.05712} \text{ g} = 28 \text{ g}$ of the oxide

But HCl reacts with MO according to the following equation:



From which 1mole of HCl reacts with 0.5 mole (28g) of MO

Thus mass of one mole of MO = $2 \times 28 \text{ g} = 56 \text{ g}$

Hence molar mass of MO is 56 g mol^{-1}

And relative atomic mass of M = $(56 - 16) = 40$

Example 7

3.000g of a mixture of sodium carbonate and sodium chloride were made up to 250 cm^3 of aqueous solution. 25 cm^3 of this solution required 21.00 cm^3 of 0.1050M hydrochloric acid (with methyl orange as indicator). Calculate the percentage by mass of sodium chloride in the mixture.

Solution

In the titration, sodium chloride is unchanged, while sodium carbonate reacts according to the following equation: $\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$

Using $n = MV$;

Number of moles of HCl used in the titration = $\frac{21}{1000} \times 0.1050 \text{ moles}$

But mole ratio of HCl to Na_2CO_3 is 2: 1;

It follows that, number of moles of Na_2CO_3 used in the titration

$$= \frac{21 \times 0.1050}{1000 \times 2} \text{ moles} = \text{number of moles of } \text{Na}_2\text{CO}_3 \text{ in } 25 \text{ cm}^3 \text{ its solution}$$

Thus number of moles of Na_2CO_3 in 250 cm^3 of its solution

$$= \frac{21 \times 0.1050 \times 250}{1000 \times 2 \times 25} \text{ moles} = 0.011025 \text{ moles}$$

Using $m = nM_r$;

Mass of Na_2CO_3 in 250 cm^3 of an impure solution = $106 \times 0.011025 \text{ g} = 1.16865 \text{ g}$

But total mass of sodium carbonate and sodium chloride = 3g.

Thus mass of NaCl in the mixture = $(3 - 1.16865) \text{ g} = 1.83135 \text{ g}$

$$\% \text{ NaCl} = \frac{m_{\text{NaCl}}}{m_T} \times 100\% = \frac{1.83135}{3} \times 100\% = 61.045\%.$$

Hence percentage by mass of NaCl in the mixture is 61.045%

Example 8

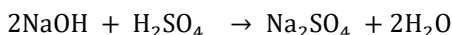
1.34g of a sample of ammonium chloride was boiled with excess of sodium hydroxide solution. The ammonia evolved was absorbed in 50 cm^3 of 0.5M sulphuric acid. The solution was then made up to 250 cm^3 with distilled water and 25 cm^3 of it required 25.1 cm^3 of 0.1M sodium hydroxide for neutralisation. Calculate the percentage of ammonia (as NH_3) in the ammonium chloride.

Solution

Number of moles of NaOH in 25.1cm³ of its solution

$$= \frac{25.1}{1000} \times 0.1 \text{ moles} = 2.51 \times 10^{-3} \text{ moles} \quad (\text{Using } n = MV)$$

NaOH reacts with H₂SO₄ according to the following equation



From which mole ratio of NaOH to H₂SO₄ is 2: 1

Thus number of moles of H₂SO₄ in 25cm³ of its solution

$$= \frac{2.51 \times 10^{-3}}{2} \text{ moles} = 1.255 \times 10^{-3} \text{ moles}$$

Then number of moles of H₂SO₄ in 250cm³ of its solution

$$= \frac{1.255 \times 10^{-3} \times 250}{25} \text{ moles} = 1.255 \times 10^{-2} \text{ moles}$$

These are number of moles of unreacted H₂SO₄ in its reaction with NH₃.

But total number of moles H₂SO₄ before the reaction = $\frac{50}{1000} \times 0.5 \text{ moles} = 0.025 \text{ moles}$

Thus number of moles of H₂SO₄ which reacted in its reaction with NH₃

$$= (0.025 - 1.255 \times 10^{-2}) \text{ moles} = 0.01245 \text{ moles}$$

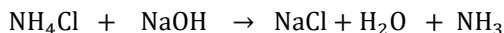
H₂SO₄ reacts with NH₃ according to the following equation:



Where mole ratio of NH₃ to H₂SO₄ is 2: 1;

Thus number of moles of NH₃ was $(2 \times 0.01245) \text{ moles} = 0.0249 \text{ moles}$

The ammonia (NH₃) was produced by the reaction between ammonium chloride (NH₄Cl) and sodium hydroxide according to the following equation:



Using $m = nM_r$;

Mass of NH₃ in 1.34g of NH₄Cl = $0.0249 \times 17 \text{ g} = 0.4233 \text{ g}$

$$\text{Thus } \% \text{ NH}_3 = \frac{0.4233}{1.34} \times 100\% = 31.6\%$$

Hence the percentage of NH₃ in the ammonium chloride is 31.6%

Note: Theoretically the percentage can be simply found by using the fact that; molar mass of NH₄Cl is 53.5gmol⁻¹ out of which 17g is the mass of NH₃. Then using; $\% \text{NH}_3 = \frac{m_{\text{NH}_3}}{M_{\text{NH}_4\text{Cl}}} \times 100\% = \frac{17}{53.5} \times 100\% = 31.8\%$. However, this question requires finding the percentage practically and hence the 'shortcut' is not allowed.

Example 9

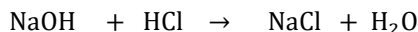
Hydrochloric acid was standardized in the following way: 1.010g of pure calcium carbonate was allowed to react with 50cm³ of the hydrochloric acid. The excess of the acid was neutralised by 24.6cm³ of a sodium hydroxide solution. 25cm³ of this sodium hydroxide solution needed 23.7cm³ of the hydrochloric acid solution for neutralisation. Calculate the molarity of the acid.

Solution

Let molarity of sodium hydroxide be M_b;

Then number of moles of NaOH in 24.6cm^3 of its solution $= \frac{24.6}{1000} M_b = 0.0246M_b$

NaOH reacts with HCl according to the following equation:



From which mole ratio of NaOH to HCl is 1:1;

Thus number of moles of unreacted HCl was also $0.0246M_b$

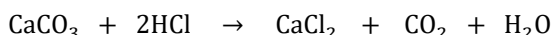
Total number of HCl before its reaction with $\text{CaCO}_3 = \frac{50}{1000} M_a = 0.05M_a$

Where, M_a is the molarity of the hydrochloric acid.

Thus number of moles of HCl reacted with $\text{CaCO}_3 = 0.05M_a - 0.0246M_b$

But number of moles of CaCO_3 reacted with HCl $= \frac{1.010\text{g}}{100\text{gmol}^{-1}} = 0.01010\text{ mol}$

And CaCO_3 reacts with HCl according to the following equation



From which mole ratio of CaCO_3 to HCl is 1:2.

Thus number of moles of HCl reacted $= 2 \times 0.01010\text{mol} = 0.0202\text{ mol}$

And hence $0.05M_a - 0.0246M_b = 0.0202$ (i)

But also, 25cm^3 of NaOH reacts with 23.7cm^3 of HCl:

Number of moles of NaOH $= \frac{25}{1000} M_b = 0.025M_b$

Number of moles of HCl $= \frac{23.7}{1000} M_a = 0.0237M_a$

From the equation of their reaction; mole ratio of NaOH to HCl is 1:1

It follows that, $0.025M_b = 0.0237M_a$

Or $M_b = 0.948M_a$ (ii)

Substituting (ii) to (i) gives $M_a = 0.757M$

Hence molarity of the acid is $0.757M$

Example 10

25cm^3 of solution of sodium hydroxide and potassium hydroxide containing 5g of solid per dm^3 required 24.2cm^3 of $0.1M\text{HCl}$ for neutralisation. Calculate the concentration of each compound in gdm^{-3} of solution.

Solution

Total mass of KOH and NaOH in 1dm^3 (1000cm^3) is 5g

Thus a mass of the mixture in $25\text{cm}^3 = \frac{25}{1000} \times 5\text{g} = 0.125\text{g}$

Let mass of KOH in 25cm^3 be x in grams

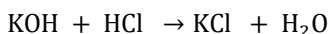
And mass of NaOH in 25cm^3 y in grams

Then $x + y = 0.125$ (i)

Number of moles of KOH in $25\text{cm}^3 = \frac{x}{56}$

Number of moles of NaOH in $25\text{cm}^3 = \frac{y}{40}$

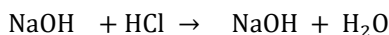
KOH reacts with HCl according to the following equation:



From which mole ratio of KOH to HCl is 1: 1

Thus number of moles of HCl reacted with KOH was $\frac{x}{56}$

NaOH reacts with HCl according to the following equation:



From which mole ratio of NaOH to HCl is 1:1

Thus number of moles of HCl reacted with NaOH was $\frac{y}{40}$

But total volume of 24.2cm^3 of 0.1M HCl was used for neutralisation of the two which give a total number of moles of $\frac{24.2}{1000} \times 0.1\text{mol} = 0.00242\text{ mol}$

Whence $\frac{x}{56} + \frac{y}{40} = 0.00242$ (ii)

Solving (i) and (ii) simultaneously;

$$x = 0.0987 \text{ and } y = 0.0263$$

$$\text{Concentration in gdm}^{-3} = \frac{\text{Mass in g}}{\text{Volume of solution in dm}^3}$$

$$\text{Thus concentration of KOH} = \frac{0.0987 \times 1000}{25} \text{gdm}^{-3} = 3.948 \text{gdm}^{-3}$$

$$\text{And concentration of NaOH} = \frac{0.0263 \times 1000}{25} \text{gdm}^{-3} = 1.052 \text{gdm}^{-3}$$

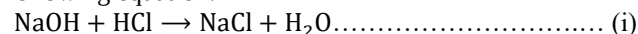
Titration by double indicator

Titration by using two different indicators can be used in:

- Estimation of a mixture of sodium hydroxide and sodium carbonate
- Estimation of a mixture of sodium carbonate and sodium hydrogencarbonate

Estimation of a mixture of sodium hydroxide and sodium carbonate by double indicators

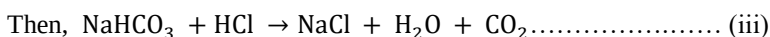
The reaction between sodium hydroxide and hydrochloric acid occurs in a single stage according to the following equation:



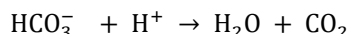
Or ionically $\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$

Where NaOH and HCl being strong base and strong acid respectively, any indicator (**methyl orange** or **phenolphthalein**) can be used to determine the equivalence point of reaction (i).

The reaction between sodium carbonate and hydrochloric acid occurs in two stages, with the hydrogen carbonate ion as intermediate product.



Or ionically, $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$

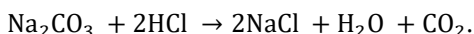


Where:

- Na_2CO_3 and HCl being strong base and strong acid respectively, either methyl orange or phenolphthalein indicator can be used to determine the equivalence point of reaction (ii).
- NaHCO_3 being weak base and HCl being strong acid, only methyl orange indicator is suitable for determination of equivalence point of reaction (iii).
- Since mole ratio of Na_2CO_3 to HCl, NaHCO_3 to HCl as well as Na_2CO_3 to NaHCO_3 is 1:1, the amount (volume) of the acid (HCl) required for reaction (ii) and (iii) is the same.

Conclusion....!

- With **phenolphthalein** as indicator, the end point is registered at the completion of **reaction (i) and (ii)**.
- With **methyl orange** as an indicator, the end point is registered at the completion of **all three reactions**.
- Since the amount of acid required for reaction (ii) and (iii) is the same, and **the amount of acid used in the reaction (iii) is the difference between the titrations with methyl orange and phenolphthalein, it follows that twice this difference is the amount of acid which titrates the whole carbonate, Na₂CO₃**, according to equation,

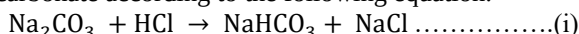


- The rest titrates the sodium hydroxide.

Estimation of a mixture of sodium carbonate and sodium hydrogen carbonate by double indicator

The same concept of the first case can be applied in this case as follows:

With **phenolphthalein as indicator**, the end point is given when all the carbonate is converted to hydrogen carbonate according to the following equation.



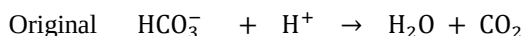
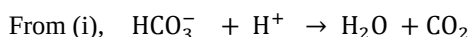
or ionically, $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$

With **methyl orange as indicator**, the end point is given when the original hydrogen carbonate and that produced in (i) as an intermediate product are both converted to CO₂ and H₂O according to the following equation:

Intermediate NaHCO₃ from (i), $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \dots\dots\text{(ii)}$

Original NaHCO₃ in the mixture, $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \dots\dots\text{(iii)}$

Or ionically;



That is the end point with **methyl orange indicator** is obtained after completion of **all three reaction (i), (ii), (iii)** while that of **phenolphthalein indicator** is obtained after reaction (i) only.

Since the amount of acid required for reactions (i) and (ii) is the same, **twice the phenolphthalein titration is the amount of which titrates the carbonate, Na₂CO₃**, according to equation: $\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$

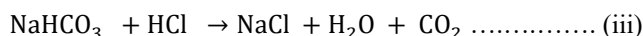
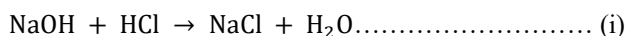
The rest titrates the original hydrogencarbonate (NaHCO₃) which was originally present in the mixture with Na₂CO₃.

Worked examples on the titration by double indicators**Example 11**

25cm³ of a solution containing sodium hydroxide and sodium carbonate required 21.5cm³ of 1M HCl with phenolphthalein as indicator and 27.85cm³ of the same with methyl orange as indicator. Calculate the concentration of each compound in gdm⁻³ of the solution.

Solution

Equations for reactions;



Titre volume used in reaction (iii) = $(27.85 - 21.5)\text{cm}^3 = 6.35\text{cm}^3$

Thus the volume of acid required to titrate $\text{Na}_2\text{CO}_3 = 2 \times 6.35\text{cm}^3 = 12.7\text{cm}^3$

Whence, the acid required to titrate the sodium hydroxide in the same volume of solution = $(27.85 - 12.7)\text{cm}^3 = 15.15\text{cm}^3$

Number of moles of HCl reacted in (i) = $\frac{15.15}{1000} \times 1\text{mol} = 0.01515\text{mol}$

But from (i), mole ratio of NaOH to HCl is 1:1

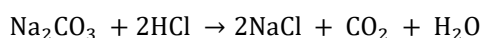
Then number of moles of NaOH reacted was also 0.01515 mol

Using; mass concentration in $\text{gdm}^{-3} = [\]M_r$

Then mass concentration of NaOH = $\frac{0.01515 \times 1000 \times 40}{25} \text{gdm}^{-3} = 24.24\text{gdm}^{-3}$

Hence the concentration of sodium hydroxide solution was 24.24gdm^{-3}

The overall reaction equation between Na_2CO_3 and HCl is;



From which mole ratio of Na_2CO_3 to HCl is 1:2

But number of moles of HCl reacted with $\text{Na}_2\text{CO}_3 = \frac{12.7}{1000} \times 1\text{mol} = 0.0127\text{mol}$

Thus number of moles of Na_2CO_3 reacted = $\frac{0.0127}{2} \text{mol} = 0.00635\text{mol}$

Then, $[\text{Na}_2\text{CO}_3] = \frac{0.00635 \times 1000}{25} \text{M} = 0.254\text{M}$

Using; mass concentration in $\text{gdm}^{-3} = [\]M_r = 0.254 \times 106\text{gdm}^{-3} = 26.924\text{gdm}^{-3}$

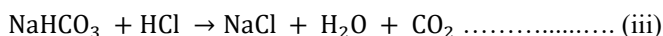
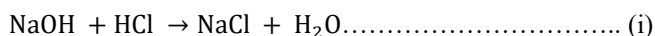
Hence the mass concentration of solution of sodium carbonate was 26.924gdm^{-3}

Example 12

20cm^3 of a solution containing sodium hydroxide and sodium carbonate required 19.2cm^3 of 0.5MHCl with phenolphthalein as indicator. With methyl orange, a further 5.1cm^3 of the acid were needed. What is the concentration of each compound in the original solution, in grams of anhydrous solid per dm^3 ?

Solution

Equations for reactions:



From above equations:

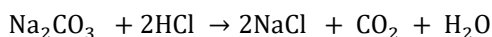
The volume of acid required to titrate $\text{Na}_2\text{CO}_3 = 2 \times 5.1\text{cm}^3 = 10.2\text{cm}^3$

And the volume of acid required to titrate NaOH

= $(19.2 - 5.1)\text{cm}^3$ or $(19.2 + 5.1 - 10.2)\text{cm}^3 = 14.1\text{cm}^3$

Number of moles of HCl reacted with $\text{Na}_2\text{CO}_3 = \frac{10.2}{1000} \times 0.5\text{mol} = 0.0051\text{mol}$

The overall reaction equation between Na_2CO_3 and HCl is



From which mole ratio of Na_2CO_3 to HCl is 1:2

Thus number of moles of Na_2CO_3 reacted = $\frac{0.0051\text{mol}}{2} = 0.00255\text{mol}$

And mass concentration of $\text{Na}_2\text{CO}_3 = \frac{0.00255 \times 106 \times 1000}{20} \text{gdm}^{-3} = 13.515\text{gdm}^{-3}$

Hence the concentration of anhydrous sodium carbonate was 13.515gdm^{-3}

Number of moles of HCl reacted with $\text{NaOH} = \frac{14.1}{1000} \times 0.5\text{mol} = 0.00705\text{mol}$

From (i), mole ratio of NaOH to HCl is 1:1

Thus number of moles of NaOH reacted was also 0.00705mol

And mass concentration of $\text{NaOH} = \frac{0.00705 \times 40 \times 1000}{20} \text{gdm}^{-3} = 14.1\text{gdm}^{-3}$

Hence mass concentration of NaOH was 14.1gdm^{-3}

Example 13

Anhydrous sodium carbonate contaminated with sodium hydrogencarbonate was made up to 250cm^3 of solution. 25cm^3 of this solution required 11.2cm^3 of $1\text{M}\text{HCl}$ with phenolphthalein as indicator and 24.5cm^3 of the same acid with methyl orange as indicator. Calculate the percentage by mass of sodium hydrogen carbonate in the mixture.

Solution

Equations for reactions: $\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaHCO}_3 + \text{HCl} \dots\dots\dots$ (i)

From (i) $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{CO}_2 + \text{H}_2\text{O} \dots\dots\dots$ (ii)

Original $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{CO}_2 + \text{H}_2\text{O} \dots\dots\dots$ (iii)

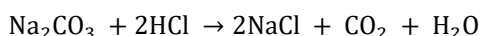
From above equation:

Volume of HCl required to titrate $\text{Na}_2\text{CO}_3 = 2 \times 11.2\text{cm}^3 = 22.4\text{cm}^3$

Thus volume of HCl used to titrate original NaHCO_3 which was present in the mixture as impurity = $(24.5 - 22.4)\text{cm}^3 = 2.1\text{cm}^3$

Number of moles of HCl reacted with $\text{Na}_2\text{CO}_3 = \frac{22.4}{1000} \times 1\text{mol} = 0.0224\text{mol}$

The overall reaction equation between Na_2CO_3 and HCl is



From which mole ratio of Na_2CO_3 to HCl is 1: 2

It follows that:

Number of moles of Na_2CO_3 in 25cm^3 reacted with $\text{HCl} = \frac{0.0224}{2} \times 0.0112\text{mol}$

And mass of Na_2CO_3 in $25\text{cm}^3 = 0.0112\text{mol} \times 106\text{gmol}^{-1} = 1.1872\text{g}$

Number of moles of HCl reacted with the original $\text{NaHCO}_3 = \frac{2.1}{1000} \times 1\text{mol} = 0.0021\text{mol}$

From equation (iii), mole ratio of NaHCO_3 to HCl is 1: 1

Thus number of moles of the NaHCO_3 in 25cm^3 was also 0.0021mol

And mass of the original $\text{NaHCO}_3 = 0.0021 \times 84\text{g} = 0.1764\text{g}$

Total mass of Na_2CO_3 and its impurity (NaHCO_3) in 25cm^3

$$= (1.1872 + 0.1764)\text{g} = 1.3636$$

Then $\% \text{NaHCO}_3 = \frac{0.1764}{1.3636} \times 100\% = 12.9\%$

Hence the percentage by mass of NaHCO_3 in the mixture was 12.9%.

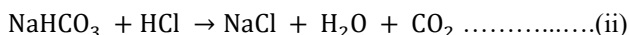
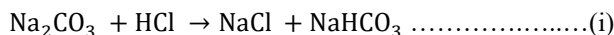
(In the above problem there is no necessity of using the 250cm^3 ; the important thing is to have mass of each component of mixture in any equal volume of solution)

Example 14

8.58g of impure sodium carbonate were made up to 250cm^3 of aqueous solution. 25cm^3 of this solution required 15cm^3 of 0.2M HCl for neutralisation with phenolphthalein (**POP**) as an indicator. Calculate percentage purity of the carbonate.

Solution

The reaction between sodium carbonate takes place in two stages as per equations:

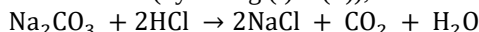


With POP indicator, the end point is registered after completion of reaction (i) only. Thus 15cm^3 is the volume of HCl used in reaction (i) only.

Since mole ratio of Na_2CO_3 to HCl, NaHCO_3 to HCl as well as Na_2CO_3 to NaHCO_3 is 1:1, the (volume) of the acid (HCl) required for reaction (i) and (ii) is the same.

Thus volume of HCl required to react with the whole carbonate (the volume at the end point if MO would be used) = $2 \times 15\text{cm}^3 = 30\text{cm}^3$

And the overall reaction equation become (by taking (i) + (ii));



From which mole ratio of Na_2CO_3 to HCl is 1:2

Number of moles of HCl required to react completely with the carbonate

$$= \frac{30}{1000} \times 0.2 \text{ moles} = 6 \times 10^{-3} \text{ moles}$$

$$\text{And from the mole ratio number of moles (in } 25\text{cm}^3) \text{ of the carbonate} = \frac{6 \times 10^{-3}}{2} = 0.003\text{mol}$$

$$\text{So number of moles of the } \text{Na}_2\text{CO}_3 \text{ in } 250\text{cm}^3 = \frac{0.003 \times 250}{25} \text{ mol} = 0.03\text{mol}$$

Using $m = nM_r$;

$$\text{Mass of } \text{Na}_2\text{CO}_3 \text{ in } 250\text{cm}^3 = 0.03\text{mol} \times 106\text{gmol}^{-1} = 3.18\text{g}$$

But total mass of the impure sodium carbonate in 250cm^3 is 8.58g

$$\text{Hence the percentage purity} = \frac{3.18}{8.58} \times 100\% = 37.06\%$$

Alternative solution (By using equation (i) only)

Number of moles of HCl reacted at the end point with POP indicator

$$= \frac{15}{1000} \times 0.2 \text{ moles} = 3 \times 10^{-3} \text{ moles}$$

But from (i); mole ratio of Na_2CO_3 to HCl is 1:1;

Therefore, number of moles of in 25cm^3 of Na_2CO_3 was also 3×10^{-3}

(On your own you may continue as in the first solution to get the same answer)

DIGGING DEEPER EXERCISE 15

EXERCISE 15A: BINDER QUESTIONS

Question 1

Classify each reactant as either a Bronsted-Lowry acid or base for the following reactions:

- (a) $\text{HCN} + \text{H}_2\text{O} \rightarrow \text{CN}^- + \text{H}_3\text{O}^+$
(b) $\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{NH}_3^+ + \text{OH}^-$

Question 2

Write the formula for the following:

- (a) Conjugate base of H_2SO_3 b) conjugate acid of CN^- c) conjugate acid of S^{2-} d) Conjugate base of HClO
(e) Conjugate acid of HCO_3^- f) conjugate base of NH_3 g) conjugate acid of H_2PO_4^- h) conjugate base of H_3O^+

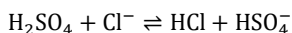
Question 3

Write conjugate acid and conjugate base of each of the following:

- (i) OH^-
(ii) H_2O
(iii) NH_3
(iv) HCO_3^-

Question 4

Concentrated sulphuric acid reacts with sodium chloride as follows:



- (a) Identify the conjugate acid/base pairs in this reaction.
(b) What would be the observable result of this reaction?
(c) Explain why this reaction goes almost completely to the right despite the hydrochloric and sulphuric acids are strong acids.

Question 5

- (a) What indicator should be used in titration of hydrochloric acid with ammonia solution?
(b) There is no suitable indicator for the titration of ethanoic acid with ammonia. Why this?

Question 6

Why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

EXERCISE 15B: REAL QUESTIONS

Question 7

If someone in your family is suffering from a problem of acidity after overeating, which of the following substances would you suggest as a remedy? Lemon juice, vinegar or baking soda solution. Mention the property on the basis of which you will choose the remedy.

Question 8

Your friend, **Kipute** tested water from a pond and told you these results. When tested with phenolphthalein, it stays clear. When litmus paper is dipped in the pond water, the paper turns blue. What can you conclude from **Kipute's** result about pH of the pond water?

Question 9

You are given with two unknown solutions labelled 'A' and 'B'. Then you tested the two solutions and found that an aqueous solution 'A' turns phenolphthalein solution pink. On addition of an aqueous solution 'B' to 'A' the pink colour disappears. What can you conclude about the nature of solution 'A' and 'B'?

Question 10

Mr. Akilikubwa added two drops of phenolphthalein to a solution of sodium hydroxide in a test tube.

- (i) State the colour change he observed.
- (ii) If he then added dilute HCl dropwise to the solution, what will be the colour change?
- (iii) On adding few drops of NaOH solution to the above mixture, he found that the colour of the solution reappears. Why?

Question 11

Curry powder and tumeric are spices that contain a bright yellow pigment called curcumin and therefore they can be used natural acid-base indicators. The curcumin turns from yellow at pH 7.4 to red at pH 8.6.

- (i) Can curry powder and tumeric be used in acid-base titrations? Give a reason to support your answer.
- (ii) Can the spices be used to detect the equivalence point of the reaction between acetic acid solution and caustic soda solution? Explain.
- (iii) *Natural indicators like curry powder and tumeric are less common in use in scientific settings such as laboratories than synthetic indicators like methyl orange and phenolphthalein.* Outline at least three reasons to justify this statement.

Question 12

Blueberry is the natural acid-base indicator whose colour change from blue (around pH 2.8 – 3.2) to red in a strongly acidic solution. Based on this information alone answer the following questions:

- (i) Can blueberries be used to detect acid and base? Rationalise your answer.
- (ii) Can blueberries be used as an indicator in methanoic acid–potassium hydroxide titration? Explain.
- (iii) Nowadays more research on the natural indicators are done so that uses of synthetic indicators can be reduced. Suggest any two possible reasons for this.

EXERCISE 15C: HOT QUESTIONS**Question 13**

A solution of sodium hydroxide contained 0.25 mol dm^{-3} . Using phenolphthalein indicator, titration of 25 cm^3 of this solution required 22.5 cm^3 of a hydrochloric acid solution for complete neutralisation.

- (a) Write the equation for the titration reaction.
- (b) What apparatus would you use to measure out (i) the sodium hydroxide solution? (ii) the hydrochloric acid solution?
- (c) What would you rinse your apparatus out with before doing the titration?
- (d) What is the indicator colour change at the end-point?
- (e) Calculate the moles of sodium hydroxide neutralised.
- (f) Calculate the moles of hydrochloric acid neutralised.
- (g) Calculate the concentration of the hydrochloric acid in mol/dm^3 .

Question 14

A bulk solution of hydrochloric acid was standardized using pure anhydrous sodium carbonate (Na_2CO_3 , a primary standard). 13.25 g of sodium carbonate was dissolved in about 150.0 cm^3 of deionised water in a beaker. The solution was then transferred, with appropriate washings, into a graduated flask, and the volume of water made up to 250 cm^3 , and thoroughly shaken (with stopper on!) to ensure complete mixing. 25.0 cm^3 of the sodium carbonate solution was pipetted into a conical flask and screened methyl orange indicator added. The aliquot required 24.65 cm^3 of a hydrochloric acid solution, of unknown molarity, to completely neutralise it.

- (a) Calculate the molarity of the prepared sodium carbonate solution.
- (b) How many moles of sodium carbonate were titrated?
- (c) How many moles of hydrochloric acid were used in the titration?
- (d) What is the molarity of the hydrochloric acid?

Question 15

50.0 cm^3 sample of sulphuric acid was diluted to 1.00 dm^3 . A sample of the diluted sulphuric acid was analysed by titrating with aqueous sodium hydroxide. In the titration, 25.0 cm^3 of 1.00 M aqueous sodium hydroxide required 20.0 cm^3 of the diluted sulphuric acid for neutralisation.

- (a) Calculate how many moles of sodium hydroxide were used in the titration?
- (b) Calculate the concentration of the diluted acid.
- (c) Calculate the concentration of the original concentrated sulphuric acid solution.

Question 16

Magnesium oxide is not very soluble in water, and is difficult to titrate directly. Its purity can be determined by use of a '**back titration**' method. 4.06 g of impure magnesium oxide was completely dissolved in 100 cm³ of hydrochloric acid, of concentration 2.00M (in excess).

The excess acid required 19.7 cm³ of sodium hydroxide (0.200M) for neutralisation.

This second titration is called a '**back-titration**', and is used to determine the unreacted acid.

- (a) Calculate the moles of hydrochloric acid added to the magnesium oxide.
- (b) Calculate the moles of excess hydrochloric acid titrated.
- (c) Calculate the moles of hydrochloric acid reacting with the magnesium oxide.
- (d) Calculate the moles and mass of magnesium oxide that reacted with the initial hydrochloric acid.
- (e) Hence the % purity of the magnesium oxide.
- (f) What compounds could be present in the magnesium oxide that could lead to a false value of its purity? Explain.

Question 17

0.279g of an organic monobasic aromatic carboxylic acid, containing only the elements C, H and O, was dissolved in aqueous ethanol. A few drops of phenolphthalein indicator were added and the mixture titrated with 0.100M sodium hydroxide solution. It took 20.5 cm³ of the alkali to obtain the first permanent pink.

- (a) How many moles of sodium hydroxide were used in the titration?
- (b) How many moles of the organic acid were titrated?
- (c) Calculate the molecular mass of the acid.
- (d) Suggest possible structures of the acid with your reasoning.

Question 18

A sample of sodium hydrogencarbonate was tested for purity using the following method. 0.400g of the solid was dissolved in 100.0 cm³ of water and titrated with 0.20M hydrochloric acid using methyl orange indicator. 23.75cm³ of acid was required for complete neutralisation.

- (a) Calculate the moles of acid used in the titration and the moles of sodium hydrogencarbonate titrated.
- (b) Calculate the mass of sodium hydrogen carbonate titrated and hence the purity of the sample.

Question 19

A 5.00g sample of dry mixture of potassium hydroxide, potassium carbonate, and potassium chloride is reacted with 0.100L of 2.0MHCl solution.

- (a) A 249mL sample of dry CO₂ gas, measured at 22°C and 740mmHg, is obtained from the reaction. What is the percentage of potassium carbonate in the mixture?
- (b) The excess HCL is found by titration to be chemically equivalent to 86.6mL of 1.5 MNaOH.calculate the percentages of:
 - (i) Potassium hydroxide and
 - (ii) Potassium chloride in the original mixture.

Question 20

A solution contains Na₂CO₃ and NaHCO₃. 10mL of this solution required 2mL of 0.1MH₂SO₄ for neutralisation using phenolphthalein as indicator. Methyl orange is then added when a further 2.5mL of 0.2MH₂SO₄ was required. Calculate the mass concentration of Na₂CO₃ and NaHCO₃ in solution.

Chapter 16

WEAK ELECTROLYTES

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called **electrolytes**. Electrolytes can be acids, bases or salts as they all give ions when dissolved in water. These substances conduct electricity due to mobility of ions (cations and anions) they possess. In some cases, they conduct electricity even in their molten state too. Substances that do not yield ions when dissolved are called **non-electrolytes**. If the physical or chemical process that generates the ions is almost hundred percent efficient (all of the dissolved compound yields ions), then the substance is known as a **strong electrolyte**. If only a relatively small fraction of the dissolved substance ionises, it is called a **weak electrolyte**. Behaviour of weak electrolyte is well explained by Arrhenius theory of weak electrolyte.

ASSUMPTIONS OF ARRHENIUS THEORY

Assumption 1: A weak electrolyte is electrically neutral.

Assumptions 2: When dissolved in solution, the electrolyte tends to ionise yielding cations and anions.

Assumptions 3: The process of ionisation of the weak electrolyte in the solution is reversible. That is the ions formed after ionisation tends to recombine giving unionised molecule again.

e.g. (i) $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+$

Or may be written as; $\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$

(The reader should note that: in aqueous solution, the hydrogen proton, H^+ is always hydrated to give hydronium ions, H_3O^+ , according to the equation, $\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+$, thus $\text{H}^+(\text{aq})$ is equivalent to H_3O^+)

(ii) $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

(iii) $\text{AgCl}(\text{s}) + \text{H}_2\text{O} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

Assumption 4: After ionisation, cations are attracted towards negative electrode while anions are attracted towards positive electrode.

Assumption 5: At any time of the ionisation process, there is a ratio of concentration of molecules ionised (dissociated) to form free ions to that of unionised (undissociated) molecule which is known as a degree of ionisation (dissociation).

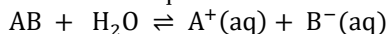
That is: Degree of dissociation, $\alpha = \frac{\text{concentration of free ions}}{\text{Original concentration of molecules before dissociation, } C}$

Thus concentration of free ions = αC

Application of Arrhenius theory in derivation of Ostwald's dilution law

Arrhenius theory can be applied in deriving Ostwald's dilution law as follows:

Consider a binary weak electrolyte, A^+B^- which ionises in aqueous solution according to the following equation:



Initial number of moles before dissociation	1	0	0
At equilibrium (After dissociation)	$1 - \alpha$	α	α
[] of each at the equilibrium	$(1 - \alpha)C$	αC	αC

(The reader should recognise that: if the initial amount is 1mole then numerical value of number of moles dissociated must be equal to the degree of dissociation, α).

From the above equilibrium: $K_c = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}][\text{H}_2\text{O}]}$

The equilibrium constant expression can be rearranged as follows: $K_c[H_2O] = \frac{[A^+][B^-]}{[AB]}$

But for every dilute solution, $[H_2O] = \text{constant}$.

Thus $K_c[H_2O]$ give another constant, K and the constant is known as **dissociation (or ionisation) constant**. So $K = \frac{[A^+][B^-]}{[AB]}$

From which $K = \frac{\alpha C \times \alpha C}{(1-\alpha)C} = \frac{\alpha^2 C}{1-\alpha}$ (by substituting values of $[A^+]$, $[B^-]$ and $[AB]$ to the above equation of the equilibrium constant expression)

But weak electrolytes ionise only partially and most part of the molecules remain undissociated (unionised) thus α becomes too small and hence $1 - \alpha \approx 1$ (**The assumption is true if and only if $\alpha \leq 0.1$; otherwise Ostwald's dilution law does not hold because when $\alpha > 0.1$, the value of α cannot be neglected compared to 1**).

It follows that: $K = \alpha^2 C$

And hence $\alpha = \sqrt{\frac{K}{C}}$

The result is known as **Ostwald dilution law** and the law states that: *The degree of dissociation of weak electrolyte varies inversely proportional to square root of its concentration.*

Also it should be remembered that, the reciprocal of concentration is known as **dilution**.

That is $\frac{1}{C} = V$ (**Dilution**) = Volume of solution in dm^3 (or L) which contains one mole of the solute

Whence Ostwald dilution law can be rewritten as; $\alpha = \sqrt{KV}$ where V is the dilution of the electrolyte

Thus according to Ostwald dilution law; **the degree of dissociation of a weak electrolyte increases with an increase of dilution of the electrolyte.**

Definition of dissociation constant

Quantitatively, **dissociation constant** may be defined as *an equilibrium constant which is given as a ratio of product of concentration of free ions to that of unionised molecules in a solution of weak electrolyte.*

Or qualitatively, the constant may be defined as *a factor (constant) which expresses the extent of ionisation of a weak electrolyte to give free ions when dissolved in aqueous solution.*

That is if the dissociation constant is large, it implies that there is more ionisation and if the constant is small, there is less ionisation.

So the significance of dissociation constant is to give the extent of ionisation of weak electrolyte yielding free ions which take part in the chemical reaction.

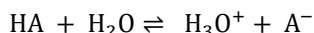
Don't forget this fact!

Ostwald's dilution law and hence the equation; $\alpha = \sqrt{\frac{K}{C}}$ is applicable if and only if the value of degree of dissociation, α is less than 0.1, i.e. It is negligible compared to 1 such that $1 - \alpha \approx 1$; otherwise the relationship: $K = \frac{\alpha^2 C}{1-\alpha}$, must be used as such.

DISSOCIATION CONSTANT FOR ACID AND BASE

Dissociation constant for acid, K_a

Consider a weak acid, HA which ionises partially in aqueous solution as follows;



Initial number of moles before ionisation	1	0	0
At equilibrium (After ionisation)	$1 - \alpha$	α	α
[] of each at equilibrium	$(1 - \alpha)C$	αC	αC

Where C is the concentration of the acid before ionisation (dissociation)

$$\text{From the above equilibrium: } K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \text{ Or } K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

But for very dilute solution, $[H_2O]$ is constant,

Thus $K_c[H_2O]$ gives another constant and the constant is known as **dissociation (or ionisation) constant for the acid, K_a**

$$\text{Whence } K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Substituting values of $[HA]$, $[A^-]$ and $[H_3O^+]$ to the above dissociation constant expression gives:

$$K_a = \frac{\alpha C \times \alpha C}{(1 - \alpha)C} = \frac{\alpha^2 C}{1 - \alpha}$$

But for weak electrolyte, α is too small;

Thus $1 - \alpha \approx 1$ and therefore $K_a = \alpha^2 C$

$$\text{And hence } \alpha = \sqrt{\frac{K_a}{C}}$$

The final result is equivalent to **Ostwald's dilution law**

Definition of dissociation constant for acid, K_a

Quantitatively the constant may be defined as *the ratio of product of concentration of free ions to that of undissociated weak acid in aqueous solution*

Or qualitatively the constant may be defined as *the factor which expresses the extent to which the weak acid ionises to give hydrogen ions (H^+) in aqueous solution.*

Significance of dissociation constant for acid, K_a

Dissociation constant for acid, K_a , is important in determining the extent to which the acid tends to ionise in aqueous solution to give hydrogen ions (H^+) thus knowing acidic strength of the acid.

- If K_a of the one acid is large than that of another acid, then the acid become stronger acid.
- Generally if $K_a > 10^{-7}$ (At 25°C), the dilute solution is then acidic
- If K_a of one acid is smaller than that of another acid, the acid is then become weaker acid.
- Generally if $K_a < 10^{-7}$ (At 25°C), the dilute solution is then basic (not acidic).
- K_a values for strong acids like HNO_3 , H_2SO_4 , HI and HCl are very large (Generally the acid is said to be strong if its $K_a > 10$).
- K_a values for weak acids like CH_3COOH and $\text{CH}_3\text{CH}_2\text{COOH}$ are very small.
- Since K_a value for weak acid are very small, to avoid confusion which may arise in dealing with very small value; the values are always given as $\text{p}K_a$ which is obtained by taking negative of common logarithm of K_a value

That is $\text{p}K_a = -\log K_a$

Hence:

For strong acid; K_a is large and pK_a is small

For weak acid; K_a is small and pK_a is large

Generally:

For acidic dilute solution; $K_a > 10^{-7}$ and $pK_a < 7$ (At 25°C)

For basic dilute solution; $K_a < 10^{-7}$ and $pK_a > 7$ (At 25°C)

The reader should note that:

Dissociation constant (whether for acid or base) is equilibrium constant so it is temperature dependent like any other equilibrium constants.

Dissociation constant for base, K_b

Consider a weak base, B^-

	$B^- + H_2O$	$\rightleftharpoons$	$HB + OH^-$
Initially	1		0
At equilibrium	$1 - \alpha$		α
[] of each at equilibrium	$(1 - \alpha)C$		αC

Where C is the initial concentration of the base

From the above equilibrium: $K_c = \frac{[HB][OH^-]}{[B^-][H_2O]}$

From which: $K_c [H_2O] = \frac{[HB][OH^-]}{[B^-]}$;

But for very dilute solution, $[H_2O] = \text{constant}$.

Thus $K_c[H_2O]$ gives another constant which is known as **dissociation constant for the base K_b**

Whence $K_b = \frac{[HB][OH^-]}{[B^-]}$

Substituting values for $[HB]$, $[OH^-]$ and $[B^-]$ gives: $K_b = \frac{\alpha C \times \alpha C}{(1 - \alpha)C} = \frac{\alpha^2 C}{1 - \alpha}$

But for very weak base, α is too small

Then $1 - \alpha \approx 1$

It follows that, $K_b = \alpha^2 C$

And hence $\alpha = \sqrt{\frac{K_b}{C}}$

The final result is equivalent to Ostwald's dilute law

Definition of dissociation constant for base, K_b

Quantitatively, the constant may be defined as *the equilibrium constant which is given as a ratio of the product of the concentration of free ions to that of undissociated weak base in aqueous solution.*

Or qualitatively, the constant may be defined as *the factor which expresses the extent to which a weak base tends to ionise in aqueous solution to give hydroxyl ions (OH^-).*

Significance of dissociation constant for base, K_b

Dissociation constant for base is important in determining the extent to which the base tends to ionise in aqueous solution to give hydroxyl ions (OH^-) thus knowing the basic strength of the base.

- If K_b of the base is large, then the base become strong and vice – versa.
- K_b values of strong bases like NaOH and KOH are very large.
- Generally if $K_b > 10^{-7}$, the dilute solution is then basic and if $K_b < 10^{-7}$, the dilute solution is then acidic for measurement taken at 25°C .

To avoid confusion of dealing with small values of K_b for very weak bases like ammonia solution, the values are always given as $\text{p}K_b$ which are obtained by taking negative of common logarithm of K_b value.

That is $\text{p}K_b = -\log K_b$

Hence:

For strong base; K_b is large and $\text{p}K_b$ is small

For acidic base; K_b is small and $\text{p}K_b$ is large

Generally:

For basic dilute solution: $K_b > 10^{-7}$ and $\text{p}K_b < 7$ (At 25°C)

For acidic dilute solution; $K_b < 10^{-7}$ and $\text{p}K_b > 7$ (At 25°C)

pH AND pOH FOR ACIDS AND BASES

pH (**p** stands for ‘potential’ and **H** stands for ‘hydrogen’) is *negative of common logarithm of hydronium ions (H_3O^+) concentration in very dilute solution.*

That is $\text{pH} = -\log[\text{H}_3\text{O}^+]$

Since H_3O^+ (hydronium ion) is formed when hydrogen proton is formed in water, i.e is the same as $\text{H}^+(\text{aq})$;

Whence the above equation can be rewritten as follows: $\text{pH} = -\log[\text{H}^+]$

pH is also termed as the **hydrogen ion index**

pOH is *negative logarithm of hydroxyl ions (OH^-) concentration in very dilute solution*

That is $\text{pOH} = \log[\text{OH}^-]$

For Acids:

- If $[\text{H}^+]$ is large then the acid is strong acid and hence pH which is $-\log[\text{H}^+]$ become small for strong acid and vice – versa.
- Generally if $[\text{H}^+] > 10^{-7} \text{ moldm}^{-3}$ then the dilute solution becomes acidic.

So $-\log[\text{H}^+] < -\log 10^{-7}$ and hence **pH < 7 for acidic solution**

- If $[\text{OH}^-]$ is small then the solution is more acidic (less basic) and its **pOH** is large.
- Generally if $[\text{OH}^-] < 10^{-7} \text{ moldm}^{-3}$, then the dilute solution become acidic.

$-\log[\text{OH}^-] > -\log 10^{-7}$ and hence **pOH > 7 for acidic solution**

For bases:

- If $[\text{OH}^-]$ is large, then the base become strong and its pOH which is $-\log[\text{OH}^-]$ become small and vice – versa.
- Generally if $[\text{OH}^-] > 10^{-7} \text{ moldm}^{-3}$, the dilute solution is basic

Then $-\log[\text{OH}^-] < -\log 10^{-7}$ and hence **pOH < 7 for basic solution**

- If $[H^+]$ is very small, then the solution is more basic (less acidic) and its pH is large.
- Generally if $[H^+] < 10^{-7} \text{ mol dm}^{-3}$, then the dilute solution become basic

So $-\log [H^+] > -\log 10^{-7}$ and hence **pH > 7 for basic solution**

IONIC PRODUCT OF WATER

Water is very weak electrolyte and it is amphoteric. It undergoes **self-ionisation** partially yielding equal concentration of H_3O^+ and OH^- (The reaction is also known as **auto-ionisation of water**).

That is: $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ (or $2H_2O \rightleftharpoons H_3O^+ + OH^-$)

From which it is clearly understood that:

$[H_3O^+] = [OH^-]$ and the equality explains neutral character of water.

An introduction of an acid which ionises to give H^+ which combine with H_2O (In left hand side of the above equilibrium) to give H_3O^+ (which appears in right hand side of the above equilibrium) is equivalent to lowering the concentration of H_2O while concentration of H_3O^+ is increased. To restore the equilibrium more OH^- needs to combine with added H_3O^+ so to form water thus shifting the position of chemical equilibrium to the left making $[H_3O^+] > [OH^-]$.

Hence $[H_3O^+] > [OH^-]$ **for acidic solution**

By similar explanation, the addition of base in water makes $[H_3O^+] < [OH^-]$ when the new equilibrium is re-established and hence $[H_3O^+] < [OH^-]$ for basic solution.

It should be noted that: At standard conditions (25°C and 1atm),

$[OH^-] = [H_3O^+] = 10^{-7} \text{ mol dm}^{-3}$. This derives the following facts:

- $pH = pOH = -\log 10^{-7} = 7$ for pure water (neutral solution) at 25°C.
- For acidic solution, $[H_3O^+] > 10^{-7} \text{ mol dm}^{-3}$ and hence its $pH < 7$ as mentioned earlier.
- For basic solution, $[H_3O^+] < 10^{-7} \text{ mol dm}^{-3}$ and hence its $pH > 7$

Derivation of ionic product of water

From the equation of self ionisation of water: $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Rearranging the above equilibrium constant expression gives: $K_c [H_2O]^2 = [H_3O^+][OH^-]$

Since at given temperature, density of water is constant

So the concentration of pure water, $[H_2O]$, must be constant too.

Whence $K_c [H_2O]^2$ gives another constant which is known as the ionic product of water, K_w .

Hence **$K_w = [H_3O^+][OH^-]$**

But at 25°C, $[H_3O^+] = [OH^-] = 10^{-7} \text{ mol dm}^{-3}$.

It follows that;

$K_w = 10^{-7} \text{ mol dm}^{-3} \times 10^{-7} \text{ mol dm}^{-3} = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 25°C and **the product is always true even for non-neutral (acidic or basic solution) because like any other equilibrium constant, K_w is only temperature dependent and its value does not depend on the initial concentration of H_3O^+ or OH^- .** According to the equilibrium law, the equilibrium constant does not depend on the initial concentration of reagents present in the system, it is only temperature dependent.

Definition of ionic product of water, K_w

Quantitatively, *it is the equilibrium constant which is given as the product of concentration hydronium ions (H_3O^+) and hydroxyl ions (OH^-) in self-ionisation of water at given temperature.*

That is; $K_w = [H_3O^+][OH^-]$

Qualitatively, is the factor which expresses the ability of water to undergo self-ionisation yielding hydronium ions $[H_3O^+]$ and hydroxyl ions $[OH^-]$ at given temperature.

Relationship between pH and pOH

From the ionic product of water: $K_w = [H_3O^+][OH^-]$

Taking – log both sides of the above K_w expression:

$$-\log K_w = -\log[H_3O^+][OH^-]$$

$$-\log K_w = -\log[H_3O^+] + -\log[OH^-]$$

But; $-\log K_w = pK_w$, $-\log[H_3O^+] = pH$ and $-\log[OH^-] = pOH$

Hence **$pK_w = pH + pOH$**

But at 25°C, $K_w = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

It follows that $pK_w = -\log 10^{-14} \text{ mol}^2 \text{ dm}^{-6} = 14$

Hence at 25°C; **$pH + pOH = 14$**

RELATIONSHIP BETWEEN K_a and K_b FOR CONJUGATE PAIRS

Consider two dilute solutions; one with HA and another with A^- which are conjugate pairs;

For HA: $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

From which: $K_a = \frac{[H_3O^+][A^-]}{[HA]}$ (i)

For A^- : $A^- + H_2O \rightleftharpoons HA + OH^-$

From which; $K_b = \frac{[HA][OH^-]}{[A^-]}$ (ii)

But from (ii); $[HA] = \frac{[A^-]K_b}{[OH^-]}$ (iii)

Then substituting (iii) into (i): $K_a = \frac{[H_3O^+][A^-][OH^-]}{[A^-]K_b}$ or $K_a K_b = [H_3O^+][OH^-]$

But $[H_3O^+][OH^-] = K_w$

Hence **$K_a K_b = K_w$ for conjugate pairs**

Introducing –log both sides in above equation:

$$-\log K_a K_b = -\log K_w \text{ or } -\log K_a + -\log K_b = -\log K_w$$

But $-\log K_a = pK_a$, $-\log K_b = pK_b$ and $-\log K_w = pK_w$

Hence **$pK_a + pK_b = pK_w$ for conjugate pairs**

At 25°C, $K_w = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ and $pK_w = 14$

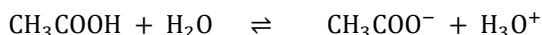
Thus **$K_a K_b = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ and $pK_a + pK_b = 14$**

WORKED EXAMPLES**Example 1**

Using ethanoic acid as the weak electrolyte, derive Ostwald's dilution law.

Solution

Ethanoic acid being weak electrolyte, (weak acid) ionises in aqueous solution according to the following equation:



Number of moles before dissociation 1 0 0

Number of moles at equilibrium $1 - \alpha$ α α

(After dissociation)

[] of each at equilibrium $(1 - \alpha)C$ αC αC

Where C is the concentration of ethanoic acid before dissociation and α is numerically equal to the degree of dissociation of the acid.

Then from the above equilibrium: $K_c = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]}$ or $K_c [\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$

But for every dilute solution, $[\text{H}_2\text{O}]$ is constant.

So $K_c [\text{H}_2\text{O}]$ gives another constant which is known as the dissociation constant for the acid, K_a .

Thus $K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$

But at equilibrium: $[\text{CH}_3\text{COOH}] = (1 - \alpha)C$, $[\text{CH}_3\text{COO}^-] = \alpha C$ and $[\text{H}_3\text{O}^+] = \alpha C$

It follows that: $K_a = \frac{\alpha C \times \alpha C}{(1 - \alpha)C} = \frac{\alpha^2 C}{1 - \alpha}$

For weak electrolyte (weak acid), α is too small.

Therefore $1 - \alpha \approx 1$

Whence $K_a = \alpha^2 C$

And hence $\alpha = \sqrt{\frac{K_a}{C}}$ which is Ostwald's dilution law

Example 2

Calculate the degree of dissociation of CH_3COOH in (a) 0.5M (b) 0.125M (c) 0.031M. Comment on the value obtained ($K_a = 1.8 \times 10^{-5}$).

Solution

Using $\alpha = \sqrt{\frac{K_a}{C}}$

Where α is the degree of dissociation of the acid,

K_a is the dissociation constant for the acid,

C is the initial concentration of the acid before dissociation.

$$(a) \alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.5}} = 6 \times 10^{-3} \text{ or } 0.6\%$$

$$(b) \alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.125}} = 0.012 \text{ or } 1.2\%$$

$$(c) \alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.031}} = 0.024 \text{ or } 2.4\%$$

Comment: Degree of dissociation increases as concentration of CH_3COOH decrease from (a) to (c), i.e. degree of dissociation increase with an increases of dilution of the acid.

Example 3

Show that figures below satisfy the dilution law:

Volume in dm^3 containing 1 mole	5.4	10.6	24.9	63.3
Degree of dissociation, α	0.0098	0.0138	0.0212	0.03375

Solution

If the solution obey Ostwald's dilution law; $\alpha = \sqrt{\frac{K}{C}}$

From which; $1/C = V$ (Volume in dm^3 containing 1 mole)

It follows that; $\alpha = \sqrt{KV}$

Rearranging the equation gives; $K = \frac{\alpha^2}{V}$ and its value should be constant for every given set of values of α and V if the solution obeys Ostwald's dilution law.

Volume of solution in dm^3 containing 1 mole, V	5.4	10.6	24.9	63.3
Degree of dissociation, α	0.0098	0.0138	0.0212	0.03375
$K = \frac{\alpha^2}{V}$	1.78×10^{-5}	1.8×10^{-5}	1.8×10^{-5}	1.8×10^{-5}

Hence the solution obeys Ostwald's dilution law as the value of $\frac{\alpha^2}{V}$ is almost the same which is equal to the dissociation constant.

Example 4

Calculate pH of 0.01M CH_3COOH ($K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$).

Solution

$$[\text{H}^+] = \alpha C = C \sqrt{\frac{K_a}{C}} = \sqrt{CK_a}$$

$$\text{pH} = -\log[\text{H}^+] = -\log\sqrt{CK_a} = -\log\sqrt{0.01 \times 1.8 \times 10^{-5}} = 3.37$$

Hence pH of 0.01M CH_3COOH is 3.37

Example 5

Calculate the pH of:

(i) 0.01M HCl

(ii) 0.01M H_2SO_4

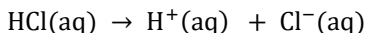
(iii) A solution prepared by dissolving 2.5g of H_2SO_4 in 250mL of water

(iv) If pH of solutions are determined experimentally, the results are often not exactly the same as the results obtained from calculations. Explain why the calculated pH of H_2SO_4 in ((ii) and (iii))

diverges more from the measured pH than the calculated pH of HCl. What should be given to improve the sulphuric acid calculations?

Solution

(i) Hydrochloric acid (HCl) being strong electrolyte (strong acid) ionises completely (its degree of dissociation is 100%) according to the following equation:



From which mole ratio of HCl to H^+ is 1:1

And hence $[\text{HCl}] = [\text{H}^+] = 0.01\text{M}$

Then $\text{pH} = -\log[\text{H}^+] = -\log 0.01\text{M} = 2$

So the pH of 0.01MHCl is 2

(ii) Sulphuric acid (H_2SO_4) being strong electrolyte (strong acid) ionises completely by 100% according to the following equation: $\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

From which mole ratio of H_2SO_4 to H^+ is 1: 2

And hence $[\text{H}^+] = 2[\text{H}_2\text{SO}_4] = 2 \times 0.01\text{M} = 0.02\text{M}$.

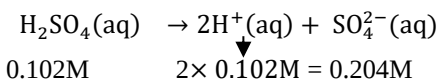
Using; $\text{pH} = -\log[\text{H}^+]$

Then the required pH of the acid = $-\log 0.02\text{M} = 1.7$

Hence the pH of 0.01MH $_2$ SO $_4$ is 1.7

$$\text{(iii) } [\text{H}_2\text{SO}_4] = \frac{m_{\text{H}_2\text{SO}_4}}{M_{\text{H}_2\text{SO}_4} \times V_{\text{soln}}} = \frac{2.5\text{g}}{98\text{gmol}^{-1} \times 0.25\text{L}} = 0.102\text{M}$$

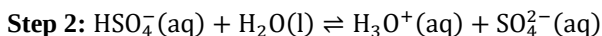
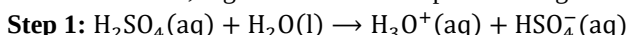
Equation for ionisation of H_2SO_4



Then $\text{pH} = -\log [\text{H}^+] = -\log 0.204\text{M} = 0.69$

Hence pH of the solution is 0.69

(iv) Sulphuric acid being diprotic acid (HCl is monoprotic) does not give all two hydrogen ions per molecule at once; it gives the ions in steps according to the following equations:



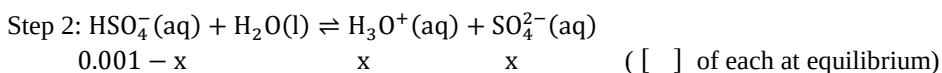
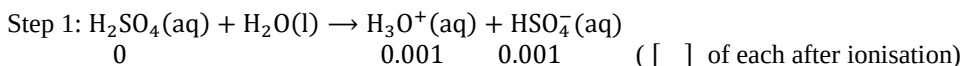
Since the second step involves the weak acid, HSO_4^- , the actual total $[\text{H}^+]$ is smaller than that used in the calculation making the calculated pH of sulphuric acid smaller than the measured pH. To reduce the difference, the dissociation constant (K_a) for HSO_4^- should be given.

Example 6

What is the pH of a 0.001M solution of H_2SO_4 ? $K_a(\text{HSO}_4^-) = 1.2 \times 10^{-2}$

Solution

Ionisation of H_2SO_4 takes place in the two steps:



From the step 2;

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

Where:

$K_a = 1.2 \times 10^{-2}$ (Here the dissociation constant which is an equilibrium constant is not very small and lies between 10^{-3} and 10^3 , thus there is appreciable concentration of both reactants and products, nothing is going to be neglected).

$$[\text{HSO}_4^-] = 0.001 - x$$

$$[\text{H}_3\text{O}^+] = x + 0.001$$

$$[\text{SO}_4^{2-}] = x$$

$$\text{Substituting } 1.2 \times 10^{-2} = \frac{(x+0.001)x}{0.001-x}$$

$$\text{From which; } x^2 + 0.013x - (1.2 \times 10^{-5}) = 0$$

$$\text{Solving above quadratic equation, gives } x = 8.6546 \times 10^{-4}$$

$$\text{Then } \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(x + 0.001) = -\log(8.6546 \times 10^{-4} + 0.001) = 2.73$$

Hence the pH is 2.73

Example 7

Calculate pH of :

(a) 0.01M NaOH

(b) 0.01M NH_4OH ($K_b = 1.78 \times 10^{-5}$)

Solution

(a) NaOH being strong electrolyte (strong base), ionises completely in the solution according to the following equation: $\text{NaOH(aq)} \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$

From which mole ratio of NaOH to OH^- is 1:1;

$$\text{And hence } [\text{NaOH}] = [\text{OH}^-] = 0.01\text{M}$$

$$\text{It follows that; } \text{pOH} = -\log[\text{OH}^-] = -\log 0.01\text{M} = 2$$

$$\text{But from } \text{pH} + \text{pOH} = 14; \text{pH} = 14 - \text{pOH} = 14 - 2 = 12$$

Hence pH of 0.01M NaOH is 12.

(b) NH_4OH being weak electrolyte (weak base), its degree of dissociation is given by Ostwald dilution

$$\text{law whereby: } \alpha = \sqrt{\frac{K_b}{C}}$$

So by using the fact that; $[\text{OH}^-] = \alpha C$

$$\text{It follows that: } [\text{OH}^-] = C \sqrt{\frac{K_b}{C}} = \sqrt{CK_b}$$

$$\text{And } \text{pOH} = -\log[\text{OH}^-] = -\log\sqrt{0.01 \times 1.78 \times 10^{-5}} = 3.4$$

$$\text{Then } \text{pH} = 14 - \text{pOH} = 14 - 3.4 = 10.6$$

Hence the pH of 0.01M NH_4OH is 10.6

Example 8

Calculate hydrogen ion index of 0.01M ammonia solution, given that; $\text{p}K_a$ value of NH_4^+ is 9.301.

Solution

In this question we are given with pK_a value of NH_4^+ instead of more useful value of pK_b of its conjugate base, $NH_3(aq)$.

So since NH_4^+ and $NH_3(aq)$ is conjugate pair, their pK_a and pK_b respectively are related by the following equation:

$$pK_a + pK_b = 14$$

$$\text{From which; } pK_b = 14 - pK_a = 14 - 9.301 = 4.699$$

$$\text{But } pK_b = -\log K_b;$$

$$\text{From which } K_b = \log^{-1}(-pK_b) = \log^{-1}(-4.699) = 2 \times 10^{-5}$$

$$\text{Thus } K_b \text{ of } NH_3(aq) \text{ is } 2 \times 10^{-5}.$$

$$\text{Then } [OH^-] = \alpha C = C \sqrt{\frac{K_b}{C}} = \sqrt{CK_b};$$

$$\text{Whence } pOH = -\log \sqrt{0.01 \times 2 \times 10^{-5}} = 3.35$$

Hydrogen ion index is pH whose value is related to pOH by the following equation:

$$pH = 14 - pOH; \text{ then } pH = 14 - 3.35 = 10.65$$

Hence the hydrogen ion index, pH of the ammonia solution is 10.65

Example 9

0.01M solution of methanoic acid had an osmotic pressure of 28350 Nm^{-2} at 25°C . Calculate the pH of the solution.

Solution

$$\text{Expected osmotic pressure} = \frac{nRT}{V}$$

$$\text{But } \frac{n}{V} = [\quad]; \text{ then the expected osmotic pressure} = [\quad]RT$$

$$\text{But } [\quad] = 0.01 \text{ mol/dm}^3 = \frac{0.01}{10^{-3}} \text{ mol/m}^3 = 10 \text{ mol/m}^3$$

$$\text{So the expected osmotic pressure} = 10 \times 8.314 \times 298 \text{ Nm}^{-2} = 24775.72 \text{ Nm}^{-2}$$

$$\text{But the observed osmotic pressure} = 28350 \text{ Nm}^{-2}$$

$$\text{Vant Hoff's factor, } i = \frac{\text{observed osmotic pressure}}{\text{expected osmotic pressure}} = \frac{28350}{24775.72} = 1.144$$

One mole methanoic acid ionises (dissociates) to produce two moles of ions according to the following equation: $\text{HCOOH} \rightleftharpoons \text{HCOO}^- + \text{H}^+$; $N = 2$

$$\text{Then } \alpha = \frac{i-1}{N-1} = \frac{1.144-1}{2-1} = 0.144 \text{ or } 14.4\%$$

$$\text{Using; } pH = -\log[H^+]; \text{ but } [H^+] = \alpha C;$$

$$\text{Then } pH = -\log \alpha C = -\log(0.144 \times 0.01) = 2.84$$

Hence, pH of 0.01M HCOOH is 2.84.

Example 10

Find pH of non – reacting mixture which is obtained by mixing two strong acidic solutions; one with pH of 1.8 and another of pH of 2.4 by taking 1 dm^3 of each solution.

Solution

From $\text{pH} = -\log[\text{H}^+]$; $[\text{H}^+] = \log^{-1}[-\text{pH}]$

For first solution: $[\text{H}^+] = \log^{-1}(-1.8) = 0.0158\text{M}$

For second solution: $[\text{H}^+] = \log^{-1}(-2.4) = 0.003981\text{M}$

Thus number of moles of H^+ taken from the first solution

$$= 0.0158\text{M} \times 1\text{dm}^3 = 0.0158 \text{ moles}$$

And number of moles of H^+ taken from the second solution

$$= 0.003981\text{M} \times 1\text{dm}^3 = 0.003981\text{moles}$$

Total number of moles of H^+ in the mixture $(0.0158 + 0.003981) \text{ moles} = 0.019781 \text{ moles}$

$$[\text{H}^+] \text{ in the mixture} = \frac{n_{\text{Total}}}{V_{\text{Total}}} = \frac{0.019781\text{moles}}{(1+1)\text{dm}^3} = 9.8905 \times 10^{-3}\text{M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(9.8905 \times 10^{-3}) = 2$$

Hence pH of the mixture is 2

Example 11

500 cm³ of 0.1M HCl is added to a 500 cm³ of 0.1M CH₃COOH. Calculate following:

- CH₃COO⁻ concentration in the solution mixture.
- pH of the solution mixture.

Dissociation constant (K_a) of CH₃COOH is 1.8×10^{-5}

Solution

$$n_{\text{HCl}} = \frac{500}{1000} \text{dm}^3 \times 0.1 \text{mol dm}^{-3} = 0.05 \text{mol}$$

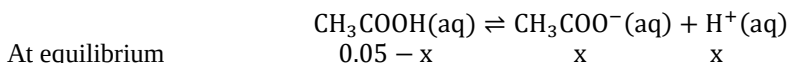
$$\text{Then } [\text{HCl}] = \frac{n_{\text{HCl}}}{V_{\text{soln}}}; \text{ where } V_{\text{soln}} = (500 + 500)\text{cm}^3 = 1000\text{cm}^3 = 1\text{dm}^3$$

$$\text{Substituting } [\text{HCl}] = \frac{0.05\text{mol}}{1\text{dm}^3} = 0.05\text{M}$$

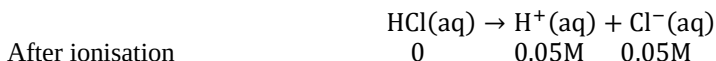
$$\text{Also } n_{\text{CH}_3\text{COOH}} = \frac{500}{1000} \text{dm}^3 \times 0.1 \text{mol dm}^{-3} = 0.05 \text{mol}$$

$$\text{Then } [\text{CH}_3\text{COOH}] = \frac{n_{\text{CH}_3\text{COOH}}}{V_{\text{soln}}} = \frac{0.05\text{mol}}{1\text{dm}^3} = 0.05\text{M}$$

CH₃COOH being weak acid ionises partially according to the following equation:



HCl being strong acid ionises completely according to the following equation:



Thus in CH₃COOH|HCl mixture:

$[\text{CH}_3\text{COOH}] = 0.05 - x \approx 0.05$ (Amount the weak acid dissociated is too small compared to its original amount because the equilibrium constant (in this case, dissociation constant) is less than 10^{-3}).

$$[\text{CH}_3\text{COO}^-] = x$$

$[\text{H}^+] = x + 0.05\text{M} \approx 0.05\text{M}$ (With **equal** concentration of both HCl and CH₃COOH, $[\text{H}^+]$ from CH₃COOH which is the weak acid can be neglected compared to $[\text{H}^+]$ which comes from strong acid).

Then from the equation of ionisation of CH₃COOH;

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{0.05x}{0.05} = 1.8 \times 10^{-5} \text{ or } x = 1.8 \times 10^{-5}$$

Hence:

$$[\text{CH}_3\text{COO}^-] = x = 1.8 \times 10^{-5} \text{ M}$$

$$\text{And pH} = -\log[\text{H}^+] = -\log(0.05 \text{ M}) = 1.3$$

Be aware with the fact that:

In this example, we were able to neglect $[\text{H}^+]$ coming from the weak acid because the two acids had equal concentration. If the concentration of weak acid is very large compared to that of strong acid, $[\text{H}^+]$ will be accounted by both acids. To have better understanding of this, study **example 12**.

Example 12

500 cm³ of 0.001 M HCl is added to a 500 cm³ of 0.1 M CH₃COOH. Calculate following:

- CH₃COO⁻ concentration in the solution mixture.
- pH of the solution mixture.

Dissociation constant (K_a) of CH₃COOH is 1.8×10^{-5}

Solution

$$n_{\text{HCl}} = \frac{500}{1000} \text{ dm}^3 \times 0.001 \text{ mol dm}^{-3} = 5 \times 10^{-4} \text{ mol}$$

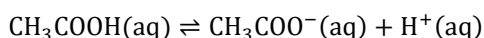
$$\text{Then } [\text{HCl}] = \frac{n_{\text{HCl}}}{V_{\text{soln}}}; \text{ where } V_{\text{soln}} = (500 + 500) \text{ cm}^3 = 1000 \text{ cm}^3 = 1 \text{ dm}^3$$

$$\text{Substituting } [\text{HCl}] = \frac{5 \times 10^{-4} \text{ mol}}{1 \text{ dm}^3} = 5 \times 10^{-4} \text{ M}$$

$$\text{Also } n_{\text{CH}_3\text{COOH}} = \frac{500}{1000} \text{ dm}^3 \times 0.1 \text{ mol dm}^{-3} = 0.05 \text{ mol}$$

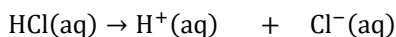
$$\text{Then } [\text{CH}_3\text{COOH}] = \frac{n_{\text{CH}_3\text{COOH}}}{V_{\text{soln}}} = \frac{0.05 \text{ mol}}{1 \text{ dm}^3} = 0.05 \text{ M}$$

CH₃COOH being weak acid ionises partially according to the following equation:



$$\text{At equilibrium} \quad \quad \quad 0.05 - x \quad \quad \quad x \quad \quad \quad x$$

HCl being strong acid ionises completely according to the following equation:



$$\text{After ionisation} \quad \quad \quad 0 \quad \quad \quad 5 \times 10^{-4} \text{ M} \quad \quad \quad 5 \times 10^{-4} \text{ M}$$

Thus in CH₃COOH|HCl mixture:

$$[\text{CH}_3\text{COOH}] = 0.05 - x \approx 0.05 \text{ (Here the same reasoning of the previous example applies)}$$

$$[\text{CH}_3\text{COO}^-] = x$$

$[\text{H}^+] = x + 5 \times 10^{-4}$ (In this case, $[\text{H}^+]$ from the weak acid cannot be neglected because the concentration of strong acid is very small compared to the concentration of weak acid).

Then from the equation of ionisation of CH₃COOH;

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$\text{Substituting } 1.8 \times 10^{-5} = \frac{x(x + 5 \times 10^{-4})}{0.05}$$

$$\text{From which: } x^2 + 5 \times 10^{-4}x - 9 \times 10^{-7} = 0$$

From the above quadratic equation; practical value of $x = 7.31 \times 10^{-4}$

Thus $[H^+] = x + 5 \times 10^{-4} = (7.31 \times 10^{-4} + 5 \times 10^{-4})M = 1.231 \times 10^{-3}M$

Hence:

$$[CH_3COO^-] = x = 7.31 \times 10^{-4}M$$

$$\text{And } pH = -\log[H^+] = -\log(1.231 \times 10^{-3}M) = 2.9$$

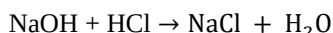
Example 13

Calculate pH of the following solution mixture of NaOH and HCl:

- (a) 25cm^3 of $0.1M$ NaOH is mixed with 50cm^3 of $0.1MHCl$
 (b) 51cm^3 of $0.1M$ NaOH is mixed with 50cm^3 of $0.1MHCl$

Solution

- (a) NaOH reacts with HCl according to the following equation:



From which mole ratio of NaOH to HCl is 1:1; so with equal concentration of NaOH and HCl, HCl having greater volume must be in excess.

That is $(50 - 25)\text{cm}^3 = 25\text{cm}^3$ of $0.1MHCl$ remain unreacted at the end of neutralisation reaction and hence the solution will be acidic.

$$\text{Number of moles of unreacted HCl} = \frac{25}{1000} \times 0.1\text{moles} = 2.5 \times 10^{-3}\text{moles}$$

$$\text{And total volume of solution mixture} = (25 + 50)\text{cm}^3 = 75\text{cm}^3$$

$$\text{Then } [HCl] = \frac{n}{V} = \frac{2.5 \times 10^{-3}\text{moles}}{75 \times 10^{-3}\text{dm}^3} = 0.033M$$

HCl being strong acid (strong electrolyte) ionises according to the following equation in the solution mixture:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

$$0.033M \qquad \qquad 0.033M$$

$$pH = -\log[H^+] = -\log 0.033M = 1.5$$

Hence the pH of the solution mixture is 1.5

- (b) In this case, $(51 - 50)\text{cm}^3 = 1\text{cm}^3$ of $0.1M$ NaOH remain unreacted at the end of neutralisation reaction and hence the solution mixture will be acidic.

$$\text{Number of moles of unreacted NaOH} = \frac{1}{1000} \times 0.1\text{mole} = 1 \times 10^{-4}\text{moles}$$

$$\text{And total volume of solution mixture} = (51 + 50)\text{cm}^3 = 101\text{cm}^3$$

$$\text{Then } [HCl] = \frac{n}{V} = \frac{1 \times 10^{-4}\text{moles}}{101 \times 10^{-3}\text{dm}^3} = 0.0009901M$$

$$\text{Then } pOH = -\log[OH^-] = -\log 0.0009901M = 3$$

$$\text{From } pH + pOH = 14; pH = 14 - pOH = 11$$

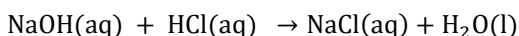
Hence pH of the solution mixture is 11

Example 14

100cm^3 of $0.05M$ NaOH is mixed with 150cm^3 of $0.04M$ HCl. Calculate pH of the solution mixture.

Solution

NaOH reacts with HCl according to the following equation:



From which mole ratio of NaOH to HCl is 1:1

But from given data:

$$\text{Number of mole of HCl} = \frac{150}{1000} \times 0.04 \text{ moles} = 0.006 \text{ moles}$$

$$\text{Number of moles of NaOH} = \frac{100}{1000} \times 0.05 \text{ moles} = 0.005 \text{ moles}$$

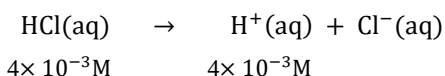
Thus HCl present in excess and the solution mixture is acidic.

Number of moles of HCl which remains unreacted

$$= (0.006 - 0.005) \text{ moles} = 0.001 \text{ moles}$$

$$\text{Then } [\text{HCl}] = \frac{n_{\text{HCl}}}{V_{\text{mixture}}} = \frac{0.001 \text{ moles}}{(100+150) \times 10^{-3} \text{ dm}^3} = 4 \times 10^{-3} \text{ M}$$

Equation for ionisation of HCl;



$$\text{pH} = -\log[\text{H}^+] = -\log(4 \times 10^{-3}) = 2.4$$

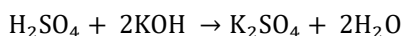
Hence pH of the solution mixture is 2.4

Example 15

80cm³ of 0.1M H₂SO₄ is mixed with 120cm³ of 0.1MKOH. Calculate pH of the solution mixture.

Solution

H₂SO₄ reacts with KOH according to the following equation:



From which mole ratio of H₂SO₄ to KOH is 1: 2

$$\text{Number of moles of H}_2\text{SO}_4 = \frac{80}{1000} \times 0.1 \text{ moles} = 8 \times 10^{-3} \text{ moles}$$

$$\text{Number of moles of KOH} = \frac{120}{1000} \times 0.1 \text{ moles} = 1.2 \times 10^{-2} \text{ moles}$$

From the mole ratio:

1.2×10^{-2} moles of KOH needs $\frac{1.2 \times 10^{-2}}{2}$ moles or 6×10^{-3} of H₂SO₄ for its complete neutralisation. Thus given amount of H₂SO₄ (8×10^{-3}) exceed the required amount and hence H₂SO₄ present in excess.

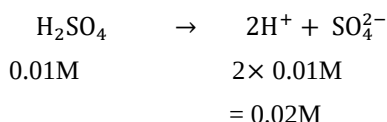
Number of moles of H₂SO₄ which remain unreacted

$$= (8 - 6) \times 10^{-3} \text{ moles} = 2 \times 10^{-3} \text{ moles}$$

$$\text{Total volume of the solution mixture} = (80 + 120) \text{ cm}^3 = 200 \text{ cm}^3$$

$$\text{Then } [\text{H}_2\text{SO}_4] = \frac{n_{\text{H}_2\text{SO}_4}}{V_{\text{mixture}}} = \frac{2 \times 10^{-3} \text{ moles}}{200 \times 10^{-3} \text{ dm}^3} = 0.01 \text{ M}$$

H₂SO₄ ionises in the solution according to the following equation:



$$\text{pH} = -\log[\text{H}^+] = -\log 0.02 \text{ M} = 1.7$$

Hence pH of the solution mixture is 1.7.

Example 16

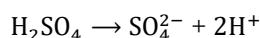
$x\text{cm}^3$ of a 0.01M solution of sulphuric acid were put into the volumetric flask of capacity 500cm^3 . Into this solution, distilled water was added until the mark. The pH of the solution made was found to be 3. Calculate the volume x used to make the solution.

Solution

From $\text{pH} = -\log[\text{H}^+]$; $[\text{H}^+] = \log^{-1}(-\text{pH})$

Thus $[\text{H}^+]$ in the diluted solution $= \log^{-1}(-3) = 10^{-3}\text{M}$

H_2SO_4 ionises according to the following equation:



From which mole ratio of H_2SO_4 to H^+ is 1:2

Thus concentration of diluted solution, M_d of $\text{H}_2\text{SO}_4 = \frac{10^{-3}\text{M}}{2} = 5 \times 10^{-4}\text{M}$

So $M_d = 5 \times 10^{-4}\text{M}$, $V_d = 500\text{cm}^3$, $M_c = 0.01\text{M}$, $V_c = x\text{cm}^3$.

By dilution principle; $M_c V_c = M_d V_d$

From which; $V_c = \frac{M_d V_d}{M_c}$; thus $x = \frac{5 \times 10^{-4} \times 500}{0.01} = 25$

The value of x is 25

Example 17

Calculate how many cm^3 of:

- Hydrochloric acid of concentration 1mol/dm^3 is needed to change the pH of 1dm^3 of HCl of concentration $1.0 \times 10^{-3} \text{mol/dm}^3$ by 1 unit.
- NaOH of concentration 1mol/dm^3 is needed to change the pH of 1dm^3 of HCl of concentration of $1.0 \times 10^{-3} \text{mol/dm}^3$ by 1 unit.

Solution

(a) pH of $1 \times 10^{-3} \text{mol/dm}^3$ HCl $= -\log(1 \times 10^{-3}) = 3$.

On addition of the acid, pH value decreases; thus the new pH value $= 3 - 1 = 2$

So using $[\text{H}^+] = \log^{-1}(-\text{pH})$

The new $[\text{H}^+] = \log^{-1}(-2) = 10^{-2}\text{M}$

Let the volume needed be $V\text{cm}^3$

Then number of moles of HCl added $= \frac{V}{1000} \times 1 = 0.001V$

Total number of moles of HCl in the mixture $= 0.001V + 0.001$

Total volume of the solution mixture $= (V + 1000)\text{cm}^3 = \frac{(V+1000)}{1000} \text{dm}^3$

Thus $10^{-2} = \left(\frac{0.001V + 0.001}{V + 1000} \right) \times 1000$

Solving the above equation gives $V = 9.09\text{cm}^3$

Hence 9.09cm^3 of HCl is needed.

(b) $\text{pH of } 1 \times 10^{-3} \text{M HCl} = -\log(1 \times 10^{-3}) = 3$

On addition of base, pH value increases; so the new pH value = $3 + 1 = 4$

The new $[\text{H}^+] = 10^{-4} \text{M}$

The $[\text{H}^+]$ decreases due to addition of OH^- from the alkaline solution which eliminates H^+ such that
number of moles of OH^- added = number of moles of H^+ eliminated.

But number of moles of OH^- added in a litre of solution = $\frac{V}{1000} \times 1 = 0.001V$

Where V is the volume of the base in cm^3 ;

Then number of moles HCl in the mixture = $0.001 - 0.001V$

Total volume of the solution mixture = $(V + 1000)\text{cm}^3 = \left(\frac{V+1000}{1000}\right) \text{dm}^3$

Thus $10^{-4} = \left(\frac{0.001-0.001V}{V+1000}\right) \times 1000$

From which $V = 0.9 \text{ cm}^3$

Hence 0.9 cm^3 of NaOH is required.

DIGGING DEEPER EXERCISE 16

EXERCISE 16A: BINDER QUESTIONS

Question 1

Calculate the pH for each of the solution with the following concentration:

(a) $[H^+] = 1 \times 10^{-3}M$ (b) $[H^+] = 1 \times 10^{-9}M$ (c) $[OH^-] = 1 \times 10^{-5}M$

Question 2

Solution "A" has a $[H^+] = 3.9 \times 10^{-5}M$. Solution "B" has a pH of 5.70. Which is more acidic? Which is more basic?

Question 3

Calculate the pH and pOH of a solution prepared by dissolving 0.93 g of HCl in enough water to give 0.40L of solution.

Question 4

A 1000mL solution of HCl has a pH of 1.30. How many grams of HCl are dissolved in the solution?

Question 5

How many times more acidic is a solution with pH = 4.80 as compared to one with pH = 6.33?

Question 6

Two solutions are mixed: 5.00 mL of 2.50 M HBr and 7.00 mL of 2.00 M LiOH. What is the final pH after mixing?

Question 8

- (a) What feature of the ammonia molecule enables it to react as a base?
(b) Calculate the pH of a 0.100M solution of ammonia if its $K_b = 1.8 \times 10^{-5}M$

Question 9

100mL of a solution with pH of 2 is mixed with 300mL of another solution with pH of 7. What is the pH of the mixture?

Question 10

10mL of HCl solution was mixed with 20mL of NaOH solution that has pH 12. After mixing, the pH of the mixture was 7. What was the pH of the hydrochloric acid solution?

EXERCISE 16B: REAL QUESTIONS

Question 11

Why should temperature be specified when doing weak acid pH calculations?

Question 12

Kipute was asked to calculate pH of pure water at 100°C and she found the **correct** answer to be 6. She then argued to you that; pure water is only neutral at 25°C where its pH is 7. Do you agree or disagree with Kipute's argument? Explain.

Question 13

The antacid called "Milk of Magnesia" contains 800mg of $Mg(OH)_2$ per 2 teaspoons. The typical stomach pH is 1.420. How many mL of stomach acid (HCl) are neutralised by 2 Tablespoons of Milk of Magnesia? (1 Tablespoon = 3 teaspoon).

Question 14

White vinegar in a kitchen is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm³, what is the pH? $K_a(\text{acetic acid}) = 1.8 \times 10^{-5}$

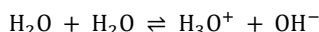
Question 15

On another day, **Kipute** was asked to calculate pH of 10^{-2}M HCl and of 10^{-8}M HCl and she got 2 and 8 respectively by taking negative logarithm of each concentration. However, the second answer made her to doubt everything she learned about calculating pH of solutions. *"I'm certain that hydrochloric acid is acid; even its name is the confirmation of this. And without any doubt, pH of 8 that was found in my calculation is the pH of base, I'm confused indeed! Please do you have any explanation to this contradiction?"* She asked.

- By applying a knowledge of chemical equilibrium on self-ionisation of water, re-calculate the pH of 10^{-2}M HCl and show to Kipute that her simplification on the calculation of pH was correct in this case.
- Explain to **Kipute**, how the simplification is incorrect in the case of 10^{-8}M HCl and hence calculate the correct pH value.

EXERCISE 16C: HOT QUESTIONS**Question 16**

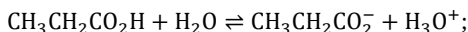
The equation to show auto-ionisation of water can be represented by using the following equation:



Give three pieces of information which can be deduced from the above equation:

Question 17

Propanoic acid dissociates in aqueous solution according to



- Write the expression for K_a for propanoic acid.
- Given that K_a for this reaction is $3.5 \times 10^{-5} \text{mol dm}^{-3}$ at 298 K, calculate the pH of a 0.100M solution of propanoic acid at this temperature.
- If the solution referred to in (ii) were to be diluted tenfold, it might be expected that the pH would rise by one unit. In fact, it rises by less than this. Explain.

Question 18

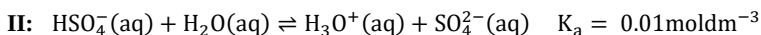
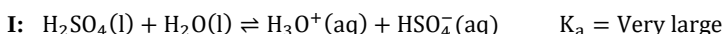
Water self-ionises: $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

At 0°C , $K_w = 1 \times 10^{-15} \text{mol}^2 \text{dm}^{-6}$ and at 100°C , $K_w = 5 \times 10^{-13} \text{mol}^2 \text{dm}^{-6}$.

- Deduce with reasons whether the dissociation of water is exothermic or endothermic.
- The pH of a $1 \times 10^{-2} \text{mol dm}^{-3}$ solution of hydrochloric acid is 2 and that of $1 \times 10^{-3} \text{mol dm}^{-3}$ hydrochloric acid is 3. However the pH of a solution of $1 \times 10^{-8} \text{mol dm}^{-3}$ hydrochloric acid is **not** equal to 8. Suggest an explanation for this observation.

Question 19

Acids differ in the number of hydrogen ions that can be liberated from one molecule of the undissociated acid. Hydrochloric acid is a strong monobasic, or monoprotic acid, liberating one hydrogen ion per molecule. Sulphuric acid is a dibasic, or diprotic acid, its ionisation in aqueous solution being:



K_a values are quoted for 25°C .

- State the hydrogen ion concentration in 0.01mol dm^{-3} hydrochloric acid, which is a strong acid, and hence find the pH of this solution.
- State the hydrogen ion concentration of 0.1mol dm^{-3} sulphuric acid arising from the first stage of ionisation, **I**.
- A solution of sodium hydrogensulphate, NaHSO_4 , of concentration 0.1mol dm^{-3} , ionises according to equation **II** above. Find the hydrogen ion concentration in this solution, and **hence** state what you would expect the hydrogen ion concentration in 0.1mol dm^{-3} sulphuric acid to be.
- In fact the pH of 0.1mol dm^{-3} sulphuric acid is about 0.98. This indicates a hydrogen ion concentration of 0.105mol dm^{-3} . By considering the reactions, **I** and **II** in the presence of one another explain why this is so. You are not expected to perform any further calculations.

Question 20

Calculate the depression in freezing point of water when 10g of $\text{CH}_3\text{CH}_2\text{CHClCOOH}$ is added to 250g of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86$

Question 21

19.5g of CH_2FCOOH (fluoroacetic acid) is dissolved in 500g of water. The depression of freezing point of water observed is 1°C . Calculate the Van't Hoff factor and dissociation constant of fluoroacetic acid.

$$K_f = 1.86$$

Question 22

Calculate the fluoride ion concentration and pH of a solution that is 1M in HF and 0.01M in HCl.

$$K_a(\text{HF}) = 6.8 \times 10^{-4}$$

Question 23

30mL of a solution with pH of 2 is mixed with 20mL of another solution with pH of 13. What is the pH of the mixture?

Question 24

Consider the reaction of $\text{Ba}(\text{OH})_2$ and HCl. You are mixing 2L of HCl solution that has pH of 1.52 and a solution of $\text{Ba}(\text{OH})_2$ that has pH = 13.3. What volume of the $\text{Ba}(\text{OH})_2$ solution is required to completely react with the HCl solution with no HCl or $\text{Ba}(\text{OH})_2$ remaining?

Question 25

At a certain temperature, a 0.01M solution of sodium hydroxide has a pH of 11. Calculate a value for ionic product of water at this temperature.

Chapter 17

BUFFER SOLUTION

In everyday life, there are various systems which function properly under certain specified narrow range of pH. A constant pH is required for many biological and chemical reactions to proceed. In these systems, substances called **buffers** or **buffer solutions** are extremely useful to maintain pH. Literally *buffer* is something that lessens or absorbs the shock of an impact. Buffer solution lessens the impact of acid and base on the pH of the solution. So it can be defined as *the solution which can maintain its pH value on addition of small amount of acid or base*. That is, it is the solution whose pH value does not change significantly on addition of acid or base provided that **buffer capacity** is not exceeded. Because it controls pH of the solution, buffer solution is also known **pH buffer** or **hydrogen ion buffer**.

Examples of buffer solution are:

- **Acetate buffer solution** which is the mixture of ethanoic acid (acetic acid) and sodium ethanoate (sodium acetate) which is usually shortened as $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffer system.
- **Ammonium buffer solution** which is the mixture of ammonium hydroxide and ammonium chloride which is usually shortened as $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer system.
- A solution mixture of ammonium hydroxide and ammonium sulphate ($\text{NH}_4\text{OH}/((\text{NH}_4)_2\text{SO}_4$ buffer system).
- A solution mixture of hydrogen cyanide and sodium cyanide (HCN/NaCN buffer system).

CHARACTERISTICS OF A BUFFER SOLUTION

Characteristics of a buffer solution include the following:

- 1) It has a definite pH.
- 2) Its pH remains the same on standing for a long time.
- 3) Its pH does not change on dilution.
- 4) Its pH changes negligibly by the addition of a small amount of acid or base.

TYPES OF BUFFER SOLUTION

Depending on their pH value, buffer solutions can be classified into two categories, namely:

- Acidic buffer solution
- Basic buffer solution

Acidic buffer solution

This is the buffer solution whose pH value is less than 7. It is used to maintain pH of the system which works properly in the acidic condition.

- It is prepared by mixing weak acid and its strong salt (the salt containing anion which is conjugate base of the acid and strong electropositive metal cation derived from strong base).

Examples of acidic buffer solution are:

- $\text{CH}_3\text{COOH}/\text{CH}_3\text{COOK}$ buffer system
- $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffer system
- HCN/KCN buffer system
- HCN/NaCN buffer system

Basic buffer solution

This is buffer solution whose pH value is greater than 7. It is used to maintain pH of the system which works properly in the basic condition.

- It is prepared by mixing a weak base and its strong salt (the salt containing its conjugate acid cation and strong electronegative anion derived from strong acid).

Examples of basic buffer solution are:

- $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer system
- $\text{NH}_4\text{OH}/(\text{NH}_4)_2\text{SO}_4$ buffer system

MECHANISM OF BUFFER SOLUTION TO CONTROL ITS pH VALUE

Acidic buffer solution mechanism

To understand this consider acetate buffer solution i.e. $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffer system which is acidic.

Determination of pH value of the buffer solution

- Before addition of strong salt (CH_3COONa), ethanoic acid being weak acid, ionises partially according to the following equation: $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$
- After addition of strong salt (CH_3COONa), the salt ionises completely according to the following equation: $\text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+$
- The ionisation of the strong salt is equivalent to an increase in concentration of CH_3COO^- which disturbs the position of the equilibrium of the ionisation of the weak acid through **common ion effect**.
- Thus more H^+ should combine with added CH_3COO^- to restore the equilibrium.
- The concentration of H^+ which remains after re-establishment of new equilibrium is the one which determine the pH of the buffer solution.

Definition of common ion effect

This is the lowering in the dissociation of a weak electrolyte due to addition of a strong electrolyte which contains a cation or anion which is also found in the weak electrolyte.

Addition of strong acid to the acidic buffer solution

- Consider strong acid like hydrochloric acid (HCl) is added to the buffer solution (our $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffer system)
- The strong acid (HCl) ionises completely in the solution according to the following equation:
 $\text{HCl}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- The ionisation of HCl is equivalent to an increase of concentration of hydrogen ions (H^+) to the buffer solution. This disturbs the position of chemical equilibrium in the buffer solution.
- Thus more ethanoate ions (CH_3COO^-) should combine with added H^+ to restore the equilibrium.
- But the added H^+ are from strong acid which ionises completely; so ethanoate ions (CH_3COO^-) from the weak acid (CH_3COOH) are not enough to combine with added hydrogen ions from the strong acid.
- However presence of sodium ethanoate which ionises completely like $\text{HCl}(\text{aq})$ provides higher concentration of CH_3COO^- which are enough to combine with added H^+ from strong acid to re-establish the equilibrium and hence pH value of the buffer solution is maintained.

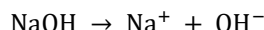
This resistance to change in pH on the addition of a strong acid is called as **reserve basicity** and is due to CH_3COO^- ions.

By definition: **reserve basicity** is the resistance of a buffer solution to change in pH upon addition of a strong acid.

Addition of strong base to the acidic buffer solution

Consider strong base like NaOH is added to the buffer solution:

- NaOH being strong base ionises completely according to the following equation:



- Hydroxyl ions (OH^-) produced in the above ionisation combine with hydrogen ions (H^+) in the buffer solution.
- This disturbs the position of chemical equilibrium in the buffer solution, so more ethanoic acid will ionise to give hydrogen ions so as to re-establish the equilibrium and hence the pH value of the buffer solution is maintained.

This resistance to change in pH on the addition of base is called **reserve acidity** and is due to CH_3COOH .

By definition: **reserve acidity** is the resistance of a buffer solution to change in pH upon addition of a strong base.

So what are uses of weak acid and strong salt in the buffer solution?

- The use of weak acid is to provide the dynamic system of the chemical equilibrium and to eliminate OH^- on addition of the strong base.
- The use of strong salt (CH_3COONa) is to provide enough concentration of anions (CH_3COO^-) to combine with H^+ on addition of the strong acid.

Basic buffer solution mechanism

To understand this consider ammonium buffer solution i.e. $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer system which is basic.

Determination of pH value of the solution

- Before addition of strong salt (NH_4Cl), NH_4OH being weak base ionises partially according to the following equation: $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
- After addition of strong salt (NH_4Cl), the salt ionises completely according to the following equation: $\text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^-$
- The ionisation of strong salt is equivalent to an increase of concentration of ammonium ions (NH_4^+) which disturbs the position of chemical equilibrium of the ionisation of NH_4OH through **common ion effect**.
- Thus more OH^- should combine with added (NH_4^+) to restore the equilibrium.
- To concentration of OH^- which remains after re-establishment of the new equilibrium is the one which determine the pOH which eventually determine pH of the buffer solution.

Addition of strong base to the basic buffer solution

Consider the strong base like NaOH is added to the buffer solution:

- The strong base ionises completely in the solution according to the following equation: $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$
- The ionisation of NaOH is equivalent to an increase of concentration of hydroxyl ions (OH^-) to the buffer solution. This disturbs the position of chemical equilibrium in the buffer solution.
- Thus more ammonium ions (NH_4^+) should combine with added OH^- to restore the equilibrium.
- But the added OH^- are from strong base which ionises completely; so ammonium ions (NH_4^+) from the weak base (NH_4OH) are not enough to combine with added hydroxyl ions from the strong base.
- However presence of ammonium chloride which ionises completely like NaOH provides higher concentration of NH_4^+ which are enough to combine with added OH^- from the strong base to re-establish the equilibrium and hence pH value of the buffer solution is maintained.

In this case, the reserve acidity and is due to NH_4^+ ions in a solution.

Addition of strong acid to the basic buffer solution

Consider strong acid like HCl is added to the buffer solution

- HCl being strong acid ionises completely according to the following equation

$$\text{HCl(aq)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$$
- Hydrogen ions (H^+) produced in the above ionisation combine with hydroxyl ions, OH^- in the buffer solution. This disturbs the position of chemical equilibrium in the buffer solution.
- So more ammonium hydroxide will ionise to give hydroxyl ions so as to re-establish the equilibrium and hence the pH value of the buffer solution is maintained.

Here, the reserve basicity and is due to NH_4OH in the buffer solution.

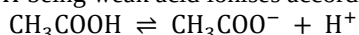
So what are uses of weak base and strong salt in the buffer solution?

- The use of weak base is to provide the dynamic system of the chemical equilibrium and to eliminate H^+ on addition of the strong base.
- The use of strong salt (NH_4Cl) is to provide enough concentration of cations (NH_4^+) to combine with OH^- on addition of strong base.

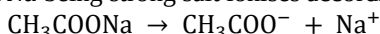
EQUATION FOR CALCULATING pH OF ACIDIC BUFFER SOLUTION

Consider $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffer system which is acidic:

CH_3COOH being weak acid ionises according to the following equation:



CH_3COONa being strong salt ionises according to the following equation:



From the equation of the ionisation of the weak acid: $K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$

From which, $[\text{H}^+] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$

Introducing $-\log$ both sides;

$$-\log [\text{H}^+] = -\log \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$\text{Or } -\log [\text{H}^+] = -\log K_a + -\log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$\text{But } -\log [\text{H}^+] = \text{pH}; -\log K_a = \text{p}K_a \text{ and } -\log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\text{Thus } \text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Since CH_3COONa ionises completely while CH_3COOH ionises partially to give CH_3COO^- , it can be concluded that; approximately all CH_3COO^- are from CH_3COONa (salt).

And since mole ratio of CH_3COONa to CH_3COO^- is 1:1;

$$[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COONa}] = [\text{Salt}].$$

Hence for acidic buffer solution:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{Acid}]} \rightarrow \text{Henderson - Hasselbalch equation}$$

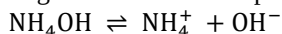
The above final formula applicable without any modification if and only if the mole ratio of salt to its anion is 1:1.

Note that the pH is determined by the ratio of concentrations, $\frac{[\text{salt}]}{[\text{Acid}]}$, but the buffering capacity of the solution can be increased by increasing the concentrations of both components in the same molar concentration ratio.

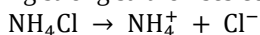
EQUATION FOR CALCULATING pH OF BASIC BUFFER SOLUTION

Consider $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ buffer system which is basic:

NH_4OH being weak base ionises partially in the solution according to the following equation:



NH_4Cl being strong salt ionises completely in the solution according to the following equation:



From the equation of ionisation of NH_4OH ; $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$

From which; $[\text{OH}^-] = \frac{K_b[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$

Introducing $-\log$ both sides; $-\log[\text{OH}^-] = -\log \frac{K_b[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$

Or $-\log[\text{OH}^-] = -\log K_b - \log \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$

So **pOH** = **pK_b** + **log** $\frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$

Since NH_4Cl ionises completely while NH_4OH ionises only partially yielding NH_4^+ ; it may be assumed that the whole concentration of NH_4^+ is from NH_4Cl (salt).

Also since mole ratio of NH_4Cl to NH_4^+ is 1:1; $[\text{NH}_4^+] = [\text{NH}_4\text{Cl}] = [\text{salt}]$

Hence for basic buffer solution: **pOH** = **pK_b** + **log** $\frac{[\text{salt}]}{[\text{base}]}$

But $\text{pH} + \text{pOH} = 14$ or $\text{pH} = 14 - \text{pOH}$

Whence for basic buffer solution; **pH** = **14** - **(pK_b + log $\frac{[\text{salt}]}{[\text{base}]}$)**

Again the above final formula is applicable without any modification if and only if the mole ratio of the salt to its cation is 1:1. (Carefully study **Example 5** to understand how to deal with the situation when the ratio is not 1:1).

EFFICIENCY OF BUFFER SOLUTION

When a buffer solution can afford greater amount of strong acid or strong base without drastic change in its pH, then the buffer is said to work more efficiently. Also, when the buffer solution shows smaller change in the pH after adding given amount of strong acid or base, then the buffer is said to be more efficient. The two scenarios are related to **buffer capacity** and **buffer range** which are main determinant of efficiency of buffer solution.

Buffer capacity is the relative ability of a buffer solution to resist pH change upon addition of acid or base. Usually the change is counted as insignificant when does not exceed one unit. As a result, buffer capacity can also be defined as the number of moles of acid or base required to change the pH of the buffer solution by one unit.

Buffer capacity depends on the amounts of the weak acid (or base) and its conjugate base (or acid) that are in a buffer mixture. For example, 1L of a solution that is 1M in acetic acid and 1M in sodium acetate has a greater buffer capacity than 1L of a solution that is 0.1M in acetic acid and 0.1M in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

Buffer range is the pH range over which the buffer acts effectively. For the buffer to be effective, the pH range must not diverge by more than 1 from the pK_a (or pK_b) value; i.e. It must lie between one pH unit above and below the pK_a (or pK_b) value.

Thus, **pH of the buffer** = **pK_a** (or **pK_b**) ± 1 .

The closer the buffer pH is to the outer limits of the range, the less effective the buffer will be as it will be reaching the limits of its ability to counter acid or base; what does this imply? This implies that, it is best to have almost equal concentrations of weak acid or base and its conjugate base or acid so that

the buffer pH is closer to the pK_a (or pK_b) value. To have better understanding of this consider Henderson – Hasselbalch equation for acetate buffer;

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

When $[CH_3COO^-] = [CH_3COOH]$; the above equation becomes;

$$pH = pK_a + \log 1 = pK_a$$

Hence the buffer solution is most effective when $[CH_3COO^-] = [CH_3COOH]$ such that $pH = pK_a$.

Another advantage of the equality in the concentration is that the buffer attains equal ability of eliminating both acid and base; that is, it attains equality in the reverse basicity and the reserve acidity.

So we can conclude that, buffer solution works more efficiently when the following conditions are met:

- 1) High concentrations of both of its components. (This ensures that high buffer capacity is achieved).
- 2) Equal concentrations of both of its components such that $pH = pK_a$. (A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other).

CALCULATIONS INVOLVING BUFFER SOLUTION

Example 1

Taking the pK_a value of NH_4^+ as 9.301, calculate the change in hydroxide ion concentration produced by adding 10g of ammonium chloride to 1dm³ of 0.1M ammonia. Assume the salt is fully ionised.

Solution

Using $pK_a + pK_b = 14$

$$\text{Then } pK_b = 14 - pK_a = 14 - 9.301 = 4.699$$

$$\text{But } pK_b = -\log K_b$$

$$\text{From which } K_b = \log^{-1}(-pK_b) = \log^{-1}(-4.699) = 2 \times 10^{-5}$$

Thus K_b of NH_4OH (conjugate base of NH_4^+) is 2×10^{-5}

Before addition of the salt:

From the equation of ionisation of NH_4OH in the solution: $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

But from the above equation of the ionisation; mole ratio of NH_4^+ to OH^- is 1:1

$$\text{Thus } [NH_4^+] = [OH^-]$$

$$\text{It follows that; } K_b = \frac{[OH^-]^2}{[NH_4OH]}$$

$$\text{So } [OH^-] = \sqrt{K_b[NH_4OH]} = \sqrt{2 \times 10^{-5} \times 0.1} = 1.414 \times 10^{-3} M$$

Thus the $[OH^-]$ before addition of the salt is $1.414 \times 10^{-3} M$

After addition of the salt $[NH_4Cl]$:

$$\text{From } K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

Since NH_4Cl is fully ionised, it may be assumed that the whole NH_4^+ comes from the salt (NH_4Cl). And since mole ratio of NH_4^+ to NH_4Cl in the ionisation of the salt is 1:1 $[NH_4^+] = [NH_4Cl]$

$$\text{Whence } K_b = \frac{[NH_4Cl][OH^-]}{[NH_4OH]} \text{ or } [OH^-] = \frac{K_b[NH_4OH]}{[NH_4Cl]}$$

$$\text{But } [\text{NH}_4\text{Cl}] = \frac{m_{\text{NH}_4\text{Cl}}}{M_{\text{NH}_4\text{Cl}} \times V_{\text{soln}}} = \frac{10\text{g}}{53.5\text{g mol}^{-1} \times 1\text{dm}^3} = 0.1869\text{M}$$

$$\text{So } [\text{OH}^-] = \frac{2 \times 10^{-5} \times 0.1}{0.1869}\text{M} = 1.07 \times 10^{-5}\text{M}$$

Hence hydroxide ion concentration decreases from $1.414 \times 10^{-3}\text{M}$ to $1.07 \times 10^{-5}\text{M}$ after addition of the salt.

Example 2

The dissociation constant of ammonia is $1.8 \times 10^{-5}\text{mol dm}^{-3}$. Calculate pH of decimolar ammonia solution. Also calculate the pH of the solution obtained by adding 2.5g of ammonium chloride to the 250cm^3 of decimolar solution.

Solution

$$[\text{OH}^-] = \alpha C; \text{ where } C = 0.1\text{M (decimolar solution)}$$

$$\text{But from Ostwald's dilution law, } \alpha = \sqrt{\frac{K_b}{C}}$$

$$\text{Then } [\text{OH}^-] = C \sqrt{\frac{K_b}{C}} = \sqrt{CK_b}$$

$$\text{So pOH} = -\log[\text{OH}^-] = -\log\sqrt{CK_b} = -\log\sqrt{0.1 \times 1.8 \times 10^{-5}} = 2.87$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.87 = 11.13$$

Thus pH of decimolar ammonia solution is 11.13

After addition of ammonium chloride to into ammonia solution, basic buffer solution whose pH is given by the equation below is formed; $\text{pH} = 14 - \left(\text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]} \right)$

$$\text{But } [\text{salt}] = [\text{NH}_4\text{Cl}] = \frac{2.5}{53.5 \times 0.25} = 0.187\text{M}$$

$$\text{Then } \text{pH} = 14 - \left(-\log(1.8 \times 10^{-5}) + \log \left(\frac{0.187}{0.1} \right) \right) = 8.98$$

Hence pH after addition of ammonium chloride is 8.98.

Example 3

Calculate the volume of 0.1M HCOONa that must be added to 1dm^3 of 0.1M HCOOH to give a buffer solution of pH 3.5 ($\text{p}K_a$ of HCOOH is 3.75).

Solution

The mixture of HCOOH and HCOONa is acidic buffer solution whose pH value is given by the following equation: $\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

$$\text{But } [\text{salt}] = \frac{\text{number of moles of salt}}{\text{volume of buffer solution}}$$

$$\text{And } [\text{Acid}] = \frac{\text{number of moles of acid}}{\text{volume of buffer solution}}$$

$$\text{It follows that: } \frac{[\text{salt}]}{[\text{acid}]} = \frac{\text{number of moles of salt}}{\text{number of moles of acid}}$$

Thus for acidic buffer solution:

$$\text{pH} = \text{p}K_a + \log \frac{\text{number of moles of salt}}{\text{number of moles of acid}}$$

If V is the volume of the salt (HCOONa) required in dm^3

$$\text{Then } 3.5 = 3.75 + \log \frac{0.1V}{0.1 \times 1} \quad (n = [\quad]V)$$

From which; $V = 0.562 \text{ dm}^3$

Hence 0.562 dm^3 or 562 cm^3 of HCOONa is required.

Example 4

Calculate the mass of CH_3COONa that must be added to 1 dm^3 of a 0.1 M CH_3COOH to produce a solution of pH 4? (K_a of CH_3COOH is 1.8×10^{-5})

Solution

CH_3COOH and CH_3COONa form acidic buffer solution whose pH is given by the following equation:

$$\text{pH} = \text{p}K_a + \log \frac{\text{Number of moles of salt } (\text{CH}_3\text{COONa})}{\text{Number of moles of acid } (\text{CH}_3\text{COOH})}$$

Using; $n = \frac{m}{M_r}$ and $n = [\quad]V$ and then substituting given values to the above equation gives:

$$4 = -\log(1.8 \times 10^{-5}) + \log \frac{\frac{m}{84}}{0.1 \times 1}$$

Where m is the mass of CH_3COONa in g

Solving above equation gives $m = 1.512 \text{ g}$

Hence the required mass of CH_3COONa is 1.512 g

Example 5

Calculate the number of grams of ammonium sulphate which are to be added to 500 cm^3 of 0.176 M ammonia solution to give a buffer solution of pH 9.42 (assume the volume of solution does not change on addition of ammonium sulphate. Given that $\text{p}K_a$ of NH_4^+ is 9.243).

Solution

When ammonium sulphate is mixed with ammonia solution, basic buffer solution whose pH value is given by the equation below is formed.

$$\text{pH} = 14 - \left(\text{p}K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} \right) \text{ or } \text{pH} = 14 - \text{p}K_b - \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

But NH_4^+ and NH_4OH are conjugate pair;

Thus $14 - \text{p}K_b = \text{p}K_a$ of NH_4^+ ($\text{p}K_a + \text{p}K_b = 14$ for conjugate pairs)

$$\text{Therefore } \text{pH} = \text{p}K_a - \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

$$\text{Substituting the given values; } 9.42 = 9.243 - \log \frac{[\text{NH}_4^+]}{0.176}$$

From which, $[\text{NH}_4^+] = 0.117 \text{ M}$.

So number of mole of NH_4^+ in 1 L of buffer solution is 0.117 moles

Whence number of moles of NH_4^+ in 500 cm^3 (0.5 L) of the solution

$$= 0.5 \times 0.117 \text{ moles} = 0.0585 \text{ moles}$$

The ammonium ions (NH_4^+) are from $(\text{NH}_4)_2\text{SO}_4$ (ammonium sulphate) which is fully ionised according to the following equation: $(\text{NH}_4)_2\text{SO}_4 \rightarrow 2\text{NH}_4^+ + \text{SO}_4^{2-}$

From which mole ratio of $(\text{NH}_4)_2\text{SO}_4$ to NH_4^+ is 1: 2

Thus $\frac{0.0585}{2} \text{ moles} = 0.02925 \text{ mole}$ of $(\text{NH}_4)_2\text{SO}_4$ is required to produce 0.0585 moles of NH_4^+ .

But molar mass of $(\text{NH}_4)_2\text{SO}_4$ is 132g/mol.

So by using $m = nM_r$;

Required mass of $(\text{NH}_4)_2\text{SO}_4$ is $0.02925 \times 132\text{g} = 3.861\text{g}$

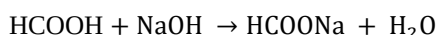
Hence 3.861g of ammonium sulphate are required.

Example 6

Calculate pH of a solution formed by mixing 24.9cm^3 of 0.1MNaOH with 25cm^3 of 0.1M HCOOH (K_a of HCOOH is 1.6×10^{-4}).

Solution

HCOOH reacts with NaOH according to the following equation:



From which mole ratio of HCOOH to NaOH is 1:1

Thus $(25 - 24.9)\text{cm}^3$ or 0.1cm^3 of 0.1MHCOOH remain unreacted at the end of chemical reaction.

Thus HCOOH is the reactant in excess while NaOH is limited reactant.

Number of moles of HCOONa formed after reaction = $\frac{24.9}{1000} \times 0.1\text{moles} = 2.49 \times 10^{-3}\text{moles}$

Number of moles of HCOOH which remain unreacted

$$= \frac{0.1}{1000} \times 0.1\text{moles} = 1 \times 10^{-5}\text{moles}$$

The formed HCOONa and unreacted HCOOH forms acidic buffer solution whose pH is given by the following equation: $\text{pH} = \text{p}K_a + \log \frac{\text{Number of moles of salt (HCOONa)}}{\text{Number of moles of acid (HCOOH)}}$

By substituting the values: $\text{pH} = -\log(1.6 \times 10^{-4}) + \log \left(\frac{2.49 \times 10^{-3}}{1 \times 10^{-5}} \right) = 6.2$

Hence the pH was 6.2.

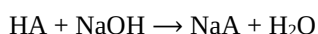
Example 7

Solution of unknown monobasic acid was titrated with the base and equivalent point reached when 36.12mL of 0.1MNaOH had been added. The 18.06mL of 0.1MHCl were added to the solution and the measured pH was found with pH meter to be 4.92. Calculate the dissociation constant of unknown acid.

Solution

Number of moles of NaOH added = $\frac{36.12}{1000} \times 0.1 = 3.612 \times 10^{-3}\text{mol}$

The acid, HA (monobasic acid) reacts with NaOH according to the following equation:

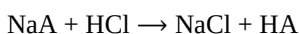


From which mole ratio of NaOH to NaA is 1:1

Thus number of moles of NaA formed was also $3.612 \times 10^{-3}\text{moles}$

Number of moles of HCl added = $\frac{18.06}{1000} \times 0.1 = 1.806 \times 10^{-3}\text{mol}$

HCl reacts with NaA according to the following equation:



From which mole ratio of NaA to HCl is 1:1. So NaA is present in excess and $(3.612 \times 10^{-3} - 1.806 \times 10^{-3})\text{moles}$ or $1.806 \times 10^{-3}\text{moles}$ of it remain unreacted at the end of chemical reaction.

Also mole ratio of HCl (limited reactant) to HA is 1:1. Thus number of moles of HA formed was also 1.806×10^{-3} moles.

Hence at the end of the above reaction, there was:

- 1.806×10^{-3} moles of HA
- 1.806×10^{-3} moles of NaA

HA being weak acid and NaA being strong salt containing conjugate base (A^-) of the acid, their mixture gives acidic buffer solution whose pH is given by the following equation:

$$pH = pK_a + \log \frac{\text{Number of moles of salt (NaA)}}{\text{Number of moles of acid (HA)}}$$

Substituting $4.92 = pK_a + \log \frac{1.806 \times 10^{-3}}{1.806 \times 10^{-3}}$; whence $pK_a = 4.92 = -\log K_a$

$$K_a = \log^{-1}(-4.92) = 1.2 \times 10^{-5}$$

Hence the dissociation constant for unknown acid is 1.2×10^{-5} .

Example 8

An CH_3COOH/CH_3COONa buffer containing 0.1M CH_3COOH has a pH of 4.742;

- Determine concentration of CH_3COONa in this solution
- To $1dm^3$ of the buffer, 0.01moles of NaOH are added. Calculate the new pH
- To $1dm^3$ of the buffer, 0.01moles of HCl are added. What is the new pH ($K_a(CH_3COOH) = 1.8 \times 10^{-5}$)

Solution

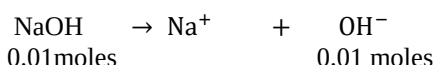
CH_3COOH/CH_3COONa buffer is acidic whose pH is given by the following equation:

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

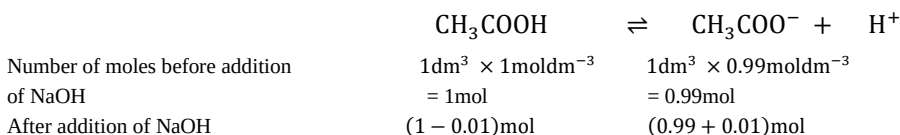
- Substituting given values: $4.742 = -\log(1.8 \times 10^{-5}) + \log \frac{[CH_3COO^-]}{1}$

From which; $[CH_3COO^-] = [CH_3COONa] = 0.99M$

- NaOH being strong base, ionises completely according to the following equation:



Introduction of OH^- shifts the position of chemical equilibrium of the buffer solution to the right as shown below



Thus at the new equilibrium:

$$[CH_3COOH] = \frac{(1-0.01)mol}{1dm^3} = 0.99M$$

$$[CH_3COO^-] = \frac{(0.99+0.01)mol}{1dm^3} = 1M$$

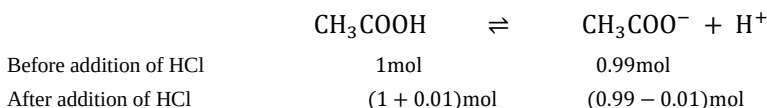
Then the new pH = $-\log(1.8 \times 10^{-5}) + \log\left(\frac{1}{0.99}\right) = 4.749$

Hence the new pH after addition of NaOH is 4.749

(c) HCl being strong acid, ionises completely according to the following equation:



An introduction of H^+ shifts the position of chemical equilibrium of the buffer solution to the left as shown below:



Thus at the new equilibrium:

$$[\text{CH}_3\text{COOH}] = \frac{(1+0.01)\text{mol}}{1\text{dm}^3} = 1.01\text{M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{(0.99-0.01)\text{mol}}{1\text{dm}^3} = 0.98\text{M}$$

$$\text{Then the new pH} = -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.98}{1.01}\right) = 4.732$$

Hence the new pH after addition of the acid is 4.732

APPLICATION OF BUFFER SOLUTIONS

Generally buffer solutions are useful in various systems which function properly under certain specified narrow range of pH. They have the following practical applications like:

- **Physiological uses in keeping correct pH for enzymes in various organisms** to work. For example, a buffer of carbonic acid and bicarbonate is present in **blood plasma** to maintain pH between 7.35 and 7.45.
- **Pharmaceutical uses** like in preparation of shampoo and baby lotion.
- **Industrial uses** like in fermentation processes and in setting the correct conditions for dyes and colouring fabrics.
- **Preparation of biological samples** that are used in research.
- **Chemical analysis and calibration of pH meters.**

DIGGING DEEPER EXERCISE 17

EXERCISE 17A: BINDER QUESTIONS

Question 1

How a buffer solution with pH of 3 manages to stabilise the pH against the addition of acid or base?

Question 2

It is known that, when water is added to acidic or basic solution, concentration of the solution and hence its pH changes. However, the change in pH is not witnessed when the dilution is done over a buffer solution.

- (i) Why pH of a buffer solution does not change on dilution?
- (ii) How the dilution affects buffer capacity?

Question 3

Does the pH of a solution increase, decrease, or stay the same when you add solid ammonium chloride to a solution of 0.10M NH_3 ?

Question 4

A buffer solution was prepared which had a concentration of 0.2mol dm^{-3} in ethanoic acid and 0.1mol dm^{-3} in sodium ethanoate. If the K_a for ethanoic acid is $1.74 \times 10^{-5} \text{mol dm}^{-3}$, calculate the theoretical hydrogen ion concentration and pH of the buffer solution.

Question 5

What is the pH of a buffer solution made from dissolving 2.0g of benzoic acid and 5.0g of sodium benzoate in 250cm^3 of water? $K_a(\text{benzoic acid}) = 6.3 \times 10^{-5} \text{mol dm}^{-3}$.

Question 6

Calculate the pH of a buffer made by mixing 100cm^3 of a 0.40 M sodium propanoate and 50cm^3 of 0.2M propanoic acid solutions. $K_a(\text{propanoic acid}) = 1.3 \times 10^{-5} \text{mol dm}^{-3}$.

Question 7

Calculate the pH of buffer solution made by mixing together 100cm^3 of 0.100M ethanoic acid and 50cm^3 of 0.400M sodium ethanoate, given that K_a for ethanoic acid is $1.74 \times 10^{-5} \text{mol dm}^{-3}$.

Question 8

What mass of sodium nitrite should be added to 1L of 1.5M nitrous acid so as to prepare buffer solution that can maintain a pH of 3.40 using? $K_a = 4.5 \times 10^{-5}$ for nitrous acid.

EXERCISE 17B: REAL QUESTIONS

Question 9

Buffers are crucial to physiology of human beings. Give three examples of buffers in the human body.

Question 10

Your friend **Kipute**, read the following statement from a chemistry book: **For buffer to be effective, it should possess equal concentrations of both of its components such that $\text{pH} = \text{p}K_a$.** "Hmmmh! Why do we study calculations of pH of buffers while in real life the pH will always be equal to $\text{p}K_a$? And why in the most of those calculations, the concentrations are different? What is the use of wasting our time and energy for applying Henderson-Hasselbalch equation while in real life only the $\text{p}K_a$ value is required to know the pH? She asked herself with small voice whispering inside her head.

If **Kipute** could ask those questions to you, what would be your response?

Question 11

You were given with four different acetate buffers. The concentration ratio, [Acetate]: [Acetic acid] for each buffer was as follows:

Buffer 1: The ratio is 2: 2

Buffer 2: The ratio is 1: 2

Buffer 3: The ratio is 3: 3

Buffer 4: The ratio is 2: 1

- (i) Which buffer has the highest pH?
- (ii) Which buffer has the greatest capacity?
- (iii) Should we add a small amount of strong acid or strong base to convert 1 to 2?
- (iv) Should we add a small amount of strong acid or strong base to convert 3 to 4?
- (v) Which buffers have the same pH?
- (vi) Which buffer(s) works best?

In each case give a reason (s) to justify your answer.

Question 12

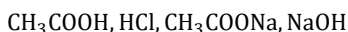
The laboratory technician, **Mr. Akilikubwa** was given a task to prepare the buffer solution which perform best at pH of 2. The following, are only acids present in the laboratory:

1. Acetic acid ($pK_a = 4.74$)
2. Chlorous acid ($pK_a = 1.95$)
3. Formic acid ($pK_a = 3.74$)

Advise **Mr. Akilikubwa** on the choice of the best acid to use.

Question 13

You have been provided with the following chemicals in the laboratory:



- (i) What a type of buffer solution can be made from given chemicals?
- (ii) Give three possible pairs of chemicals which may act as buffer solution.
- (iii) What amount should be taken for each component of pair in (ii) above to make the buffer work at best level.

EXERCISE 17C: HOT QUESTIONS**Question 14**

Increasing temperature of a buffer system is said to decrease the buffer capacity. Explain why.

Question 15

By referring to the following Henderson – Hasselbalch equation, explain factors affecting pH of buffer solution.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Question 16

In what ratio by volume should a 0.3mol dm^{-3} of ethanoic acid be mixed with a 0.3mol dm^{-3} solution of sodium ethanoate to give a buffer solution of pH 5.6? K_a for ethanoic acid is $1.74 \times 10^{-5} \text{ mol dm}^{-3}$.

Question 17

You have 100mL of 1 M ammonia solution ($pK_a=9.25$). What volume of 1 M hydrochloric acid is needed to prepare buffer with pH=9.5?

Question 18

During a titration NaOH solution of concentration 0.100M was added to 30.0cm^3 of 0.100M propanoic acid.

- (a) What property is shown by the reaction mixture when 15.0cm^3 of NaOH has been added to the propanoic acid?
- (b) Calculate the pH of the reaction mixture at this stage. Propanoic acid has $K_a = 1.35 \times 10^{-5}$.

Question 19

A buffer solution of $\text{pH} = 3.87$ contains 7.40gdm^{-3} of propanoic acid together with a quantity of sodium propanoate. K_a for propanoic acid $= 1.35 \times 10^{-5}\text{mol dm}^{-3}$ at 298K .

- (a) Calculate the concentration in gdm^{-3} of sodium propanoate, $\text{C}_2\text{H}_5\text{CO}_2\text{Na}$, in the solution, stating any assumptions made.
- (b) If the sodium propanoate were to be replaced by anhydrous magnesium propanoate, calculate the concentration of magnesium propanoate in gdm^{-3} , required to give a buffer of the same pH .

Question 20

- (a) Calculate the pH of 0.100mol dm^{-3} sodium hydroxide solution at 25°C . The value of K_w at this temperature is $1 \times 10^{-14}\text{mol}^2\text{dm}^{-6}$.
- (b) 100cm^3 of 0.100mol dm^{-3} sodium hydroxide solution was added to 100cm^3 of 0.200mol dm^{-3} ethanoic acid.
 - (i) Find the concentration of ethanoic acid in the mixture.
 - (ii) Calculate the concentration of sodium ethanoate in the mixture.
 - (iii) Calculate the pH of the mixture at 25°C ; K_a for ethanoic acid at this temperature is $1.8 \times 10^{-5}\text{mol dm}^{-3}$.
 - (iv) State and explain what happens if a small amount of hydrochloric acid is added to this mixture?

Question 21

Calculate the pH in the solution formed by adding 10mL of 0.05M NaOH to 40mL of 0.0250M benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$, $K_a = 6.3 \times 10^{-5}$).

Question 22

Calculate the pH in the solution formed by adding 10mL of 0.1M HCl to 20mL of 0.1M NH_3 .

$$K_b(\text{NH}_3) = 1.8 \times 10^{-5}$$

Question 23

For acetic acid, $K_a = 1.76 \times 10^{-5}$ at 25°C .

- (a) Calculate the pH in a solution prepared by dissolving 0.070mol of acetic acid and 0.035mol of sodium acetate in water and adjusting the volume to 500mL .
- (b) Suppose 0.015mol of HCl is added to the buffer from part a. Calculate the pH of the solution that results (assume that the total solution volume remains 500mL).
- (c) Suppose 0.015mol of HCl were added to 500.0mL of pure water instead of the buffer solution in part a. Calculate the pH of the solution that results (again, assume that the total solution volume remains 500.0mL).

Question 24

A sample of 1.25L of HCl gas at 21°C and 0.950atm is bubbled through 0.5L of 0.15M NH_3 solution. Calculate the pH of the resulting solution assuming that all the HCl dissolves and that the volume of the solution remains 0.5L . $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$

Chapter 18

SALT HYDROLYSIS

Salts are ionic compounds that result from neutralisation reaction of an acid and a base. They are composed of related numbers of cations and anions so that the product is electrically neutral. These component ions can be inorganic, such as bromide ion (Br^-) and potassium ion (K^+) or organic, such as acetate (CH_3COO^-) and can be mono-atomic, such as chloride ion (Cl^-) or polyatomic, such as nitrate (NO_3^-) and ammonium ion (NH_4^+). They can also be simple ion, such as Ag^+ or complex ion, such as $[\text{Cu}(\text{NH}_3)_4]^+$

The ion-ion interactions between cations and anions of salt, are very strong making the physical state of salt to be solid.

So **salt** can simply be defined as *the compound which consists of ions in its solid state*. Thus salts consist of **cations** and **anions**.

- Always cations are **acidic** while anions are **basic**. If cation is **the conjugate acid** of weak base, then the cation is **strong acid** and if cation is **conjugate acid** of **strong base** then the cation is **weak acid**.
- On another hand, if anion is the **conjugate base** of **weak acid** then the anion is **strong base** and if the anion is **conjugate base** of **strong acid** then the anion is **weak base**.

Examples of strong acid cations are NH_4^+ and Al^{3+} as they are derived from NH_4OH and $\text{Al}(\text{OH})_3$ respectively which are weak bases. Being strong acidic, NH_4^+ and Al^{3+} have high ability of holding OH^- (from base) to form NH_4OH and $\text{Al}(\text{OH})_3$ molecules respectively and eventually to large extent NH_4OH and $\text{Al}(\text{OH})_3$ exist as molecules and not as ions.

Examples of weak acid cations are Na^+ and K^+ as they are derived from NaOH and KOH respectively which are strong bases. Being weak acid, Na^+ and K^+ are unable (low ability) to hold OH^- (from base) to form NaOH and KOH molecules respectively and eventually the molecules do not exist as the two (NaOH and KOH) ionises completely to give their respective ions.

Examples of strong base anions are CH_3COO^- and CN^- as they are derived from CH_3COOH and HCN respectively which are weak acids. Being strong bases, CH_3COO^- and CN^- have high ability of holding H^+ (from acid) to form CH_3COOH and HCN molecules respectively and eventually to large extent CH_3COOH and HCN exist as molecules and not as ions.

Examples of weak base anions are Cl^- and NO_3^- as they are derived from HCl and HNO_3 respectively which are strong acids. Being weak acids Cl^- and NO_3^- are unable to hold H^+ (from acid) to form HCl and HNO_3 molecules respectively and eventually the molecules do not exist as the two (HCl and HNO_3) ionises completely to give their respective ions.

Strong acid cation and strong base anion can attract (or be attracted by) OH^- and H^+ respectively from self ionisation of water thus reacting with the water in **salt hydrolysis**.

- Salts which contain strong acid cation or weak base anion have significant degree of covalent characters. These salts undergo salt hydrolysis in aqueous solution yielding acidic solution or basic solution according to the nature of the salt
- Generally, ability to hydrolyse in water is covalent character, i.e. salts (ionic compounds) with high degree of polarisation undergo salt hydrolysis (the greater degree of covalence, the higher ability to hydrolyse in water).

Definition of salt hydrolysis

Salt hydrolysis is a chemical reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity.

CATIONIC AND ANIONIC SALT HYDROLYSIS

Salt hydrolysis can be classified into two main categories:

- Cationic salt hydrolysis
- Anionic salt hydrolysis

Cationic salt hydrolysis

*This is the chemical reaction between water and salt containing **strong acid cation** and **weak base anion** to give acidic solution.*

A good example of a salt which undergo cationic salt hydrolysis (or simply cationic hydrolysis) is ammonium chloride (NH_4Cl) in which NH_4^+ is strong acid cation while Cl^- is weak base anion. Salts which undergo cationic hydrolysis are known as **acidic salts**.

How acidic solution is formed after addition of NH_4Cl to water?

Before addition of the salt (NH_4Cl), water undergo self ionisation according to the following equation:
 $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \dots\dots\dots(\text{i})$

In which $[\text{H}^+] = [\text{OH}^-]$ and this explains for neutrality of the pure water.

Addition of the salt (NH_4Cl) to the water is equivalent to addition of NH_4^+ and Cl^- because NH_4Cl being strong salt ionises completely according to the following equation:



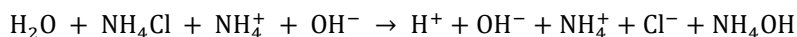
NH_4^+ being strong acid cation, combine with OH^- from self ionisation of water (from equation (i)) to form NH_4OH according to the following equation.



While Cl^- being weak base anion is unable to combine with H^+ from self ionisation of water (from equation (i)) i.e. $\text{Cl}^- + \text{H}^+ \rightarrow \text{No reaction}$

So concentration of hydroxyl ions (OH^-) is decreased while that of hydrogen ions (H^+) remain unchanged thus shifting position of chemical equilibrium in self ionisation of water to the right and eventually the concentration of hydrogen ions become greater than that of hydroxyl ions i.e. $[\text{H}^+] > [\text{OH}^-]$ and hence the solution become acidic.

The overall reaction equation can simply be obtained through combining (i), (ii) and (iii) by taking (i) + (ii) + (iii) as follows:

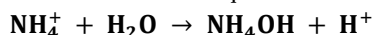


Cancelling like terms gives the overall reaction equation which is:



From the above overall reaction equation, it is clearly understood that only cation of the salt has undergone change and hence the name **cationic hydrolysis**.

The simplified overall reaction equation which shows changing species only is given below:



Where the formation of H^+ accounts for acidity of the solution.

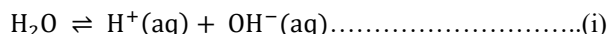
Anionic salt hydrolysis

*This is the chemical reaction between water and salt containing **strong base anion** and **weak acid cation** to give basic solution.*

A good example of salt which undergo anionic salt hydrolysis (or simply **anionic hydrolysis**) is sodium ethanoate (CH_3COONa) in which CH_3COO^- is strong base anion while Na^+ is weak acid cation. Salts which undergo cationic hydrolysis are known as **basic salts**.

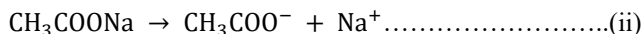
How basic solution is formed after addition of CH_3COONa to water?

Before addition of the salt (CH_3COONa), water undergo self ionisation according to the following equation:



In which $[\text{H}^+] = [\text{OH}^-]$ and hence the pure liquid is neutral.

Addition of the salt (CH_3COONa) to the water is equivalent to addition of CH_3COO^- and Na^+ because CH_3COONa being strong salt is fully ionised according to the following equation:



CH_3COO^- being strong base anion, combines with H^+ from self ionisation of water (equation (i)) to form CH_3COOH according to the following equation:



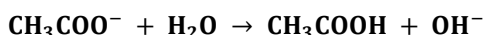
While Na^+ being weak acid cation, is unable to combine with OH^- from self ionisation of water (equation (i)) That is $\text{Na}^+ + \text{OH}^- \rightarrow \text{No reaction}$

So while concentration of hydrogen ions (H^+) is decreased, the hydroxyl ions concentration $[\text{OH}^-]$ remains unchanged thus shifting the position of chemical equilibrium in self-ionisation of water to the right and eventually the concentration of hydrogen ions become smaller than that of hydroxyl ions i.e. $[\text{H}^+] < [\text{OH}^-]$ and hence the solution become basic.

The overall reaction equation can simply be obtained through combining (i), (ii) and (iii) by taking (i) + (ii) + (iii) and cancelling like terms to give the following equation:



From the above overall reaction equation, it is clearly understood that only anionic part of the salt has undergone changes and hence the name anionic hydrolysis. The simplified overall reaction equation which shows changing species is given below as follows:



Where formation of OH^- accounts for alkalinity (basicity) of the solution

What happen when very strong ionic salt like NaCl is mixed with water?

Nothing happen as far as salt hydrolysis is taken to an account.

NaCl being strong ionic salt, contains weak acid cation (Na^+) as well as weak base anion (Cl^-) both of which are unable to combine with OH^- and H^+ from self ionisation of water thus hydroxyl and hydrogen ions concentrations remain unchanged and hence the solution become neutral.

That is: $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ where $[\text{H}^+] = [\text{OH}^-]$ (in pure water)

NaCl being strong ionic salt ionises completely according to the following equation:



However both Na^+ and Cl^- being weak acid cation and weak base anion respectively are unable to combine with either OH^- or H^+ from the water ionisation thus maintaining neutrality of the solution and hence **$\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{No reaction}$**

The same kind of explanation applies for any other strong ionic salt like KCl , CaCl_2 etc., which contain weak acid cation and weak base anion.

Salts which do not undergo hydrolysis such that they give neutral solution when dissolved in water are known as **neutral salts**.

What about salts which contain strong acid cation and strong base anion?

In this case both cation and anion are able to combine with OH^- and H^+ respectively from self ionisation of water and hence the solution may become neutral, acidic or basic depending on the difference in the strengths of bases and acids which are formed.

Examples:

- $\text{CH}_3\text{COONH}_4 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{NH}_4\text{OH}$
- $(\text{NH}_4)_2\text{CO}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{OH} + \text{H}_2\text{CO}_3$
- $\text{Al}_2(\text{CO}_3)_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2\text{CO}_3$

Salts which contain strong acid cation and strong base anion are termed as **weak salts**.

EFFECTS OF SALT HYDROSIS ON PROPERTIES OF SALT SOLUTION

When a salt hydrolyse in water, properties of resulting solution are affected in the following ways:

Colouration of litmus paper

If the salt is introduced to the solution of the salt which undergoes cationic hydrolysis, the blue litmus paper turns red verifying that the solution is acidic as result of the hydrolysis. And if the salt undergoes anionic hydrolysis to give alkaline (basic) solution, the red litmus paper turns blue.

Evolvement of hydrogen gas

When strong electropositive metal is introduced to the solution of salt which undergoes cationic hydrolysis, the hydrogen gas is evolved verifying that the solution is acidic as result of the hydrolysis.

Evolvement of carbon dioxide gas

When carbonate or bicarbonate (hydrogen carbonate) is introduced to the solution which undergoes cationic hydrolysis, the carbon dioxide is evolved verifying that the solution is acidic as result of the hydrolysis

Electrolytic conduction

Usually covalent compounds or ionic compounds (including salts) with high degree of covalence characters as result of their high degree of polarisation are incapable of doing electrolytic conduction due to lack of enough concentration ions which are responsible for doing the conduction. The statement is always true in the molten state of the compound. However, in aqueous solution the compound may conduct electricity if they are capable of undergoing hydrolysis to give enough concentration of free ions which are responsible for doing electrolytic conduction.

Formation of precipitate

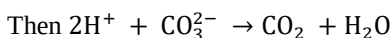
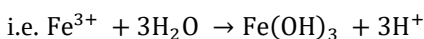
Two clear solutions may give a precipitate when they are mixed if one of the double decomposition products of the reaction between the two salts is capable of undergoing cationic hydrolysis to give the insoluble hydroxide which appears as the precipitate.

Worked examples**Example 1**

Explain what will you **observe** when sodium carbonate is introduced in the solution containing iron (III) ions (Fe^{3+}).

Solution

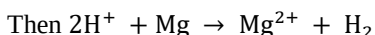
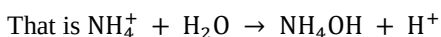
Fe^{3+} being strong acid cation, undergo cationic hydrolysis in aqueous solution to give acidic solution which evolve carbon dioxide CO_2 gas from the carbonate and the gas appears as effervescence of colourless gas which turn lime water milky.

**Example 2**

Hydrogen gas is evolved when magnesium is introduced into a beaker containing aqueous solution of ammonium chloride. Explain.

Solution

NH_4Cl contain strong acidic cation (NH_4^+) and weak basic anion (Cl^-), so in aqueous solution it undergo cationic hydrolysis yielding acidic solution which is responsible of evolving hydrogen gas when magnesium (metal) is introduced in the solution.

**Example 3**

What will you **observe** when sodium metal is introduced into a beaker containing a solution of iron (III) chloride?

Solution

Bubbles of a gas which is recognised by its pop sound, i.e. hydrogen gas is evolved.

Example 4

What will you **observe** when blue litmus paper is dipped into a beaker containing aqueous solution of AlCl_3 ?

Solution

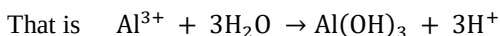
Blue litmus paper turns red

Example 5

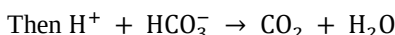
What **happen** when sodium bicarbonate (NaHCO_3) is introduced in a beaker containing aqueous solution of AlCl_3 ?

Solution

In aqueous solution, AlCl_3 undergo cationic hydrolysis yielding acidic solution which reacts with NaHCO_3 to evolve carbon dioxide gas which appears as effervescence of colourless gas that turns lime water milky.



(From AlCl_3)

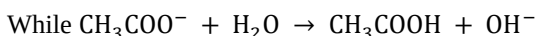
**Example 6**

Aqueous solution of AlCl_3 is acidic while that of CH_3COONa is basic. Explain.

Solution

AlCl_3 contains strong acidic cation, Al^{3+} , and weak basic anion, Cl^- , so in aqueous solution AlCl_3 undergo cationic hydrolysis yielding acidic solution while CH_3COONa contains strong basic anion, CH_3COO^- , and weak acidic cation, Na^+ ; so CH_3COONa undergo anionic hydrolysis yielding basic solution. i.e. $\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{H}^+$

Where presence of H^+ determines the acidity of solution of AlCl_3



Where presence of OH^- determines the basicity of solution of CH_3COONa .

Example 7

AlCl_3 reacts chemically with water while NaCl does not. Explain.

Solution

AlCl_3 is the salt that contains strong acid cation, Al^{3+} , and weak base anion, Cl^- . So with water, the salt undergo cationic hydrolysis yielding acidic solution while NaCl being strongly ionic as it contains weak acid cation, Na^+ , and weak base anion, Cl^- , does not hydrolyse in water.



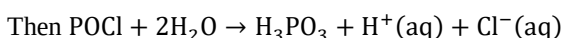
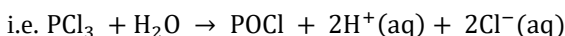
While $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{No reaction}$

Example 8

PCl_3 is covalent liquid but in aqueous solution it conducts electricity. Explain.

Solution

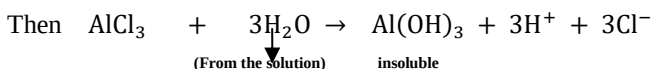
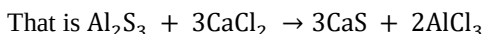
In aqueous solution, PCl_3 hydrolyse yielding enough concentration of H^+ and Cl^- to do electrolytic conduction.

**Example 9**

A precipitate of aluminium hydroxide is observed when a solution of aluminium sulphide is mixed with a solution of calcium chloride in the beaker. Explain.

Solution

After mixing the two solutions, aluminium chloride which is initially formed in the reaction of the two solutions is further undergoing cationic hydrolysis yielding insoluble aluminum hydroxide.

**HYDROLYSIS CONSTANT FOR CATIONIC HYDROLYSIS**

Consider ammonium chloride (NH_4Cl) which undergoes cationic hydrolysis according to the following equation: $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$

From which, $K = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+][\text{H}_2\text{O}]}$ or $K[\text{H}_2\text{O}] = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]}$

If $[\text{H}_2\text{O}]$ is constant, $K[\text{H}_2\text{O}]$ gives another constant which is known as hydrolysis constant, K_h .

Thus $K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]}$ (i)

But the ammonium hydroxide (NH_4OH) produced in the hydrolysis ionises according to the following equation: $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

From which $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$

Or $\frac{[\text{OH}^-]}{K_b} = \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$ (ii)

Substituting (ii) to (i) gives; $K_h = \frac{[\text{OH}^-][\text{H}^+]}{K_b}$

But $[\text{OH}^-][\text{H}^+] = K_w$

Hence for cationic hydrolysis, $K_h = \frac{K_w}{K_b}$

From K_h expression, it should be noted that: **$K_h = K_a$ of cation of the salt which is hydrolysed.**

HYDROLYSIS CONSTANT FOR ANIONIC HYDROLYSIS

Consider sodium ethanoate (CH_3COONa) which undergo anionic hydrolysis according to the following equation: $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$

$$\text{From which, } K = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-][\text{H}_2\text{O}]} \text{ or } K[\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

If $[\text{H}_2\text{O}]$ is constant, $K[\text{H}_2\text{O}]$ gives another constant which is known as hydrolysis constant, K_h .

$$\text{Thus } K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \dots\dots\dots(ii)$$

But ethanoic acid (CH_3COOH) produced in the hydrolysis ionises according to the following equation: $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$\text{From which, } K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$\text{Or } \frac{[\text{H}^+]}{K_a} = \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \dots\dots\dots(ii)$$

$$\text{Substituting (ii) to (i) gives; } K_h = \frac{[\text{H}^+][\text{OH}^-]}{K_a}$$

$$\text{But } [\text{H}^+][\text{OH}^-] = K_w$$

$$\text{Hence for anionic hydrolysis, } K_h = \frac{K_w}{K_a}$$

In this case $K_h = K_b$ for anion of the salt which is hydrolysed.

CONCENTRATION OF HYDROGEN IONS (H^+) IN CATIONIC HYDROLYSIS

Consider ammonium chloride (NH_4Cl) which undergoes cationic hydrolysis according to the following equation: $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$

$$\text{From which } K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]}$$

$$\text{Where } [\text{NH}_4\text{OH}] = [\text{H}^+] \text{ (Their mole ratio is 1:1)}$$

$$\text{And } [\text{NH}_4^+] = [\text{NH}_4\text{Cl}] = [\text{salt}] \text{ (Their mole ratio is 1:1)}$$

$$\text{Then } K_h = \frac{[\text{H}^+]^2}{[\text{salt}]} \text{ or } [\text{H}^+] = \sqrt{K_h[\text{salt}]}$$

$$\text{But } K_h = \frac{K_w}{K_b} \text{ (For cationic hydrolysis)}$$

$$\text{Hence for cationic hydrolysis } [\text{H}^+] = \sqrt{\frac{K_w}{K_b} [\text{salt}]}$$

The pH of the solution is found by taking negative logarithm of $[\text{H}^+]$ as usual,

$$\text{i.e. } \text{pH} = -\log\sqrt{K_h[\text{salt}]} \text{ where } K_h = \frac{K_w}{K_b}$$

CONCENTRATION OF HYDROGEN IONS (H^+) IN ANIONIC HYDROLYSIS

Consider sodium ethanoate (CH_3COONa) which undergoes anionic hydrolysis according to the following equation: $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$

$$\text{From which } K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$\text{Where } [\text{CH}_3\text{COOH}] = [\text{OH}^-] \text{ (Their mole ratio is 1:1)}$$

$$\text{And } [\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COONa}] = [\text{salt}] \text{ (Their mole ratio is 1:1)}$$

$$\text{Then } K_h = \frac{[\text{OH}^-]^2}{[\text{salt}]} \text{ or } [\text{OH}^-] = \sqrt{K_h [\text{salt}]}$$

$$\text{But for anionic hydrolysis, } K_h = \frac{K_w}{K_a}$$

$$\text{Thus } [\text{OH}^-] = \sqrt{\frac{K_w}{K_a} [\text{salt}]}$$

$$\text{But } [\text{OH}^-] [\text{H}^+] = K_w; \text{ from which } [\text{H}^+] = \frac{K_w}{[\text{OH}^-]}$$

$$\text{It follows that, } [\text{H}^+] = \frac{K_w}{\sqrt{\frac{K_w}{K_a} [\text{salt}]}} = \sqrt{\frac{K_a K_w}{[\text{salt}]}}$$

$$\text{Hence for anionic hydrolysis; } [\text{H}^+] = \sqrt{\frac{K_a K_w}{[\text{salt}]}}$$

The pH of the solution is found by taking negative logarithm of $[\text{H}^+]$ as usual,

$$\text{i.e. pH} = -\log \sqrt{\frac{K_a K_w}{[\text{salt}]}}$$

Don't forget that:

- For cationic hydrolysis, $K_h = K_a$ of cation of the salt which is hydrolysed.
- For anionic hydrolysis, $K_h = K_b$ of anion of the salt which is hydrolysed.

Worked examples

Example 10

4.1g of CH_3COONa was dissolved in 500cm^3 of water; calculate: $[\text{CH}_3\text{COO}^-]$, $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$ and pH of this solution.

Use $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5} \text{mol dm}^{-3}$.

Solution

$$\begin{aligned} [\text{CH}_3\text{COO}^-] &= [\text{CH}_3\text{COONa}] = \frac{\text{Mass concentration of } \text{CH}_3\text{COONa in g dm}^{-3}}{\text{Molar mass of } \text{CH}_3\text{COONa}} \\ &= \frac{4.1}{0.5 \times 82} \text{M} = 0.1\text{M} \end{aligned}$$

$$\text{Thus } [\text{CH}_3\text{COO}^-] = 0.1\text{M}$$

CH_3COONa undergoes anionic hydrolysis to give the solution whose $[\text{H}_3\text{O}^+]$ is given by the following

$$\text{equation: } [\text{H}_3\text{O}^+] = \sqrt{\frac{K_a K_w}{[\text{salt}]}} = \sqrt{\frac{1.8 \times 10^{-5} \times 10^{-14}}{0.1}} = 1.34 \times 10^{-9} \text{M}$$

$$\text{Thus } [\text{H}_3\text{O}^+] = 1.34 \times 10^{-9} \text{M}$$

$$\text{From } [\text{H}_3\text{O}^+] [\text{OH}^-] = K_w = 10^{-14}; [\text{OH}^-] = \frac{10^{-14}}{1.34 \times 10^{-9}} = 7.46 \times 10^{-6} \text{M}$$

$$\text{Thus } [\text{OH}^-] = 7.46 \times 10^{-6} \text{M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.34 \times 10^{-9}) = 8.87$$

Hence:

$$[\text{CH}_3\text{COO}^-] = 0.1\text{M}, [\text{H}_3\text{O}^+] = 1.34 \times 10^{-9} \text{M}, [\text{OH}^-] = 7.46 \times 10^{-6} \text{M}$$

pH of the solution is 8.87

Example 11

0.3M solution of NH_4Br is present in aqueous solution. Assume complete dissociation of NH_4Br . Calculate: $[\text{NH}_4^+]$, $[\text{Br}^-]$, $[\text{H}_3\text{O}^+]$, $[\text{NH}_3]$ and pH of the solution.

$$(K_a \text{ of } \text{NH}_4^+ \text{ is } 5.7 \times 10^{-10} \text{M})$$

Solution

NH_4Br is ionised according to the following equation: $\text{NH}_4\text{Br} \rightarrow \text{NH}_4^+ + \text{Br}^-$

From which mole ratio of NH_4Br to both NH_4^+ and Br^- is 1: 1;

$$\text{Thus } [\text{NH}_4\text{Br}] = [\text{NH}_4^+] = [\text{Br}^-] = 0.3\text{M}$$

NH_4Br undergoes cationic hydrolysis according to the following equation:



$(\text{NH}_3(\text{aq}) \text{ is equivalent to } \text{NH}_4\text{OH} \text{ and } \text{H}_3\text{O}^+ \text{ is equivalent to } \text{H}^+(\text{aq}))$

$$\text{From which } [\text{NH}_3] = [\text{H}_3\text{O}^+] = \sqrt{K_h [\text{salt}]}$$

But for cationic hydrolysis, $K_h = K_a$ of cation of the salt where in this case, K_a of NH_4^+ .

$$\text{It follows that } [\text{NH}_3] = [\text{H}_3\text{O}^+] = \sqrt{K_a [\text{salt}]} = \sqrt{5.7 \times 10^{-10} \times 0.3} = 1.3 \times 10^{-5} \text{M}$$

$$\text{And } \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.3 \times 10^{-5}) = 4.89$$

Hence:

$$[\text{NH}_4^+] = 0.3\text{M}, [\text{Br}^-] = 0.3\text{M}, [\text{NH}_3] = 1.3 \times 10^{-5}\text{M},$$

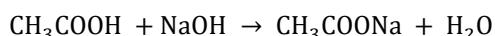
$$[\text{H}_3\text{O}^+] = 1.3 \times 10^{-5}\text{M}, \text{pH of the solution is } 4.89$$

Example 12

25cm³ of 0.1M CH_3COOH is titrated against sodium hydroxide solution and 25cm³ of the alkaline solution was found to be used at neutralisation point. Calculate pH of the solution at the end point of the neutralisation. Use K_a of $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}\text{M}$

Solution

CH_3COOH reacts with NaOH according to the following equation:



From which mole ratio of CH_3COOH to CH_3COONa is 1: 1

Thus at neutralisation point:

Number of moles of CH_3COOH = Number of moles of CH_3COONa produced

$$= \frac{25}{1000} \times 0.1 \text{moles} = 2.5 \times 10^{-3} \text{moles}$$

$$\text{And } [\text{CH}_3\text{COONa}] = \frac{n}{v} = \frac{2.5 \times 10^{-3} \text{mol}}{(25+25) \times 10^{-3} \text{dm}^3} = 0.05\text{M}$$

The CH_3COONa which is produced, undergoes anionic hydrolysis to give basic solution whose pH is given by the following equation: $\text{pH} = -\log \sqrt{\frac{K_a K_w}{[\text{salt}]}} = -\log \sqrt{\frac{1.8 \times 10^{-5} \times 10^{-14}}{0.05}} = 8.72$

Hence pH of the solution at neutralisation point is 8.72

Example 13

20cm³ of 0.05M NaOH is titrated against 0.05M HCl and 20cm³ of the acid was found to be used at neutralisation point. Calculate pH of the solution at the end point of the neutralisation.

Solution

$$\text{Number of moles of NaOH used} = \frac{20}{1000} \times 0.05 \text{ moles} = 10^{-3} \text{ moles}$$

$$\text{Number of moles of HCl used} = \frac{20}{1000} \times 0.05 \text{ moles} = 10^{-3} \text{ moles}$$

NaOH reacts with HCl according to the following equation: $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

From which mole ratio of NaOH to HCl is 1:1.

Thus neither NaOH nor HCl is in excess as the given amounts of base and acid satisfy the mole ratio.

And because NaCl is incapable of undergoing salt hydrolysis; the solution remains neutral.

$$\text{That is } [\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ mol dm}^{-3}$$

$$\text{It follows that } \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 10^{-7} = 7$$

Hence pH of the solution at neutralisation point is 7

Example 14

100cm³ of 0.01M HCOOH is titrated against 0.1M NaOH. Calculate the pH;

- Before the titration begin
- When 15cm³ of NaOH solution has been added
- When 10cm³ of NaOH solution has been added
- When 5cm³ of NaOH solution has been added

$$(\text{K}_a \text{ of HCOOH} = 1.8 \times 10^{-4})$$

Solution

$$(a) [\text{H}_3\text{O}^+] = \sqrt{\text{K}_a \text{C}}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\sqrt{\text{K}_a \text{C}} = -\log\sqrt{1.8 \times 10^{-4} \times 0.01} = 2.87$$

Thus pH of the solution before titration was 2.87.

$$(b) \text{ Number of moles of HCOOH} = \frac{100}{1000} \times 0.01 \text{ moles} = 0.001 \text{ moles}$$

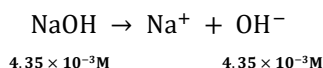
$$\text{Number of moles of NaOH} = \frac{15}{1000} \times 0.1 \text{ moles} = 0.0015 \text{ moles}$$

$$\text{Thus number of moles of unreacted NaOH} = (0.0015 - 0.001) \text{ moles} = 0.0005 \text{ moles}$$

$$\text{Total volume of solution} = (100 + 15) \text{ cm}^3 = 115 \text{ cm}^3$$

$$\text{Thus } [\text{NaOH}] \text{ after the reaction} = \frac{0.0005 \text{ mol}}{115 \times 10^{-3} \text{ dm}^3} = 4.35 \times 10^{-3} \text{ M}$$

NaOH being strong base ionises according to the following equation:



$$\text{It follows that } \text{pOH} = -\log[\text{OH}^-] = -\log(4.35 \times 10^{-3}) = 2.36$$

$$\text{But } \text{pH} = 14 - \text{pOH}; \text{ thus } \text{pH} = 14 - 2.36 = 11.64$$

Hence pH of the solution after addition of 15cm³ of NaOH was 11.64.

$$(c) \text{ Number of moles of NaOH} = \frac{10}{1000} \times 0.1 \text{ moles} = 0.001 \text{ moles}$$

That is number of moles of NaOH = number of moles HCOOH which satisfy the required mole ratio and hence neither of the reactant is in excess.

But HCOONa produced in the reaction undergoes anionic hydrolysis to give solution whose pH is given by the following equation: $\text{pH} = -\log \sqrt{\frac{K_a K_w}{[\text{salt}]}}$

$$\text{But } [\text{salt}] = [\text{HCOONa}] = \frac{0.001 \text{ moles}}{(100+10) \times 10^{-3} \text{ dm}^3} = 9.09 \times 10^{-3} \text{ M}$$

$$\text{Therefore pH} = -\log \sqrt{\frac{1.8 \times 10^{-4} \times 10^{-14}}{9.09 \times 10^{-3}}} = 7.85$$

Hence pH of the solution after addition of 10 cm^3 of NaOH was 7.85.

$$(d) \text{ Number of moles of HCOOH} = \frac{100}{1000} \times 0.01 \text{ moles} = 0.001 \text{ moles}$$

$$\text{Number of moles of NaOH} = \frac{5}{1000} \times 0.1 \text{ moles} = 0.0005 \text{ moles}$$

$$\text{Thus number of moles of unreacted HCOOH} = (0.001 - 0.0005) \text{ moles} = 0.0005 \text{ moles}$$

$$\text{Total volume of solution} = (100 + 5) \text{ cm}^3 = 105 \text{ cm}^3$$

$$\text{Thus } [\text{HCOOH}] \text{ after the reaction} = \frac{0.0005 \text{ mol}}{105 \times 10^{-3} \text{ dm}^3} = 4.7619 \times 10^{-3} \text{ M}$$

But from the mole ratio and using the fact that NaOH is limited reactant;

Number of moles of HCOONa formed after the reaction = Number of moles of NaOH reacted

Thus number of moles of HCOONa produced was 0.0005 moles

$$\text{And } [\text{HCOONa}] = \frac{0.0005 \text{ mol}}{105 \times 10^{-3} \text{ dm}^3} = 4.7619 \times 10^{-3} \text{ M}$$

The unreacted HCOOH and the produced HCOONa forms acidic buffer solution whose pH is given by the following equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{HCOONa}]}{[\text{HCOOH}]}$$

$$\text{Substituting pH} = -\log(1.8 \times 10^{-4}) + \log \frac{4.7619 \times 10^{-3} \text{ M}}{4.7619 \times 10^{-3} \text{ M}} = 3.74$$

Hence pH of the solution after addition of 5 cm^3 of NaOH was 3.74

DIGGING DEEPER EXERCISE 18

EXERCISE 18A: BINDER QUESTIONS

Question 1

Explain whether the following solutions will be acidic, basic or neutral at the equivalence point by indicating the major species that regulates the pH for each solution:

- (i) A strong acid titrated with a strong base
- (ii) A weak acid titrated with a strong base
- (iii) A weak base titrated with a strong acid

Question 2

Predict if the following salts in water would be neutral, acidic, or basic:

- a) KF b) NaNO_3 c) NaClO_4 d) NH_4Cl e) FeCl_3 f) Na_2CO_3

Question 3

Arrange the following solutions ascending order of their pH. Rationalise your arrangement.

0.01MNaBr , 0.01MKCN , $0.01\text{MNH}_4\text{Br}$

Question 4

Among the following, which compound has highest pH? Give a reason.

$0.1\text{MCH}_3\text{COONH}_4$, $0.1\text{MNa}_2\text{CO}_3$, $0.1\text{MNH}_4\text{Cl}$, 0.1MNaNO_3

Question 5

The hypothetical inorganic salt **CD** is made from strong base and weak acid. With reason and help of chemical equation, state whether an aqueous solution of CD is acidic, basic or neutral.

EXERCISE 18B: REAL QUESTIONS

Question 6

Although AlCl_3 is highly covalent in characters, its aqueous solution conducts electricity. Explain.

Question 7

Explain what happens when baking soda is introduced into an aqueous solution of NH_4Br ?

Question 8

Explain what will you observed when a litmus paper is dipped into a solution of potassium cyanide.

Question 9

When sodium methanoate solution is added to the onion juice, the onion loses its smell; why?

Question 10

Kipute introduced magnesium into a solution ammonium sulphate. Immediately after that, she brought a burning candle near the solution and then the sound of small explosion was heard. Explain.

EXERCISE 18C: HOT QUESTIONS**Question 11**

What is the pH of a 0.0500 M solution of ammonium chloride, NH_4Cl . $K_a = 5.65 \times 10^{-10}$ for NH_4^+

Question 12

What is the pH of a 0.100 M solution of methyl ammonium chloride ($\text{CH}_3\text{NH}_3\text{Cl}$). K_a of the methyl ammonium ion (CH_3NH_3^+) = 2.7×10^{-11}

Question 13

Calculate the pH of a 0.15 M solution of sodium acetate CH_3COONa . ($K_a = 1.8 \times 10^{-5}$)

Question 14

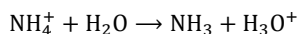
Given the $\text{p}K_a$ for ammonium ion is 9.26, what is the pH of 1.00 L of solution which contains 5.45 g of NH_4Cl ?

Question 15

Calculate the pH of a solution after 25.0mL of 0.1M hydrofluoric acid is titrated with 12.5mL of 0.200M lithium hydroxide. ($K_a = 6.8 \times 10^{-4}$ for hydrofluoric acid)

Question 16

When ammonium salts are dissolved in water, the following reaction occurs.



- Identify the acid/base conjugate pairs in this reaction by writing appropriate symbols under each of the species in the equation above.
- Write an expression for the dissociation constant, K_a , for $\text{NH}_4^+(\text{aq})$.
- Calculate the pH of a solution of ammonium chloride of concentration 0.100M at 298 K, the K_a value for NH_4^+ being $5.62 \times 10^{-10}\text{M}$ at this temperature.
- How would you modify the solution of ammonium chloride in (c) to make it more resistant to changes in pH when small amounts of acid or base are added to it?

Chapter 19

SOLUBILITY AND SOLUBILITY PRODUCT**INTRODUCTION**

In everyday life we are coming across to insoluble substances; from silver iodide, a solid that is recognised by its antiseptic properties, calcium carbonate, the active ingredient in many over-the-counter chewable antacids, magnesium hydroxide, the active ingredient in milk of magnesia to hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), the mineral which is a source of phosphate for fertilizers. These substances are not actually hundred percent insoluble in water (Remember, everything dissolve in the universal solvent called water, even if to very small extent which cannot be recognised by eyes!), they dissolve by very small amount; they are actually **sparingly soluble substances**. Because they dissolve only slightly to give free ions, they are weak electrolytes and thus they are also known as **sparingly soluble electrolytes**.

So **sparingly soluble electrolytes** are substances (compounds) which dissolve only slightly in aqueous solution to give free ions. They are approximately insoluble substances in a sense that very small portion of them go in solution as ions. Other examples of sparingly soluble substance are AgCl , BaSO_4 and $\text{Al}(\text{OH})_3$.

When the sparingly soluble substance dissolves in a solvent, usually water, the dissociated ions are present in the solvent phase in the same proportions as they are found in the solid phase. In other words, the stoichiometry of the dissociation is preserved just like it is in any chemical reaction.

Consider A_nB_m to be sparingly soluble electrolyte which dissolves according to the following equation:
 $\text{A}_n\text{B}_m(\text{s}) \rightleftharpoons n\text{A}^{m+}(\text{aq}) + m\text{B}^{n-}(\text{aq})$

From which $K_c = \frac{[\text{A}^{m+}]^n [\text{B}^{n-}]^m}{[\text{A}_n\text{B}_m]}$ or $K_c [\text{A}_n\text{B}_m] = [\text{A}^{m+}]^n [\text{B}^{n-}]^m$

A_nB_m being solid and sparingly soluble, its concentration is invariable;

i.e. $[\text{A}_n\text{B}_m] = \text{constant}$

Thus $K_c [\text{A}_n\text{B}_m]$ gives another constant, which is known as **solubility product, K_{sp}**

Hence $K_{sp} = [\text{A}^{m+}]^n [\text{B}^{n-}]^m$

Definitions of solubility and solubility product**Solubility**

Generally, **solubility** is the ability of a certain solute to be dissolved in a given solvent which is given as the amount of the substance dissolved in one litre of saturated solution at given temperature.

- It can be expressed in g/L as **mass solubility** or mol/L as **molar solubility**.

Among the two methods, the former (g/L) is more common and when we speak about 'solubility' we always refer to the one expressed in g/L (in contrary to concentration which is commonly given in mol/L).

- **Molar solubility** is the number of moles of a solute in one litre of a saturated solution
- **Mass solubility** (commonly termed as simply, **solubility**) is the number of grams of a solute in one litre of a saturated solution.

Solubility product, K_{sp}

Solubility product is an equilibrium constant which is given as the product of concentration of ions in a saturated solution of sparingly soluble electrolyte, each raised to the power of their stoichiometric coefficients in the balanced chemical equation.

- If A_nB_m is the sparingly soluble substance its solubility product, K_{sp} , is given by $[\text{A}^{m+}]^n [\text{B}^{n-}]^m$ and its unit is $(\text{mol dm}^{-3})^{n+m}$

- Like any other equilibrium constant, the value solubility product does not depend on concentration of ions present in solution, it is only temperature dependent.
- Solubility product is useful in comparing molar solubility of sparingly soluble substances with **the same number of ions per formula unit** like AgCl and ZnS or Fe(OH)₂ and PbCl₂ such that the greater the value the greater molar solubility of the salt. However solubility product cannot be used to compare molar solubility of two compounds with different formulas like ZnS and Fe(OH)₂ or AgCl and PbCl₂ which have different number of ions per formula unit. In this case it is necessary to calculate the solubility of each compound to know which compound is more soluble.

UNDERSTANDING SOLUBILITY AND SOLUBILITY PRODUCT

To build concrete foundation for understanding solubility and solubility product, it is important to have deeper understanding of the two terms. We are going to start with solubility.

Solubility

Imagine adding a small amount of table salt to a glass of water, stirring until all the salt has dissolved, and then adding a bit more. You can repeat this process until the salt amount that has been dissolved in the solution reaches its natural limit. You can be certain that you have reached this limit because, no matter how long you stir the solution, undissolved salt remains. The amount of salt that has been dissolved in the solution at this point is known as its solubility.

The solubility of a solute in a particular solvent is the maximum amount of solute that can be dissolved under given conditions when the dissolution process is at equilibrium.

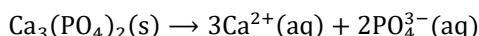
When the solute amount in the solution is equal to its solubility, the solution is said to be **saturated** with that solute. If the solute amount is less than its solubility, the solution is said to be **unsaturated**.

Solutions may be prepared in which the solute amount exceeds its solubility. Such solutions are said to be **supersaturated**, and they are good examples of non-equilibrium states. For example, immediately after opening the container of the carbonated beverage, the beverage is supersaturated with carbon dioxide gas and if the container is left open, the carbon dioxide amount will decrease until it reaches its solubility (equilibrium).

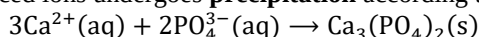
Solubility product

When sparingly soluble electrolyte, say Ca₃(PO₄)₂ is dissolved in the solution, two processes occur:

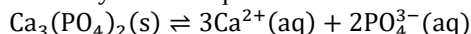
First process: The electrolyte undergoes **dissolution** according to the following equation:



Second process: The produced ions undergoes **precipitation** according to the following equation:



Thus the two processes may be combined to get the following reversible process which represents the action of dissolving the given electrolyte in the aqueous solution.

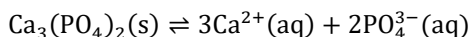


The equilibrium of the above reversible process is achieved when *the rate of dissolution is equal to the rate of precipitation* and the equilibrium constant obtained under this constant is what we call solubility product. Now, why and how 'solubility' enters to the term of our equilibrium constant resulting to 'solubility product'? Is it solubility product the product (result of multiplication) of 'solubilities' as the name suggests? To answer these crucial questions, we are going to consider the following scenario:

Imagine certain mass of our electrolyte Ca₃(PO₄)₂ is added to **1L** of water. And assume that the mass is equivalent to '**a**' moles (after dividing the mass by molar mass of the electrolyte). Also assume that amount of the electrolyte has negligible volume such that the volume of solution remains to be **1L**.

Now, let **x** represents the amount of the electrolyte that dissolves into solution after any time, **t**. The dissolution process will continue and hence **x** will increase until the equilibrium is reached where the limit of the solvent to dissolve more solute has been reached and we can call this limit amount, '**s**'

which by definition is actually the solubility of the electrolyte. This explanation can be summarised in the chemical equation as follows:



Initially (at $t = 0$)

a 0 0

After any time, t (solution is still unsaturated)

$a - x$ $3x$ $2x$

At equilibrium (when solution is saturated, x becomes s)

$a - s$ $3s$ $2s$

Now, from the definition of solubility product, the constant is directly related to concentration of ions.

That is; $K_{\text{sp}} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$

But $[\text{Ca}^{2+}] = 3s$ and $[\text{PO}_4^{3-}] = 2s$

Thus the K_{sp} can alternatively be written in terms of solubility (s) as follows:

$$K_{\text{sp}} = (3s)^3 (2s)^2 = 108s^5$$

After that discussion, now you can understand the following conclusions which are very crucial in mastering solubility and solubility product:

- Solubility product is the multiple of **molar** solubility raised to certain powers.
- Solubility which is found directly from K_{sp} is the molar solubility, to convert it to mass solubility (which is the common method of representing solubility unless stated otherwise), it must be multiplied by molar mass of the electrolyte.
- Number of moles of undissolved electrolyte (precipitate) in a litre of the solution = $a - s$; it can be converted to the mass of precipitate in the litre of the solution by multiplying it by molar mass of the electrolyte. Another sub-conclusion which goes together with this is that, if $a > s$; the solution is **supersaturated** and there is a **formation of precipitate**.
- The limit of **forming or not forming the precipitate** is found when $a = s$ and the solution is **saturated** at this point.
- If $a < s$; the solubility equilibrium will not be achieved and the solution is **unsaturated (no formation of precipitate at all)**.

Worked examples

Example 1

Given the following solubility in gdm^{-3} at 25°C , obtain the corresponding K_{sp} ;

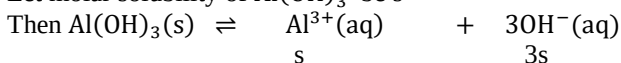
(i) $\text{Al}(\text{OH})_3$ (1.35×10^{-4})

(ii) CaF_2 (1.47×10^{-2})

Solution

$$\begin{aligned} \text{(i) Molar solubility of } \text{Al}(\text{OH})_3 &= \frac{1.35 \times 10^{-4}}{78} \text{ moldm}^{-3} \\ &= 1.73 \times 10^{-6} \text{ moldm}^{-3} \end{aligned}$$

Let molar solubility of $\text{Al}(\text{OH})_3$ be s



$$\text{And } K_{\text{sp}} = [\text{Al}^{3+}][\text{OH}^{-}]^3 = s(3s)^3 = 27s^4$$

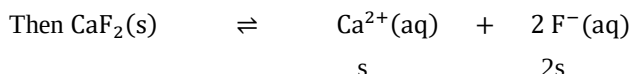
$$\text{But } s = 1.73 \times 10^{-6} \text{ moldm}^{-3}$$

$$\begin{aligned} \text{Whence } K_{\text{sp}} &= 27 \times (1.73 \times 10^{-6} \text{ moldm}^{-3})^4 \\ &= 2.42 \times 10^{-22} \text{ mol}^4 \text{ dm}^{-12} \end{aligned}$$

Hence the solubility product of $\text{Al}(\text{OH})_3$ at 25°C is $2.42 \times 10^{-22} \text{ mol}^4 \text{ dm}^{-12}$

$$(ii) \text{ Molar solubility of } \text{CaF}_2 = \frac{1.47 \times 10^{-2}}{78} \text{ moldm}^{-3} = 1.88 \times 10^{-4} \text{ moldm}^{-3}$$

Let molar solubility of CaF_2 be s



$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2 = s(2s)^2 = 4s^3$$

$$\text{But } s = 1.88 \times 10^{-4} \text{ moldm}^{-3}$$

$$\text{Whence } K_{sp} = 4 \times (1.88 \times 10^{-4} \text{ moldm}^{-3})^3 = 2.66 \times 10^{-11} \text{ mol}^3\text{dm}^{-9}$$

Hence the solubility product of CaF_2 is $2.66 \times 10^{-11} \text{ mol}^3\text{dm}^{-9}$

Example 2

A 100cm^3 sample is removed from a water solution saturated in MgF_2 at 18°C . The water is completely evaporated from sample and 7.6mg deposit of $\text{MgF}_2(s)$ is obtained. What is the K_{sp} for MgF_2 at 18°C ?

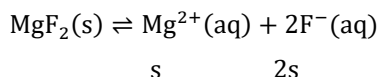
Solution

The amount of deposit after evaporation, is the amount of MgF_2 originally dissolved in the solution

$$\text{Thus mass solubility of } \text{MgF}_2 = \frac{7.6 \times 10^{-3}}{0.1} = 7.6 \times 10^{-2} \text{ gdm}^{-3}$$

$$\text{Then molar solubility of } \text{MgF}_2 = \frac{7.6 \times 10^{-2}}{62} = 1.2258 \times 10^{-3} \text{ M}$$

MgF_2 dissolves in solution according to the following equation:



$$K_{sp} = s \times (2s)^2 = 4s^3 = 4 \times (1.2258 \times 10^{-3})^3 = 7.37 \times 10^{-9} \text{ M}^3$$

Hence solubility product of magnesium fluoride is $7.37 \times 10^{-9} \text{ M}^3$

Example 3

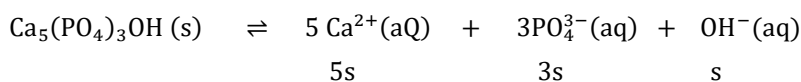
If hydroxyapatite is allowed to reach equilibrium in water, what is the concentration of calcium ion in the solution?

$$\text{Given that: } K_{sp}(\text{hydroxyapatite}) = 2.34 \times 10^{-59}$$

Ionic composition of hydroxyapatite = $\text{Ca}_5(\text{PO}_4)_3\text{OH}$

Solution

Let the solubility of hydroxyapatite be x in moldm^{-3}



$$K_{sp} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^3[\text{OH}^{-}]$$

$$\text{Then } 2.34 \times 10^{-59} = (5s)^5(3s)^3(s) = 84375s^9$$

$$\text{Or } s = \sqrt[9]{\frac{2.34 \times 10^{-59}}{84375}} = 8.67 \times 10^{-8} \text{ M}$$

$$\text{But } [\text{Ca}^{2+}] = 5s = 5 \times 8.67 \times 10^{-8} \text{ M} = 4.3 \times 10^{-7} \text{ M}$$

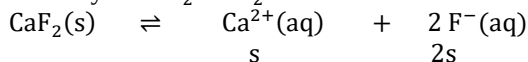
Hence concentration of calcium ions was $4.3 \times 10^{-7} \text{ M}$

Example 4

What is the greatest mass of CaF_2 can be mixed with water to make a 5L solution without forming a precipitate? $K_{\text{sp}}(\text{CaF}_2) = 4 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$

Solution

Let the solubility of CaF_2 in H_2O be s in mol dm^{-3}



$$K_{\text{sp}} = [\text{Ca}^{2+}] [\text{F}^{-}]^2$$

$$\text{Substituting } 4 \times 10^{-11} = (s) (2s)^2 = 4s^3$$

$$\text{Or } s = \sqrt[3]{\frac{4 \times 10^{-11}}{4}} = 2.3713 \times 10^{-4} \text{ mol dm}^{-3}$$

Thus the solubility of CaF_2 in water is $2.3713 \times 10^{-4} \text{ mol dm}^{-3} \times 78 \text{ g/mol} = 0.018 \text{ g/L}$

So maximum mass of CaF_2 which can be dissolved in 1L of solution without forming precipitate is 0.018g.

In 5L of the solution, the mass will be $0.018 \text{ g/L} \times 5 \text{ L} = 0.09 \text{ g}$

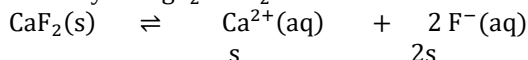
Hence the mass is 0.09g

Example 5

What is the least mass of MgF_2 is required to form the precipitate when it is mixed with water to make a 2L solution? $K_{\text{sp}}(\text{MgF}_2) = 7.37 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$

Solution

Let the solubility of MgF_2 in H_2O be s in mol dm^{-3}



$$K_{\text{sp}} = [\text{Mg}^{2+}] [\text{F}^{-}]^2$$

$$\text{Substituting } 7.37 \times 10^{-9} = (s) (2s)^2 = 4s^3$$

$$\text{Or } s = \sqrt[3]{\frac{7.37 \times 10^{-9}}{4}} = 1.3493 \times 10^{-3} \text{ mol dm}^{-3}$$

Thus the solubility of CaF_2 in water is $1.3493 \times 10^{-3} \text{ mol dm}^{-3} \times 62 \text{ g/mol} = 0.084 \text{ g/L}$

So least mass of CaF_2 which can be dissolved in 1L of solution with just about starting to form precipitate is 0.084g.

In 2L of the solution, the mass will be $0.084 \text{ g/L} \times 2 \text{ L} = 0.168 \text{ g}$

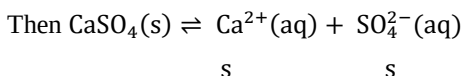
Hence the mass is 0.168g

Example 6

The solubility product, K_{sp} of $\text{CaSO}_4 = 4 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$. If 5g of calcium sulphate is mixed with water to make 500 cm^3 solution, calculate the mass of the precipitate in the solution.

Solution

Let the solubility of CaSO_4 in H_2O be s in mol dm^{-3}



It follows that: $K_{\text{sp}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$

Substituting $4 \times 10^{-4} = s^2$ or $s = \sqrt{4 \times 10^{-4}} = 2 \times 10^{-2} \text{ mol dm}^{-3}$

Solubility in g dm^{-3} = solubility in $\text{mol dm}^{-3} \times \text{molar mass}$

$$= 2 \times 10^{-2} \times 136 \text{ g dm}^{-3} = 2.72 \text{ g dm}^{-3}$$

Thus the saturated solution of CaSO_4 contains 2.72g of the sulphate in dm^3 .

So maximum mass of CaSO_4 which can be dissolved in $500 \text{ cm}^3 = \frac{500}{1000} \text{ dm}^3 \times 2.72 \text{ g dm}^{-3} = 1.36 \text{ g}$

But the given mass of 5g is greater than the limit mass of 1.36g.

Hence there is a formation of the precipitate whose mass is $(5 - 1.36) \text{ g} = 3.64 \text{ g}$

Example 7

An aqueous solution of Na_2S is gradually added to a solution containing Ca^{2+} , Cu^{2+} and Ag^+ each at concentration of 10^{-3} M . Determine $[\text{S}^{2-}]$ at which precipitation of each cations occurs.

Given that:

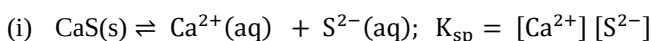
$$K_{\text{sp}} \text{ of } \text{CaS} = 1 \times 10^{-28} \text{ mol}^2 \text{ dm}^{-6}$$

$$K_{\text{sp}} \text{ of } \text{CuS} = 1 \times 10^{-36} \text{ mol}^2 \text{ dm}^{-6}$$

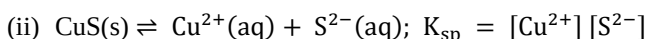
$$K_{\text{sp}} \text{ of } \text{Ag}_2\text{S} = 1 \times 10^{-50} \text{ mol}^3 \text{ dm}^{-9}$$

Hence give the order of precipitation of given compounds.

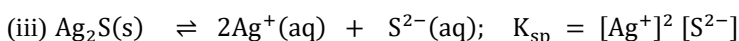
Solution



From which $[\text{S}^{2-}] = \frac{K_{\text{sp}}}{[\text{Ca}^{2+}]} = \frac{1 \times 10^{-28}}{10^{-3}} \text{ M} = 10^{-25} \text{ M}$



From which $[\text{S}^{2-}] = \frac{K_{\text{sp}}}{[\text{Cu}^{2+}]} = \frac{1 \times 10^{-36}}{10^{-3}} \text{ M} = 10^{-33} \text{ M}$



From which $[\text{S}^{2-}] = \frac{K_{\text{sp}}}{[\text{Ag}^+]^2} = \frac{1 \times 10^{-50}}{(10^{-3})^2} \text{ M} = 10^{-44} \text{ M}$

The salt with least amount of $[\text{S}^{2-}]$ precipitates first and hence Ag_2S will precipitate first, followed by CuS and finally CaS will precipitate.

Differences between solubility and solubility product

Differences between solubility and solubility product are summarised in the table below.

Table 19.1 Differences between solubility and solubility product

	SOLUBILITY		SOLUBILITY PRODUCT
01	Definition	01	Definition
02	It is depressed by common ion effect	02	It does not be affected by concentration of ions present in the solution including common ion effect
03	It can be applied for both highly soluble and sparingly soluble substances	03	It is applied for sparingly soluble substance only. Its use is not common for highly soluble substance.
04	It is measured as the amount of solute dissolved in a litre of saturated solution.	04	It is deduced from measured solubility as the product of solubility (molar solubility) raised to the power of their stoichiometric coefficients
05	It is commonly given in g/L	06	It is always given in mol/L raised to certain powers

COMMON ION EFFECT IN SOLUBILITY

When strong electrolyte is introduced into saturated solution of sparingly soluble substance which contains the same (common) ion as that present in the strong electrolyte, the solubility of the sparingly soluble substance is depressed and the precipitate is formed.

For deeper understanding of the concept, consider solution of hydrochloric acid is introduced into a beaker containing saturated solution of silver chloride:

- Silver chloride (AgCl) being sparingly soluble, dissolves slightly in aqueous solution according to the following equation:
- $\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \dots\dots\dots(\text{i})$
- Hydrochloric acid being strong electrolyte, dissolves completely in the solution according to the following equation: $\text{HCl(aq)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \dots(\text{ii})$
- Introduction of $\text{Cl}^-(\text{aq})$ from HCl(aq) increases concentration of $\text{Cl}^-(\text{aq})$ in (i) above; so according to Le Chatelier's principle the position of equilibrium will shift to the left by forming AgCl which appears as precipitate and hence the solubility of the silver chloride (sparingly soluble substance) is lowered.

It should be noted that:

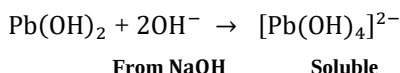
The depression of solubility of sparingly soluble substance (as result of common ion effect) is a hundred percent correct if and only if the substance is incapable of forming complex with the common ion, how?

When the metallic cation of sparingly soluble substance is capable of forming complex ion which is always soluble in aqueous solution, the precipitate will be formed on small addition of the strong electrolyte only. When the electrolyte is added until in excess, the complex is formed and the precipitate appears to dissolve.

For example:

When small amount of sodium hydroxide which is strong electrolyte is added to a solution of lead(II) hydroxide (Pb(OH)_2) which is sparingly soluble electrolyte, the following happen:

Initially, the precipitate is formed due to common ion effect and when the sodium hydroxide in large amount (until in excess) the precipitate dissolves to give clear solution due to formation of complex ion, $[\text{Pb(OH)}_4]^{2-}$ which is soluble.



Lead (II) chloride which is sparingly soluble electrolyte; is insoluble in dilute hydrochloric acid (when the strong electrolyte, HCl(aq) present in small amount) due to common ion effect. However the chloride of lead is soluble in concentrated hydrochloric acid (when the strong electrolyte present in large amount) due to formation of complex ion, $[\text{PbCl}_4]^{2-}$ which is soluble.

Worked examples

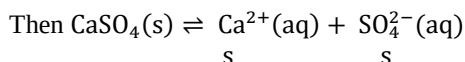
Example 8

The solubility product, K_{sp} of $\text{CaSO}_4 = 4 \times 10^{-4} \text{mol}^2 \text{dm}^{-6}$, calculate the solubility at the same temperature:

- (i) In H_2O
- (ii) In $0.10\text{MNa}_2\text{SO}_4$

Solution

(i) Let the solubility of CaSO_4 in H_2O be s in mol dm^{-3}



It follows that: $K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$

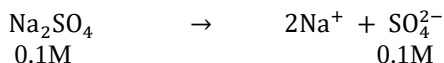
$$\text{Substituting } 4 \times 10^{-4} = s^2 \text{ or } s = \sqrt{4 \times 10^{-4}} = 2 \times 10^{-2} \text{mol dm}^{-3}$$

Solubility in $\text{g dm}^{-3} = \text{solubility in mol dm}^{-3} \times \text{molar mass}$

$$= 2 \times 10^{-2} \times 136 \text{g dm}^{-3} = 2.72 \text{g dm}^{-3}$$

Hence the solubility of CaSO_4 in H_2O is 2.72g dm^{-3}

(ii) Na_2SO_4 being strong electrolyte ionises completely according to the following equation:



So addition of Na_2SO_4 increases $[\text{SO}_4^{2-}]$, thus decreasing solubility of CaSO_4 by common ion effect

Let the new solubility of CaSO_4 be y

Then $[\text{Ca}^{2+}] = y$, $[\text{SO}_4^{2-}] = y + 0.1$

But since y comes from sparingly soluble electrolyte, its value (after common effect) can be neglected compared to 0.1 which comes from the strong electrolyte; i.e. $y + 0.1 \approx 0.1$

- And since K_{sp} does not depend on concentration of ions present in the solution, it follows that:

$$4 \times 10^{-4} = 0.1y \text{ or } y = 4 \times 10^{-3} \text{mol dm}^{-3}$$

$$\text{Thus the solubility} = 4 \times 10^{-3} \times 136 \text{g dm}^{-3} = 0.544 \text{g dm}^{-3}$$

Hence the solubility of CaSO_4 in $0.1\text{MNa}_2\text{SO}_4$ is 0.544g dm^{-3}

Interesting fact you have to understand!

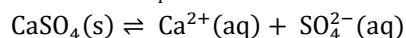
A mother of solubility product and any other concept in ionic equilibria is the chemical equilibrium we studied in **chapter 4**. So whenever you feel any sort of doubt in your consideration about problems related to ionic equilibria including solubility product, return to our mother, chemical equilibrium and then make new consideration or solve the problem from the first principle. To get clearer picture of this, we are going to re-solve the second part of this question (ii) from the first principle.

Assume we are not sure about the effect of common ion effect on calculations involving solubility product.

But we know that at initial equilibrium (saturated solution **before** involving sodium sulphate); $[Ca^{2+}] = [SO_4^{2-}] = 2 \times 10^{-2} \text{ mol dm}^{-3} = \text{Solubility}, s$

The addition of sodium sulphate, will increase $[SO_4^{2-}]$ and the new $[SO_4^{2-}]$ will be $(2 \times 10^{-2} + 0.1) \text{ M}$ or 0.12 M .

The increase in $[SO_4^{2-}]$ will shift equilibrium position to the undissolved $CaSO_4$ side.



Just after the addition of $0.1 \text{ M Na}_2\text{SO}_4$

$$0.02 \quad 0.12$$

After re-establishment of new equilibrium

$$0.02 - x \quad 0.12 - x$$

Where new molar solubility $= [Ca^{2+}] = 0.02 - x$ (It cannot be deduced from $[SO_4^{2-}]$ because **not** all SO_4^{2-} came from the $CaSO_4$).

Then our equilibrium constant, $K_{sp} = [Ca^{2+}][SO_4^{2-}] = (0.02 - x)(0.12 - x) = 4 \times 10^{-4}$

From which; $x^2 - 0.14x + 2 \times 10^{-3} = 0$.

Solving above quadratic equation gives practical value of $x = 0.016$

Then new molar solubility $= 0.02 - x = 0.02 - 0.016 = 4 \times 10^{-3} \text{ M}$ which will be converted to mass solubility to get the same answer of 0.544 g dm^{-3} .

In this particular problem, the alternative approach may seem tedious but you will find that the ability to connect with chemical equilibrium is very crucial in solving tricky problems involving solubility product.

Example 9

Calculate the solubility of CaF_2 in mol dm^{-3} :

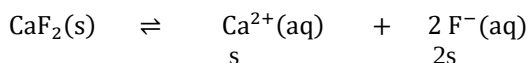
- (i) In water
- (ii) In 0.01 M NaF
- (iii) In IMHF

Given that: K_a of HF $= 5.6 \times 10^{-4} \text{ mol dm}^{-3}$

$$K_{sp} \text{ of } CaF_2 = 4 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$$

Solution

(i) Let the solubility of CaF_2 in H_2O be s in mol dm^{-3}



$$K_{sp} = [Ca^{2+}][F^{-}]^2$$

$$\text{Substituting } 4 \times 10^{-11} = (s)(2s)^2 = 4s^3$$

$$\text{Or } s = \sqrt[3]{\frac{4 \times 10^{-11}}{4}} = 2.37 \times 10^{-4} \text{ mol dm}^{-3}$$

Hence the solubility of CaF_2 in water is $2.37 \times 10^{-4} \text{ mol dm}^{-3}$

(ii) Let the solubility of CaF_2 in 0.01 M NaF be y

Then $[Ca^{2+}] = y$

$$[F^{-}] = 2y + 0.01 \approx 0.01 \text{ M}$$

$$\text{And } 4 \times 10^{-11} = 0.01^2 y \text{ or } y = 4 \times 10^{-7} \text{ mol dm}^{-3}$$

Hence the solubility of CaF_2 in 0.01 NaF is $4 \times 10^{-7} \text{ mol dm}^{-3}$

(iii) $[F^{-}]$ from HF $= \sqrt{K_a[HF]}$

$$= \sqrt{5.6 \times 10^{-4} \times 1} = 0.02\text{M}$$

So if Z is the solubility of CaF_2 in 1MHF;

$$[\text{F}^-] = 2Z + 0.02 \approx 0.02\text{M}, [\text{Ca}^{2+}] = Z$$

$$\text{And } 4 \times 10^{-11} = (0.02)^2 \times Z \text{ or } Z = 1 \times 10^{-7} \text{ moldm}^{-3}$$

Hence the solubility of CaF_2 in 1MHF is $1 \times 10^{-7} \text{ moldm}^{-3}$

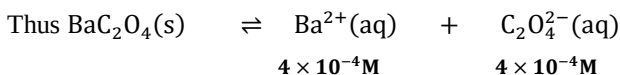
Example 10

If the solubility of barium ethanedioate of room temperature is 0.09gdm^{-3} of aqueous solution, calculate the solubility product of the salt. What mass of barium ethanedioate is precipitated by adding 2.68g of sodium ethanedioate (anhydrous) to 1dm^3 of saturated solution of barium ethanedioate at that temperature?

Solution

Molar mass of barium ethanedioate (BaC_2O_4) = 225g/mol

$$\text{Molar solubility of the salt} = \frac{0.09}{225} \text{ moldm}^{-3} = 4 \times 10^{-4} \text{ moldm}^{-3}$$



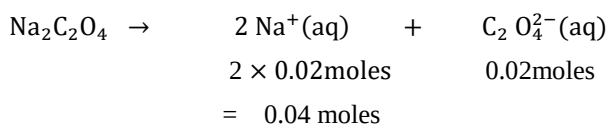
$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{C}_2\text{O}_4^{2-}] = (4 \times 10^{-4}\text{M})^2 = 1.6 \times 10^{-7}\text{M}^2$$

Hence solubility product of BaC_2O_4 is $1.6 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$.

$$\text{Using } n = \frac{m}{M_r};$$

$$\text{Number of moles of sodium ethanedioate } \text{Na}_2\text{C}_2\text{O}_4 \text{ added} = \frac{2.68}{134} \text{ moles} = 0.02 \text{ moles}$$

Being strong electrolyte, $\text{Na}_2\text{C}_2\text{O}_4$ ionises according to the following equation



Let molar solubility of BaC_2O_4 after introduction of introduction of the strong electrolyte be x

$$\text{Then } [\text{Ba}^{2+}] = x, [\text{C}_2\text{O}_4^{2-}] = x + 0.02 \approx 0.02$$

$$\text{It follows that; } 1.6 \times 10^{-7} = 0.02x \text{ or } x = 8 \times 10^{-6}$$

Then solubility of BaC_2O_4 in gdm^{-3} after introduction of $\text{Na}_2\text{C}_2\text{O}_4$

$$= 8 \times 10^{-6} \times 225\text{gdm}^{-3} = 1.8 \times 10^{-3} \text{ gdm}^{-3}$$

Thus the solubility of BaC_2O_4 reduced from $9 \times 10^{-2}\text{gdm}^{-3}$ to $1.8 \times 10^{-3}\text{gdm}^{-3}$ after introducing $\text{Na}_2\text{C}_2\text{O}_4$ to the solution. The difference is the mass of BaC_2O_4 precipitated due to the common ion effect.

$$\text{Hence mass } \text{BaC}_2\text{O}_4 \text{ precipitated in } 1\text{dm}^3 = (9 \times 10^{-2} - 1.8 \times 10^{-3}) \text{ or } 8.82 \times 10^{-2}\text{g}$$

IONIC PRODUCT OF SPARINGLY SOLUBLE SUBSTANCES

This is the product of concentration of ions of sparingly soluble electrolyte, each raised to the power of their stoichiometric coefficients in the balanced equation at any concentration of the solution.

Thus unlike solubility product, ionic product is applied in the solution which is not necessary to be saturated.

i.e. If A_nB_m is sparingly soluble substance which dissolves in a solution according to the following equation: $A_nB_m(s) \rightleftharpoons nA^{m+}(aq) + mB^{n-}(aq)$

$$Q_{sp} = [A^{m+}]_o^n [B^{n-}]_o^m$$

Where Q_{sp} the ionic product and subscripts in the molar concentration symbols insist that the concentration of ions (original concentration) not necessary to be that of saturated solution at equilibrium

Ionic product is useful in determining whether the solution of sparingly soluble substance is saturated or not by comparing its value to the solubility product (It is like comparison of reaction quotient, Q_c to equilibrium constant, K_c to determine whether the system is at equilibrium or not).

- If $Q_{sp} < K_{sp}$, the solution is **unsaturated** and no precipitate is formed.
- If $Q_{sp} = K_{sp}$, the solution is **saturated** and it is the margin of forming and not forming the precipitate i.e. if $Q_{sp} = K_{sp}$, the concentration of ions can be said as either minimum concentration for precipitate to be formed or maximum concentration of ions without forming the precipitate.
- If $Q_{sp} > K_{sp}$, the solution is **supersaturated** and the precipitate is formed.

By definition:

Saturated solution is the solution which cannot dissolve more solute without forming a precipitate at given temperature.

Supersaturated solution is the solution with more solute beyond its **saturated point**. Where, **saturated point** is the point at which a liquid cannot take up more of the solute at given temperature.

Differences between ionic product and solubility product

Differences between ionic product and solubility product are summarised in the table below.

Table 19.2 Differences between ionic product and solubility product

	IONIC PRODUCT, Q_{sp}		SOLUBILITY PRODUCT, K_{sp}
01	Definition	01	Definition
02	Its value keeps changing with concentration	02	At constant temperature, its value is constant for a given electrolyte
03	It is applicable for solution at any concentration (saturated, unsaturated and supersaturated solution)	03	It is applicable for saturated solution only

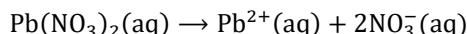
Worked examples

Example 11

Will a precipitate form when 100cm^3 of $8 \times 10^{-3}\text{M Pb(NO}_3)_2$ is added to 400cm^3 of $5 \times 10^{-3}\text{M Na}_2\text{SO}_4$? The solubility product, K_{sp} of $\text{PbSO}_4 = 6.3 \times 10^{-7}\text{M}^2$.

Solution

$\text{Pb}(\text{NO}_3)_2$ which is highly soluble salt (strong electrolyte) ionises completely according to the following equation:

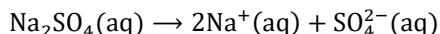


From which;

$$\text{Number of moles of } \text{Pb}(\text{NO}_3)_2 = \text{Number of moles of } \text{Pb}^{2+} = \frac{100}{1000} \times 8 \times 10^{-3} = 8 \times 10^{-4} \text{ mol}$$

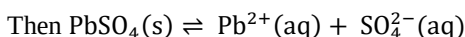
$$\text{And thus } [\text{Pb}^{2+}] \text{ in the mixture} = \frac{8 \times 10^{-4} \text{ mol}}{0.5 \text{ L}} = 1.6 \times 10^{-3} \text{ M} \quad (V_{\text{soln}} = (100 + 400) \text{ cm}^3 = 0.5 \text{ L})$$

Na_2SO_4 which is also strong electrolyte ionises according to the following equation:



$$\text{Number of moles of } \text{Na}_2\text{SO}_4 = \text{Number of moles of } \text{SO}_4^{2-} = \frac{400}{1000} \times 5 \times 10^{-3} = 2 \times 10^{-3} \text{ mol}$$

$$\text{And thus } [\text{SO}_4^{2-}] \text{ in the mixture} = \frac{2 \times 10^{-3} \text{ mol}}{0.5 \text{ L}} = 4 \times 10^{-3} \text{ M}$$



$$\text{From which; } Q_{\text{sp}} = [\text{Pb}^{2+}]_o [\text{SO}_4^{2-}]_o$$

$$\text{Substituting } Q_{\text{sp}} = (1.6 \times 10^{-3} \text{ M}) \times (4 \times 10^{-3} \text{ M}) = 6.4 \times 10^{-6} \text{ M}^2 > K_{\text{sp}}$$

Since $Q_{\text{sp}} > K_{\text{sp}}$; the precipitate will form.

Question 12

The solubility product of calcium sulphate is $6 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$ at room temperature. What mass of calcium sulphate would you expect to be precipitated if 125 cm^3 of 1M sulphuric acid and 125 cm^3 of 1M calcium chloride solution are mixed at room temperature? Assume simple summation of volumes and neglect any possible effect from the hydrochloric acid formed.

Solution**Before mixing**

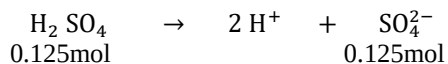
$$\text{Number of moles of } \text{H}_2\text{SO}_4 = \frac{125}{1000} \times 1 \text{ mol} = 0.125 \text{ mol}$$

$$\text{Number of moles of } \text{CaCl}_2 = \frac{125}{1000} \times 1 \text{ mol} = 0.125 \text{ mol}$$

In the solution mixture:

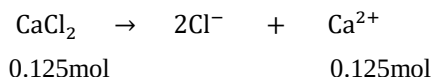
$$\text{Total volume of solution} = (125 + 125) \text{ cm}^3 = 250 \text{ cm}^3 = 0.25 \text{ L}$$

H_2SO_4 being strong electrolyte ionises completely according to the following equation:



$$\text{Thus } [\text{SO}_4^{2-}] = \frac{0.125 \text{ mol}}{0.25 \text{ L}} = 0.5 \text{ M}$$

CaCl_2 being strong electrolyte ionises completely according to the following equation:



$$\text{Thus } [\text{Ca}^{2+}] = \frac{0.125 \text{ mol}}{0.25 \text{ L}} = 0.5 \text{ M}$$

Checking whether precipitate will be formed or not:

$$Q_{sp} = [Ca^{2+}]_o [SO_4^{2-}]_o = 0.5 \times 0.5 M^2 = 0.25 M^2$$

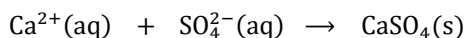
By comparing the calculated ionic product, Q_{sp} with the given solubility product, it is clearly understood the $Q_{sp} > K_{sp}$ and hence the precipitate was formed.

Calculating the mass of the precipitate:

If s is the molar solubility of $CaSO_4$;

$$K_{sp} = s^2 \text{ or } s = \sqrt{K_{sp}} = \sqrt{6 \times 10^{-5}} = 7.746 \times 10^{-3} \text{ moldm}^{-3}$$

Thus concentration of Ca^{2+} and SO_4^{2-} which appears uncombined in the solution was $7.746 \times 10^{-3} M$ of each and the remaining amount which is $(0.5 - 0.007746)$ or 0.492254 mol combines to form the precipitate of $CaSO_4$ in dm^3 according to the following equation:



Thus 0.492254 moles of $CaSO_4$ would be formed in a litre of solution.

Therefore in 250 mL ; $\frac{0.492254 \times 250}{1000}$ moles = 0.123 moles of $CaSO_4$ precipitate was formed

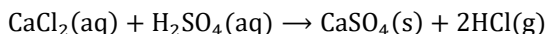
Using $m = nM_r$;

Mass of $CaSO_4$ formed = $0.123 \times 136 \text{ g} = 16.73 \text{ g}$

Hence mass of $CaSO_4$ precipitate formed was 16.73 g

Alternative solution**Calculating total amount of $CaSO_4$ that can be formed by the reaction between $CaCl_2$ and H_2SO_4 :**

$CaCl_2$ and H_2SO_4 reacts according to the following equation:



From which mole of $CaCl_2$ to H_2SO_4 is 1: 1

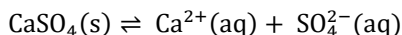
Since number of moles of H_2SO_4 = number of moles of $CaCl_2 = \frac{125}{1000} \times 1 \text{ mol} = 0.125 \text{ mol}$ (Given); nothing present in excess and hence number of moles of $CaSO_4$ formed was also 0.125 mol .

Using $m = nM_r$;

Total mass of $CaSO_4$ formed = $0.125 \times 136 \text{ g} = 17 \text{ g}$

Calculating the mass of precipitate

The $CaSO_4$ is sparingly soluble substance and thus it is in equilibrium with its ions according to the following equation:



Thus if s represents solubility of calcium sulphate; then $K_{sp} = [Ca^{2+}][SO_4^{2-}] = s^2$

From which; $s = \sqrt{K_{sp}} = \sqrt{6 \times 10^{-5}} = 7.746 \times 10^{-3} \text{ moldm}^{-3}$

Or $s = 7.746 \times 10^{-3} \text{ moldm}^{-3} \times 136 \text{ g/mol} = 1.0534 \text{ g/L}$

But total volume of solution = $(125 + 125) \text{ cm}^3 = 250 \text{ cm}^3 = 0.25 \text{ L}$

Therefore, mass of $CaSO_4$ dissolved in 0.25 L of the saturated solution is $1.0534 \text{ g/L} \times 0.25 \text{ L} = 0.26 \text{ g}$

Hence mass of the precipitate is $(17 - 0.26) \text{ g} = 16.74 \text{ g}$

FACTORS AFFECTING SOLUBILITY OF SPARINGLY SOLUBLE ELECTROLYTES

Factors affecting solubility of sparingly soluble ionic compounds includes:

- Temperature
- Common ion effect (concentration)
- Complex formation
- pH of the solution

Temperature

Dissolving sparingly soluble substances in solution is endothermic process and hence (according to Le-Chatelier's principle) their solubility is found to increase with rise in temperature.

However:

- Dissolving some highly soluble substances like magnesium chloride is exothermic process; this makes their solubility to decrease as the temperature increases.
- In gases, solubility is found to decrease with an increase in temperature because at higher temperature, kinetic energy of gas molecules become higher thus making gas particles to escape from the solution.

Common ion effect

The solubility of sparingly soluble substances is found to decrease if there is common ion effect as explained earlier. If the excess common ions are added until the ionic product is greater than solubility product, the precipitate is formed. **However, to ensure complete precipitation, the ion (if it is anion) must be only slightly excess, why?**

Reason: This is simply because in large excess of the common ion, there is complex formation which is soluble and hence the precipitate starts to dissolve.

Complex formation

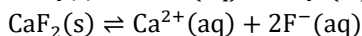
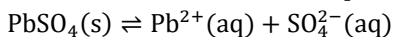
If the salt can form complex ion (which are always soluble) then its solubility is found to increase in presence of large excess anions. For example; most of amphoteric hydroxide like $\text{Al}(\text{OH})_3$ are soluble in strong alkaline solution like $\text{NaOH}(\text{aq})$ due to this reason of their ability of forming soluble complex.

pH of the solution

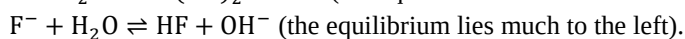
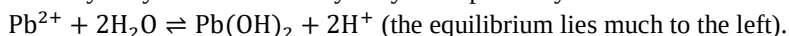
The pH affects solubility of sparingly soluble electrolyte which contains either strong acid cation (e.g. PbSO_4) or strong base anion (e.g. CaF_2). When the electrolyte contains cation from weak base (strong acid cation) or anion from weak acid (strong base anion), two things happen in relation to solubility.

First thing: When the electrolyte dissolved in water, its solubility becomes slightly higher than that predicted by solubility product.

To have better understanding of this, let us look at our two examples; PbSO_4 and CaF_2 .



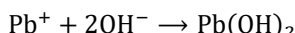
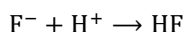
In the above examples, Pb^{2+} and F^{-} being strong acid and strong base, they are capable of undergoing cationic hydrolysis and anionic hydrolysis respectively.



The hydrolysis is therefore (by small extent) decreases concentration of ions (Pb^{2+} and F^{-}) and due to this equilibrium position shifts slightly to the ions side (in accordance with Le-Chatelier's principle) by dissolving more electrolyte.

However, the increase in solubility due to this (hydrolysis) is usually so small that we can ignore it. But when it comes to the acidic or basic solution, we cannot neglect this effect of acid-base characters of ions. Let us go to our 'second thing' to have better understanding of pH effect on solubility of sparingly soluble electrolytes.

Second thing: In acidic solution (solution with low pH), the strong base anion will react with the acid leading to significant decrease in the concentration of the anion. The same happens to strong acid cation when it is subjected to basic solution (solution with high pH).



According to Le-Chatelier's principle, the decrease in concentration of ions, shifts the equilibrium position to the ions side by dissolving more electrolyte. Consequently, *sparingly soluble electrolytes containing strong acid cation (acidic salts) are more soluble in basic solution (at high pH) whereas sparingly soluble electrolytes containing strong base anion (basic salts) are more soluble in acidic solution (at low pH).*

You should be aware with the fact that, although HSO_4^- is anion, it behaves more as an acid and thus electrolytes containing HSO_4^- are more soluble in basic solution.

Also, **the reader should note that:** there are other factors which affect solubility of substances but not of sparingly soluble weak electrolyte. This includes:

- **Pressure** (Its effect is encountered for gases only whereby solubility of gases increases with an increase in pressure. It has no effect in solid and liquid).
- **Nature of solute and solvent** (Recall: like dissolves like).
- **Molecular weight** (Generally solubility decreases with an increase in molecular weight).

Worked examples

Example 13

Which of the following slightly soluble electrolytes will be more soluble in acidic solution than in water? For those where the solubility increases, write an equation for the net chemical reaction that occurs when a strong acid is present in solution. And for those where solubility does not increase, give a reason to support your choice.

- $\text{Ni}(\text{OH})_2(\text{s})$
- $\text{CaCO}_3(\text{s})$
- $\text{BaF}_2(\text{s})$
- $\text{AgCl}(\text{s})$

Solution

Only compounds whose anions are conjugate base of weak acid are basic, their solubility will be increased in the acidic solution. So the answer of each part is as follows:

- $\text{Ni}(\text{OH})_2$ is more soluble in acidic solution because it contains OH^- which is strong base anion that reacts with strong acid according to the following equation:

$$\text{Ni}(\text{OH})_2(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$$
- CaCO_3 is more soluble in acidic solution because it contains CO_3^{2-} which is strong base anion that reacts with strong acid according to the following equation:

$$\text{CaCO}_3(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$$
- BaF_2 is more soluble in acidic solution because it contains F^- which is strong base anion that reacts with strong acid according to the following equation:

$$\text{BaF}_2(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{HF}(\text{aq})$$
- Solubility of AgCl in the acid will not increase because Cl^- being conjugate base of HCl which is very strong acid, it is very weak base and hence it cannot react with H^+ from the acid.

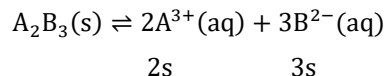
Example 14

The hypothetical ionic compound, A_2B_3 with molar mass of 200g/mol has solubility product of $4.32 \times 10^{-10} M^5$ and 9.72×10^{-4} at $20^\circ C$ and $80^\circ C$ respectively. If 5L of a saturated solution of A_2B_3 at $80^\circ C$ is cooled to $20^\circ C$; what mass of the precipitate will be formed?

Solution

Assume s represents molar solubility of the compound.

Then



At equilibrium (when solution is saturated)

$$\text{Then } K_{sp} = [A^{3+}]^2 [B^{2-}]^3 = (2s)^2 (3s)^3 = 108s^5$$

$$\text{From which } s = \sqrt[5]{\frac{K_{sp}}{108}}$$

$$\text{At } 80^\circ C; s = \sqrt[5]{\frac{9.72 \times 10^{-4}}{108}} = 0.0979 \text{ mol/L} = 0.0979 \text{ mol/L} \times 200 \text{ g/mol} = 19.58 \text{ g/L}$$

$$\text{At } 20^\circ C; s = \sqrt[5]{\frac{4.32 \times 10^{-10}}{108}} = 5.253 \times 10^{-3} \text{ mol/L} = 5.253 \times 10^{-3} \text{ mol/L} \times 200 \text{ g/mol} = 1.0506 \text{ g/L}$$

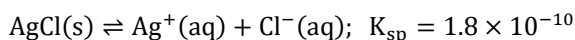
Thus the solubility of the given compound decreases from 19.58g/L to 1.0506g/L when cooled from $80^\circ C$ to $20^\circ C$. The difference is the mass of precipitate that will be formed in 1L of the solution.

Hence mass of the precipitate in 5L will be $(19.58 - 1.0506) \text{ g/L} \times 5 \text{ L} = 92.647 \text{ g}$

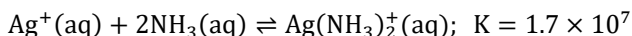
The mass will be 92.647g.

Example 15

AgCl is a sparingly soluble electrolyte which ionises in aqueous solution according to the following equation:



The $Ag^+(aq)$ is capable of reacting with NH_3 to form complex ion according to the following equation:



Use the above information to calculate an equilibrium constant for dissolution process of AgCl in ammonia solution and hence compare solubility of AgCl in the ammonia solution and the solubility in the water.

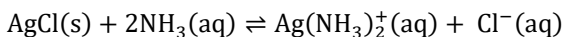
Solution

Given that:

$$K_{sp} = 1.8 \times 10^{-10} = [Ag^+][Cl^-]$$

$$\text{And } K = 1.7 \times 10^7 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

Dissolution of AgCl in the ammonia solution can be represented by the following equation:



$$\text{From which; } K_c = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} \text{ -----(i)}$$

$$\text{But from } K = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

$$\text{Or } K[Ag^+] = \frac{[Ag(NH_3)_2^+]}{[NH_3]^2} \text{ -----(ii)}$$

Substituting (ii) in (i) gives:

$$K_c = K[Ag^+][Cl^-] = K \times K_{sp} = 1.8 \times 10^{-10} \times 1.7 \times 10^7 = 3.06 \times 10^{-3}$$

Hence the equilibrium constant is 3.06×10^{-3} .

Comment: The equilibrium constant of dissolution of AgCl in ammonia is much larger (17 million times) than that in water implying that solubility of AgCl in the ammonia solution is very high compared to that in water.

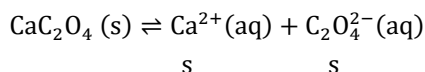
Example 16

The solubility product of calcium oxalate is $2 \times 10^{-9} \text{M}^2$. How many times calcium oxalate is more soluble in the acidic solution with pH of 2 than in pure water?

Solution

In the pure water:

Let the solubility of CaC_2O_4 be s



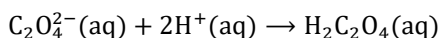
$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = s^2$$

$$s = \sqrt{K_{\text{sp}}} = \sqrt{2 \times 10^{-9} \text{M}^2} = 4.47 \times 10^{-5} \text{M}$$

In the acidic solution:

Using $[\text{H}^+] = \log^{-1}(-\text{pH})$; the pH of 2 is equivalent to $\log^{-1}(-2)$ or 0.01M of H^+ .

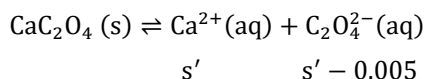
$\text{C}_2\text{O}_4^{2-}$ being strong base anion, combines with H^+ according to the following equation:



From which, mole ratio of $\text{C}_2\text{O}_4^{2-}$ to H^+ is 1: 2

$$\text{Thus } [\text{C}_2\text{O}_4^{2-}] \text{ consumed in combining with } \text{H}^+ = \frac{[\text{H}^+]}{2} = \frac{0.01}{2} \text{M} = 0.005 \text{M}$$

The decrease in $[\text{C}_2\text{O}_4^{2-}]$ will shift the equilibrium position to free ions side and thus the solubility of CaC_2O_4 will increase from s to s' .



$$\text{Then } K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = s'(s' - 0.005) = 2 \times 10^{-9}$$

$$\text{From which; } (s')^2 - 0.005s' - 2 \times 10^{-9} = 0$$

Solving the above quadratic equation gives the practical value of $s' = 0.005$

$$\text{Then } \frac{s'}{s} = \frac{0.005 \text{M}}{4.47 \times 10^{-5} \text{M}} = 112$$

Hence the solubility of calcium oxalate in the acidic solution is 112 times its solubility in the pure water.

APPLICATIONS OF SOLUBILITY PRODUCT

Solubility product is useful in:

1. Purification of common salt

Natural common salt consists of many insoluble and soluble impurities. Saturated solution of common salt is prepared and insoluble impurities are filtered off. Hydrogen chloride gas (HCl) is circulated through the saturated solution. HCl and NaCl dissociate into their respective ion, both giving Cl^- as anion.

The concentration of Cl^- ions increases considerably in solution due to ionisation HCl. Hence, the ionic product $[\text{Na}^+][\text{Cl}^-]$ exceeds the solubility product of sodium chloride and, therefore, pure sodium chloride precipitates out from solution.

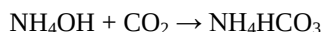
2. Salting out of soap

Soap is a sodium salt of higher carboxylic acids with general molecular formula of $C_nH_{2n+1}COONa$. From the solution, soap is precipitated by the addition of concentrated solution of sodium chloride which ionises to give Na^+ which is also produced by the salt.

Thus, the concentration of Na^+ ions increases considerably on addition of $NaCl$ solution. Hence, the ionic product $[C_nH_{2n+1}COO^-][Na^+]$ exceeds the solubility product of soap and, therefore, soap precipitates out from the solution.

3. Manufacture of sodium bicarbonate (baking soda)

In Solvay's soda process, CO_2 gas is passed through ammonical brine to precipitate out $NaHCO_3$.



Then $NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$,

$NaHCO_3$ is precipitated first because of its lower solubility product as compared to those of NH_4Cl , NH_4HCO_3 and $NaCl$.

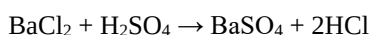
Thus, baking soda ($NaHCO_3$) can be quantifiably estimated.

4. Quantitative analysis

In quantitative analysis, solubility product is useful in estimation of:

barium as barium sulphate:

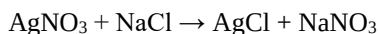
H_2SO_4 as precipitating agent is added to the aqueous solution of $BaCl_2$.



Precipitation of $BaSO_4$ takes place when its ionic product exceeds solubility product. H_2SO_4 is added in slight excess to ensure complete precipitation. Large excess of H_2SO_4 is harmful for complex formation.

silver as silver chloride:

$NaCl$ solution is added to the silver nitrate solution, slight excess of $NaCl$ is added to ensure complete precipitation.



Again, precipitation of $AgCl$ takes place when ionic product of $AgCl$ exceeds its solubility product.

In a similar manner; it is possible to estimate lead as lead chromate, calcium as calcium oxalate, etc.

Fractional precipitation

Fractional precipitation is a technique that separates ions from solution based on their different solubility and hence different solubility products, K_{sp} .

It is a technique of separating two or more ions from a solution by adding a reagent (common ion) that precipitates first one ion and then the second.

Let us suppose $0.1M Ba^{2+}$ and $0.1M Sr^{2+}$ in aqueous solution. K_2CrO_4 is added as **precipitating agent**. K_{sp} of $BaCrO_4$ is 1.2×10^{-10} and K_{sp} of $SrCrO_4$ is 3.5×10^{-5} :

$[CrO_4^{2-}]$ required to precipitate $BaCrO_4$

$$= \frac{K_{sp}}{[Ba^{2+}]} = \frac{1.2 \times 10^{-10}}{0.1} = 1.2 \times 10^{-9}M$$

$[CrO_4^{2-}]$ required to precipitate $SrCrO_4$

$$= \frac{K_{sp}}{[Sr^{2+}]} = \frac{3.5 \times 10^{-5}}{0.1} = 3.5 \times 10^{-4} M$$

Thus, $BaCrO_4$ will precipitate first because it requires low concentration of CrO_4^{2-} ions. On addition of chromate ions, $BaCrO_4$ starts precipitating when chromate ion concentration reaches $1.2 \times 10^{-9} M$. When CrO_4^{2-} ion concentration reaches up to $3.5 \times 10^{-4} M$, then $SrCrO_4$ also starts precipitating.

Remaining concentration of Ba^{2+} when $SrCrO_4$ starts precipitating

$$= \frac{K_{sp} \text{ of } BaCrO_4}{[CrO_4^{2-}] \text{ when } SrCrO_4 \text{ starts precipitating}} = \frac{1.2 \times 10^{-10}}{3.5 \times 10^{-4}} = 3.4 \times 10^{-7} M$$

% of remaining concentration of Ba^{2+}

$$= \frac{[\text{Remaining } Ba^{2+}]}{[\text{Initial } Ba^{2+}]} \times 100\% = \frac{3.4 \times 10^{-7}}{0.1} \times 100\% = 0.00034\%$$

The resulting solution can be filtered and the Ba^{2+} isolated from the original solution as the chromate salt.

Definition of fractional precipitation:

Fractional precipitation is the method for separating elements or compounds with similar solubility by a series of analytical precipitations, each one improving the purity of the desired element.

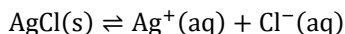
Example 17

To a solution containing $0.1 M Cl^-$ and $0.01 M CrO_4^{2-}$, a solution of $AgNO_3$ is added slowly.

- Which salt will precipitate first between $AgCl$ and Ag_2CrO_4 ? Show clearly how you arrived to your answer.
- Find the concentration of the ion that will precipitate first at the time the second ion will start precipitating. Use $K_{sp}(AgCl) = 2.72 \times 10^{-10}$ and $K_{sp}(Ag_2CrO_4) = 2.4 \times 10^{-12}$

Solution

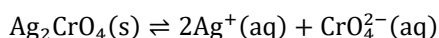
(i) For $AgCl$:



$$\text{From which } K_{sp} = [Ag^+][Cl^-] \text{ or } [Ag^+] = \frac{K_{sp}}{[Cl^-]}$$

$$\text{Thus minimum } [Ag^+] \text{ required to precipitate } AgCl = \frac{2.72 \times 10^{-10}}{0.1} M = 2.72 \times 10^{-9} M$$

For Ag_2CrO_4 :



$$\text{From which } K_{sp} = [Ag^+]^2[CrO_4^{2-}] \text{ or } [Ag^+] = \sqrt{\frac{K_{sp}}{[CrO_4^{2-}]}}$$

$$\text{Thus minimum } [Ag^+] \text{ required to precipitate } Ag_2CrO_4 = \sqrt{\frac{2.4 \times 10^{-12}}{0.01}} M = 1.55 \times 10^{-5} M$$

Therefore $AgCl$ will precipitate first because it requires lower concentration of Ag^+ ions. On addition of silver ions (from silver nitrate solution), $AgCl$ starts precipitating when silver ion concentration reaches $2.72 \times 10^{-9} M$ while until concentration of silver ions reaches up to $1.55 \times 10^{-4} M$, Ag_2CrO_4 will also start precipitating.

(ii) Remaining concentration of Cl^- when Ag_2CrO_4 starts precipitating

$$= \frac{K_{sp} \text{ of } AgCl}{[Ag^+] \text{ when } Ag_2CrO_4 \text{ starts precipitating}} = \frac{2.72 \times 10^{-10}}{1.55 \times 10^{-5}} = 1.75 \times 10^{-5} M$$

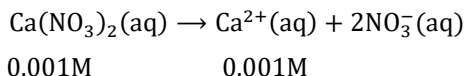
Hence the concentration of the ion that will precipitate first (Cl^-) at the time CrO_4^{2-} start to precipitate was $1.75 \times 10^{-5} M$.

MISCELLANEOUS WORKED EXAMPLES ON SOLUBILITY AND SOLUBILITY PRODUCT**Example 18**

What is the minimum mass of sodium sulphate crystals that must be dissolved in 5L of 0.001M $\text{Ca}(\text{NO}_3)_2$ solution in order to initiate precipitation of calcium sulphate? $K_{\text{sp}}(\text{CaSO}_4) = 2.6 \times 10^{-5} \text{M}^2$

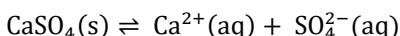
Solution

$\text{Ca}(\text{NO}_3)_2$ is highly soluble salt (strong electrolyte) which ionises completely according to the following equation;



Thus $[\text{Ca}(\text{NO}_3)_2] = [\text{Ca}^{2+}] = 0.001\text{M}$

Calcium sulphate being sparingly soluble electrolyte ionises according to the following equation;



The precipitate formation is initiated when ionic product is equal to solubility product.

$$\text{Thus } K_{\text{sp}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] \text{ or } [\text{SO}_4^{2-}] = \frac{K_{\text{sp}}}{[\text{Ca}^{2+}]} = \frac{2.6 \times 10^{-5} \text{M}^2}{0.001\text{M}} = 2.6 \times 10^{-2} \text{M}$$

So minimum $[\text{SO}_4^{2-}]$ required to initiate the precipitate is $2.6 \times 10^{-2} \text{M}$.

Na_2SO_4 is strong electrolyte and its formula suggests that for every mole of sodium sulphate there is one mole of sulphate ions. Thus, $[\text{Na}_2\text{SO}_4] = [\text{SO}_4^{2-}] = 2.6 \times 10^{-2} \text{M}$

Then mass of $\text{Na}_2\text{SO}_4 = [\text{Na}_2\text{SO}_4] \times V_{\text{soln}} \times M_r(\text{Na}_2\text{SO}_4)$

Substituting mass of $\text{Na}_2\text{SO}_4 = 2.6 \times 10^{-2} \text{mol/L} \times 5\text{L} \times 142\text{g/mol} = 18.46\text{g}$

Hence the mass is 18.46g.

Example 19

A saturated solution of $\text{Mg}(\text{OH})_2$ in contact with undissolved solid is prepared at 25 °C. The pH of the solution is found to be 10.17. Calculate solubility product for this compound.

Solution

$$[\text{OH}^{-}] = \log^{-1}(-\text{pOH}) = \log^{-1}(-(14 - \text{pH}))$$

$$= \log^{-1}(-(14 - 10.17)) = \log^{-1}(-3.83) = 1.4791 \times 10^{-4} \text{M}$$

But from mole ratio of the equation for ionisation of $\text{Mg}(\text{OH})_2$;

$$[\text{Mg}^{2+}] = \frac{[\text{OH}^{-}]}{2} = \frac{1.4791 \times 10^{-4} \text{M}}{2} = 7.3955 \times 10^{-5} \text{M}$$

$$K_{\text{sp}} = (7.3955 \times 10^{-5} \text{M})(1.4791 \times 10^{-4} \text{M})^2 = 1.62 \times 10^{-12} \text{M}^3$$

The solubility product is $1.62 \times 10^{-12} \text{M}^3$.

Example 20

If equal volume of 0.01M K_2SO_4 and 0.1M $\text{Pb}(\text{NO}_3)_2$ solutions are mixed;

(i) Will a precipitate form?

(ii) What are the concentrations of Pb^{2+} and SO_4^{2-} remaining in the solution?

Use $K_{\text{sp}}(\text{PbSO}_4) = 1.8 \times 10^{-8}$

Solution

(i) Let the volume of each solution taken in litres be V

Then:

Total volume of solution mixture will be $V + V = 2V$

$$[K_2SO_4] \text{ in the mixture} = \frac{0.01V}{2V} = 0.005M$$

$$[Pb(NO_3)_2] \text{ in the mixture} = \frac{0.1V}{2V} = 0.05M$$

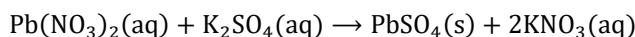
As a general rule: If equal volume of two solutions, concentration of each in the mixture will be halved.

Then from, $PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

$$Q_{sp} = [Pb^{2+}]_o [SO_4^{2-}]_o = 0.005 \times 0.05 = 2.5 \times 10^{-4} > 1.8 \times 10^{-8} (K_{sp})$$

Since $Q_{sp} > K_{sp}$, the precipitate will form.

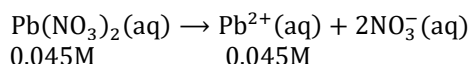
(ii) $Pb(NO_3)_2$ reacts with K_2SO_4 (to precipitate $PbSO_4$) according to the following equation:



From which their mole ratio of 1:1. But the given amount of $Pb(NO_3)_2$ is greater than that of K_2SO_4 . So $Pb(NO_3)_2$ was in excess.

$$\text{Unreacted } [Pb(NO_3)_2] = (0.05 - 0.005)M = 0.045M$$

The unreacted $Pb(NO_3)_2$ being strong electrolyte ionises according to the following equation:



So the unreacted will affect the dissolution of $PbSO_4$ by common ion effect and therefore if s is its solubility, then:

$$[Pb^{2+}] = s + 0.045 \approx 0.045M$$

$$[SO_4^{2-}] = s$$

It follows that; $K_{sp} = 0.045s = 1.8 \times 10^{-8}$ or $s = 4 \times 10^{-7}M$

Hence $[Pb^{2+}] = 0.045M$ and $[SO_4^{2-}] = 4 \times 10^{-7}M$

Alternative solution

You may find easier to solve the second part of the question from the 'first principle' as normal chemical equilibrium problem. Let us look how it is done!

We have found that just after mixing:

$$[Pb(NO_3)_2] = [Pb^{2+}] = 0.05M$$

$$[K_2SO_4] = [SO_4^{2-}] = 0.005M$$

Then the precipitation process will proceed until the equilibrium is achieved.

	$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$
Just after mixing	$\begin{array}{cc} 0.05 & 0.005 \end{array}$
At equilibrium	$\begin{array}{cc} 0.05 - x & 0.005 - x \end{array}$
$K_{sp} = (0.05 - x)(0.005 - x) = 1.8 \times 10^{-8}; x^2 - 0.055x + 2.499982 \times 10^{-4} = 0$	
Solving above quadratic equation, gives practical value of $x = 0.0049996$	
Hence: $[Pb^{2+}] = 0.05 - x = (0.05 - 0.0049996)M = 0.045M$	
And $[SO_4^{2-}] = 0.005 - x = (0.005 - 0.0049996)M = 4 \times 10^{-7}M$	

Example 21

Lead chromate, PbCrO_4 , is a yellow pigment used in paints. Suppose 0.5L of a $1 \times 10^{-5}\text{M}$ $(\text{CH}_3\text{COO})_2\text{Pb}$ and 0.5L of a $1 \times 10^{-3}\text{M}$ K_2CrO_4 solution are mixed.

- Calculate the equilibrium concentration of Pb^{2+} ion remaining in the solution after PbCrO_4 precipitates.
- What is the percentage of Pb^{2+} remaining in solution after the precipitation has occurred and hence state whether the precipitation of Pb^{2+} was complete or not.

Use $K_{\text{sp}}(\text{PbCrO}_4) = 1.8 \times 10^{-14}$

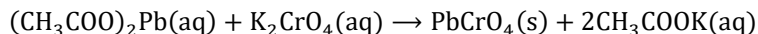
Solution

- Since equal volume (0.5L) of each solution was taken, their concentrations in the mixture will be halved. Thus:

$$[(\text{CH}_3\text{COO})_2\text{Pb}] \text{ in the mixture} = \frac{1 \times 10^{-5}\text{M}}{2} = 5 \times 10^{-6}\text{M}$$

$$[\text{K}_2\text{CrO}_4] \text{ in the mixture} = \frac{1 \times 10^{-3}\text{M}}{2} = 5 \times 10^{-4}\text{M}$$

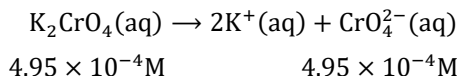
$(\text{CH}_3\text{COO})_2\text{Pb}$ reacts with K_2CrO_4 (to precipitate PbCrO_4) according to the following equation:



From which their mole ratio of 1:1. But the given amount of K_2CrO_4 is greater than that of $(\text{CH}_3\text{COO})_2\text{Pb}$. So K_2CrO_4 was in excess.

$$\text{Unreacted } [\text{K}_2\text{CrO}_4] = (5 \times 10^{-4} - 5 \times 10^{-6})\text{M} = 4.95 \times 10^{-4}\text{M}$$

The unreacted K_2CrO_4 being strong electrolyte ionises according to the following equation:



So the unreacted will affect the dissolution of PbSO_4 by common ion effect and because PbCrO_4 ionises according to the equation; $\text{PbCrO}_4(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$; it follows that, if s is its solubility, then:

$$[\text{CrO}_4^{2-}] = s + 4.95 \times 10^{-4}\text{M} \approx 4.95 \times 10^{-4}\text{M}$$

$$[\text{Pb}^{2+}] = s$$

$$\text{It follows that; } K_{\text{sp}} = 4.95 \times 10^{-4}s = 1.8 \times 10^{-14} \text{ or } s = 3.6363 \times 10^{-11}\text{M}$$

$$\text{Hence the equilibrium } [\text{Pb}^{2+}] = 3.6363 \times 10^{-11}\text{M}$$

$$\text{(ii) Original } [\text{Pb}^{2+}] = [(\text{CH}_3\text{COO})_2\text{Pb}] = 5 \times 10^{-6}\text{M}$$

$$\text{Then \%remained} = \frac{\text{remained } [\text{Pb}^{2+}]}{\text{original } [\text{Pb}^{2+}]} \times 100\% = \frac{3.6363 \times 10^{-11}\text{M}}{5 \times 10^{-6}\text{M}} \times 100\% = 0.00073\%$$

The percentage of Pb^{2+} remaining is 0.00073% which is extremely small and hence the precipitation of Pb^{2+} was complete.

Example 22

A solution prepared by mixing 150mL of $1 \times 10^{-2}\text{M}$ $\text{Mg}(\text{OH})_2$ and 250mL of $1 \times 10^{-1}\text{M}$ NaF . Calculate the concentration of Mg^{2+} and F^- at equilibrium with solid MgF_2 . (K_{sp} at 298K is $6.4 \times 10^{-9}\text{M}^2$).

Solution

Number of moles of $\text{Mg}(\text{OH})_2$ was $\frac{150}{1000} \times 1 \times 10^{-2} \text{mol} = 1.5 \times 10^{-3} \text{mol}$

Number of moles NaF was $\frac{250}{1000} \times 1 \times 10^{-1} \text{mol} = 2.5 \times 10^{-2} \text{mol}$

$\text{Mg}(\text{OH})_2$ reacts with NaF according to the following equation:



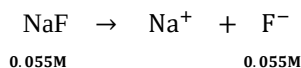
From which mole ratio of $\text{Mg}(\text{OH})_2$ to NaF is 1:2

Thus $1.5 \times 10^{-3} \text{mol}$ of $\text{Mg}(\text{OH})_2$ reacted with $2 \times 1.5 \times 10^{-3}$ or $3 \times 10^{-3} \text{mol}$ of NaF and $(2.5 \times 10^{-2} - 3 \times 10^{-3})$ moles or $2.2 \times 10^{-2} \text{mol}$ of NaF remain unreacted at the end of the reaction

Total volume of solution mixture = $(150 + 250) \text{mL} = 400 \text{mL}$

Thus $[\text{NaF}]$ after the reaction = $\frac{2.2 \times 10^{-2}}{400} \times 1000 \text{M} = 0.055 \text{M}$

NaF being strong electrolyte ionises according to the following equation



So if x is the molar solubility of MgF_2 (which is formed in the double decomposition reaction) in 0.055M of unreacted NaF

$$[\text{Mg}^{2+}] = x$$

$$[\text{F}^-] = 2x + 0.055 \approx 0.055$$

And from: $\text{MgF}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{F}^-(\text{aq}); K_{\text{sp}} = [\text{Mg}^{2+}][\text{F}^-]^2$

$$\text{Then } 6.4 \times 10^{-9} = x(0.055)^2 \text{ or } x = 2.1157 \times 10^{-6} \text{ mol dm}^{-3}$$

Hence $2.1157 \times 10^{-6} \text{M}$ of Mg^{2+} and 0.055M of F^- are at equilibrium with solid MgF_2 .

Example 23

Calculate milligrams of precipitate of calcium fluoride that will formed when 1L of $2 \times 10^{-2} \text{M}$ NaF is mixed with 200mL of $1 \times 10^{-2} \text{M}$ $\text{Ca}(\text{NO}_3)_2$. Given that: $K_{\text{sp}}(\text{CaF}_2) = 3.9 \times 10^{-9} \text{M}^3$.

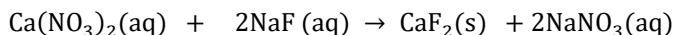
Solution

Calculating total mass of CaF_2 that can be formed by the reaction between NaF and $\text{Ca}(\text{NO}_3)_2$:

Number of moles of $\text{Ca}(\text{NO}_3)_2$ was $\frac{200}{1000} \times 1 \times 10^{-2} \text{mol} = 2 \times 10^{-3} \text{mol}$

Number of moles NaF was $1 \times 2 \times 10^{-2} \text{mol} = 2 \times 10^{-2} \text{mol}$

$\text{Ca}(\text{NO}_3)_2$ reacts with NaF according to the following equation:



From which mole ratio of $\text{Ca}(\text{NO}_3)_2$ to NaF is 1:2

Thus $2 \times 10^{-3} \text{mol}$ of $\text{Ca}(\text{NO}_3)_2$ reacted with $2 \times 2 \times 10^{-3}$ or $4 \times 10^{-3} \text{mol}$ of NaF and $(2 \times 10^{-2} - 4 \times 10^{-3}) \text{mol}$ or 0.016mol of NaF remain unreacted at the end of the reaction.

So $\text{Ca}(\text{NO}_3)_2$ is the limited reactant and therefore it is going to determine the amount of CaF_2 produced.

From the same equation; mole ratio of $\text{Ca}(\text{NO}_3)_2$ to CaF_2 is 1:1.

Thus number of moles of CaF_2 produced = Number of moles of $\text{Ca}(\text{NO}_3)_2$ reacted = $2 \times 10^{-3} \text{mol}$

Using $m = nM_r$;

Total mass of CaF_2 produced just after reaction between $\text{Ca}(\text{NO}_3)_2$ and NaF

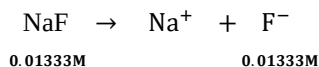
$$= 2 \times 10^{-3} \text{ mol} \times 78 \text{ g/mol} = 0.156 \text{ g}$$

Calculating the mass of precipitate

Total volume of solution mixture = $(200 + 1000) \text{ mL} = 1200 \text{ mL} = 1.2 \text{ L}$

Thus $[\text{NaF}]$ after the reaction (concentration of unreacted NaF) = $\frac{0.016 \text{ mol}}{1.2 \text{ L}} = 0.01333 \text{ M}$

NaF being strong electrolyte ionises according to the following equation:



So if s is the molar solubility of CaF_2 , then:

$$[\text{Ca}^{2+}] = s$$

$$[\text{F}^-] = 2s + 0.01333 \approx 0.01333 \text{ M}$$

And from: $\text{CaF}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{F}^-(\text{aq}); K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2$

$$\text{Then } 3.9 \times 10^{-9} \text{ M}^3 = s (0.01333)^2$$

$$\text{Or } s = 2.1948 \times 10^{-7} \text{ mol/L} = 2.1948 \times 10^{-5} \text{ mol/L} \times 78 \text{ g/mol} = 0.001712 \text{ g/L}$$

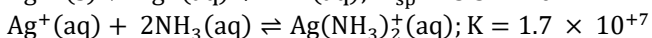
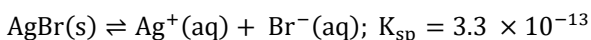
Thus mass of CaF_2 that dissolves in 1.2L of the solution = $0.001712 \text{ g/L} \times 1.2 \text{ L} = 0.002 \text{ g}$

Thus only 0.002g out of the total mass of 0.156g is dissolved in the solution and hence the solution is supersaturated and the mass of precipitate = $(0.156 - 0.002) \text{ g} = 0.154 \text{ g} = 154 \text{ mg}$

There are 154 milligrams of precipitate of calcium fluoride.

Example 24

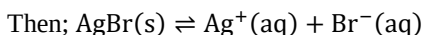
Below are data which can be used to compare solubility of AgBr in water and in ammonia solution.



- How many grams of silver bromide, AgBr can be dissolved in 50 millilitres of water?
- How many grams of silver bromide can be dissolved in 50 millilitres of $10 \text{ M NH}_3(\text{aq})$?
- How many times is silver bromide more soluble in the ammonia solution than in water?

Solution

If s is the molar solubility of AgBr in water;



$$K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-] = s^2$$

$$\text{From which } s = \sqrt{K_{\text{sp}}} = \sqrt{3.33 \times 10^{-13}} = 5.744 \times 10^{-7} \text{ M}$$

The solubility of AgBr = Molar solubility $\times$ Molar mass

$$= 5.744 \times 10^{-7} \times 188 \text{ g/dm}^3 = 1.1 \times 10^{-4} \text{ g/dm}^3$$

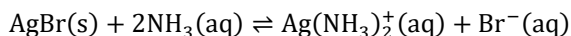
$$\text{Thus mass of AgBr dissolved in 50 mL} = \frac{50}{1000} \times 1.1 \times 10^{-4} \text{ g} = 5.5 \times 10^{-6} \text{ g}$$

(i) Hence mass of AgBr dissolved in 50 mL of water is $5.5 \times 10^{-6} \text{ g}$.

$$K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-] = 3.3 \times 10^{-13} \dots\dots (i)$$

And $K = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+][\text{NH}_3]^2} = 1.7 \times 10^7 \dots\dots (ii)$

AgBr dissolves in $\text{NH}_3(\text{aq})$ according to the following equation:



At equilibrium $10 - 2s' \qquad s' \qquad s'$

Where s is the molar solubility of AgBr in $\text{NH}_3(\text{aq})$

Then $K_s = \frac{[\text{Ag}(\text{NH}_3)_2]^+[\text{Br}^-]}{[\text{NH}_3]^2} = \frac{(s')^2}{(10-2s')^2}$

But $K_{sp} \times K = \frac{[\text{Ag}(\text{NH}_3)_2]^+[\text{Ag}^+][\text{Br}^-]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{[\text{Ag}(\text{NH}_3)_2]^+[\text{Br}^-]}{[\text{NH}_3]^2} = K_s$

Thus $K_s = K_{sp} \times K = 3.3 \times 10^{-13} \times 1.7 \times 10^7$

Then $\frac{(s')^2}{(10-2s')^2} = 5.61 \times 10^{-6}$

From which $(s')^2 + 2.244 \times 10^{-4}s' - 5.61 \times 10^{-6} = 0$; and $s' = 0.0236\text{M}$

Then mass solubility of AgBr in $\text{NH}_3(\text{aq}) = 0.0236 \times 188\text{gdm}^{-3} = 4.4368\text{gdm}^{-3}$

And mass of AgBr dissolved in 50mL = $\frac{50}{1000} \times 4.4368\text{gdm}^{-3} = 0.22\text{g}$

(i) Hence mass of AgBr dissolved in 50mL of ammonia solution is 0.22g.

(ii) Taking $\frac{\text{solubility of AgBr in ammonia}}{\text{solubility of AgBr in water}} = \frac{4.4368\text{gdm}^{-3}}{1.1 \times 10^{-4}\text{g/dm}^3} = 40335$

Hence the solubility of silver bromide in the given ammonia solution is about forty thousand times its solubility in water.

DIGGING DEEPER EXERCISE 19

EXERCISE 19A: BINDER QUESTIONS

Question 1

The solubility of Zn(OH)_2 is not the same in the following solutions as it is in pure water. In each case state whether the solubility is greater or less than that in water and briefly account for the change in solubility.

- (a) 1-molar HCl (c) 1-molar NaOH
(b) 1-molar $\text{Zn(NO}_3)_2$ (d) 1-molar NH_3

Question 2

One litre of water is able to dissolve $2.5 \times 10^{-3} \text{ mol}$ of PbF_2 . What is the K_{sp} for PbF_2 ?

Question 3

What is the molar solubility of Fe(OH)_3 in a solution with a hydroxide ion concentration of 0.05 M ?

$$K_{\text{sp}} = 1.6 \times 10^{-39} \text{ M}^4$$

Question 4

Will a precipitate of CaSO_4 form in a solution if the Ca^{2+} concentration is 0.0025 M and the SO_4^{2-} concentration is 0.030 M ? For CaSO_4 , $K_{\text{sp}} = 2.4 \times 10^{-5} \text{ M}^2$.

Question 5

Will a precipitate of PbSO_4 form if 100 mL of $1 \times 10^{-3} \text{ M}$ $\text{Pb(NO}_3)_2$ solution is added to 100 mL of $2 \times 10^{-3} \text{ M}$ MgSO_4 solution? $K_{\text{sp}} = 6.3 \times 10^{-7}$

Question 6

For the equilibrium; $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$; $K_{\text{sp}} = 5 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$.

- (a) What is the molarity of calcium carbonate in a saturated solution at 298 K ?
(b) What is the solubility of calcium carbonate in 0.1 mol dm^{-3} sodium carbonate solution?

Question 7

A 50.0 mL sample of a saturated aqueous solution of lead bromide, PbBr_2 , was evaporated to dryness. 0.422 g of solid PbBr_2 was obtained. Calculate the value of K_{sp} (PbBr_2).

EXERCISE 19B: REAL QUESTIONS

Question 8

Silver bromide dissolves more in ammonia solution than in pure water. Explain the difference.

Question 9

Explain why addition of NH_3 or HNO_3 to a saturated solution of Cu(OH)_2 in contact with solid Cu(OH)_2 increases the solubility of the solid.

Question 10

Supersaturated solution of calcium sulphate in water are prepared by cooling its saturated solution. Supersaturated solution of carbon dioxide in water is prepared by heating its saturated solution. Explain the reasons for the difference in the two procedures.

Question 11

When hydrochloric acid solution is added to a supersaturated solution of calcium carbonate, the precipitate dissolves into clear solution but when it is added to a saturated solution of silver chloride, the solution becomes supersaturated accompanied with clear formation of precipitate. Explain.

Question 12

You were discussing the following question with your friend **Kipute**;

Two hypothetical salts, X_2Y and PQ , have the same molar solubility in water. If the solubility product for X_2Y is 1.08×10^{-7} , what is the solubility product for PQ ?

In the discussion, **Kipute** argued that because the two compounds have the same molar solubility; the solubility product of PQ will be also 1.08×10^{-7} . With a reason, state whether you agree or disagree with **Kipute**. If you agree, explain clearly your reason and if you disagree, help **Kipute** to find the solubility product.

EXERCISE 19C: HOT QUESTIONS**Question 13**

For the equilibrium; $\text{CaSO}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$; $K_{\text{sp}} = 2 \times 10^{-5} \text{mol}^2 \text{dm}^{-6}$

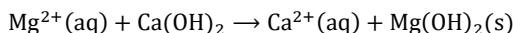
- What is the solubility of calcium sulphate in a saturated solution of the salt in gcm^{-3} ?
- Assuming equal volumes of solutions are mixed, what is the minimum concentration of sodium sulphate (Na_2SO_4) solution that when added to a $1 \times 10^{-4} \text{mol dm}^{-3}$ solution of calcium sulphate, will just begin to cause precipitation of calcium sulphate?

Question 14

What is the pH in a saturated solution of $\text{Ca}(\text{OH})_2$? $K_{\text{sp}} = 5.5 \times 10^{-6} \text{M}^3$

Question 15

A useful commercial source of magnesium is sea water, where $[\text{Mg}^{2+}(\text{aq})]$ is 0.054mol dm^{-3} . The magnesium is precipitated from solution by adding calcium hydroxide.



- Write an expression for the K_{sp} of $\text{Mg}(\text{OH})_2$, including its units.
- The numerical value for K_{sp} is 2×10^{-11} . Calculate $[\text{Mg}^{2+}(\text{aq})]$ in a saturated solution of $\text{Mg}(\text{OH})_2$.
- Hence calculate the maximum percentage of the original magnesium in the seawater that this method can extract.

Question 16

At 25°C the solubility product constant, K_{sp} , for strontium sulphate, SrSO_4 , is 7.6×10^{-7} . The solubility product constant for strontium fluoride, SrF_2 , is 7.9×10^{-10} .

- What is the molar solubility of SrSO_4 in pure water at 25°C ?
- What is the molar solubility of SrF_2 in pure water at 25°C ?
- An aqueous solution of $\text{Sr}(\text{NO}_3)_2$ is added slowly to 1 litre of a well-stirred solution containing 0.02mole F^- and $0.1 \text{mole SO}_4^{2-}$ at 25°C . (You may assume that the added $\text{Sr}(\text{NO}_3)_2$ solution does not materially affect the total volume of the system.)
 - Which salt precipitates first?
 - What is the concentration of strontium ion, Sr^{2+} , in the solution when the first precipitate begins to form?
- As more $\text{Sr}(\text{NO}_3)_2$ is added to the mixture in (c) a second precipitate begins to form. At that stage, what percent of the anion of the first precipitate remains in solution?

Question 17

A saturated solution of lead iodate in pure water has a lead ion concentration of 4×10^{-5} mole per litre at 25°C.

- (a) Calculate the value for the solubility-product constant of $\text{Pb}(\text{IO}_3)_2$ at 25°C.
- (b) Calculate the molar solubility of $\text{Pb}(\text{IO}_3)_2$ in a 0.10molar $\text{Pb}(\text{NO}_3)_2$ solution at 25°C.
- (c) To 333millilitres of a 0.120-molar $\text{Pb}(\text{NO}_3)_2$ solution, 667 millilitres of 0.435-molar KIO_3 is added. Calculate the concentrations of Pb^{2+} and IO_3^- in the solution at equilibrium at 25°C.

Question 18

Barium ions are poisonous. Patients with digestive tract problems are sometimes given an X-ray after they have swallowed a 'barium meal', consisting of a suspension of BaSO_4 in water. The $[\text{Ba}^{2+}(\text{aq})]$ in a saturated solution of BaSO_4 is too low to cause problems of toxicity.

- (a) Write an expression for the solubility product, K_{sp} , for BaSO_4 , including its units.
- (b) The numerical value of K_{sp} is 1.3×10^{-10} . Calculate $[\text{Ba}^{2+}(\text{aq})]$ in a saturated solution of BaSO_4 .
- (c) The numerical value of K_{sp} for BaCO_3 (5×10^{-10}) is not significantly higher than that for BaSO_4 , but barium carbonate is very poisonous if ingested. Suggest a reason why this might be so.

EXAMINATION QUESTIONS FOR PART FIVE

Question 1

- (a) Explain why the neutralisation reaction of a strong acid and a weak base gives an acidic solution.
- (b) 0.16g of an acid, of relative molecular mass 118, was made up to 250cm^3 of aqueous solution. 25cm^3 of this solution required 27.1cm^3 of 0.1M sodium hydroxide for neutralisation. Calculate the mass of acid reacting with 1 mole of sodium hydroxide and hence basicity of acid.

Question 2

- (a) Classify whether aqueous solutions of the following salts are acidic, basic or neutral:
 $\text{FeCl}_3, \text{K}_2\text{CO}_3, \text{NH}_4\text{Br}, \text{KClO}_4, \text{KCl}, \text{HCOOK}$
- (b) 100cm^3 of vinegar at 15°C were diluted to 250cm^3 with distilled water. 25cm^3 of the diluted solution required 16.9cm^3 of 0.5MNaOH for neutralisation with phenolphthalein as indicator. Assuming that all the acidity of vinegar is caused by ethanoic acid; calculate the percentage by mass of this acid in the original vinegar. (Density of vinegar at 15°C is 1.02gcm^{-3}).

Question 3

- (a) Why do the salts of strong acid and strong base not hydrolyse in the solution?
- (b) 8.58g of washing soda were made up to 250cm^3 of aqueous solution. 25cm^3 of this solution required 30cm^3 of 0.2MHCl for neutralisation with methyl orange as indicator. Calculate x in the formula, $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$, for washing soda.

Question 4

- (a) Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present:
 $\text{PbCO}_3, \text{CuI}, \text{KClO}_4, \text{AgCl}, \text{BaSO}_4, \text{CaF}_2$
- (b) A potassium salt has the formula, $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{KHC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$
Calculate x from the following data. 1.923g of potassium salt was neutralised by 22.7cm^3 of 1M NaOH, phenolphthalein as indicator.

Question 5

- (a) Suggest at least three practical facts which make salt to dissolve slowly in water.
- (b) 1.5g of a sample of limestone was dissolved in 50cm^3 of 1M hydrochloric acid. The resulting solution was made up to 250cm^3 with distilled water. 25cm^3 of this solution required 21.05cm^3 of 0.1M sodium hydroxide for neutralisation. Assuming all the basic material in the rock to be calcium carbonate, calculate the percentage of calcium carbonate present.

Question 6

- (a) Explain why NaCl cannot be a component in either an acidic or basic buffer.
- (b) Calculate the relative molecular mass of the carbonate of divalent metal X and hence the relative atomic mass of X from the data: 1g of the anhydrous normal carbonate of X was added to 50cm^3 of 1MHCl. The excess acid required 30cm^3 of 1MNaOH for neutralisation.

Question 7

- (a) Which solute combinations can make a buffer? Assume all are aqueous solutions.
 HNO_3 and KNO_3 , NaHCO_3 and Na_2CO_3 , NH_4NO_3 and NH_3 , H_3PO_4 and Na_3PO_4 , HClO_4 and NaClO_4
- (b) Calculate the percentage of ammonium sulphate in a sample of this compound contaminated with sodium sulphate from the following data: 1.65g of the ammonium sulphate was made up to 250cm^3 of aqueous solution. 25cm^3 of this solution were boiled with 50cm^3 of 0.1 M NaOH and the excess alkali neutralised by 25.4cm^3 of 0.1MHCl.

Question 8

- (a) Why weak acid alone cannot act as buffer solution?
- (b) 25cm^3 of solution of sodium carbonate and sodium hydroxide required 18.6cm^3 of 0.1M hydrochloric acid for the end point as determined by phenolphthalein as indicator. Another 25cm^3 of the same solution required 22.7cm^3 of 0.1M HCl, using methyl orange as indicator. Calculate the concentration of each in the original liquid in gdm^{-3} .

Question 9

Find pH of:

- (i) 0.05M CH_3COOH ($K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}\text{M}$)
- (ii) 0.05M HCl

Comment on difference in two values obtained.

Question 10

A 0.1M solution of aqueous ammonia is 1.4% dissociated at 25°C;

- (a) Calculate the dissociation constant of the base at this temperature, hence its pK_b
- (b) Obtain a value for degree of dissociation of $\text{NH}_3(\text{aq})$ in 0.002M solution, hence its pH of the solution.

Question 11

- (a) Why the mixture of sulphuric acid and salt containing its conjugate base like sodium hydrogensulphate is not a buffer solution?
- (b) What is the degree of ionisation and pH of a 0.01M solution of ethanoic acid at 25°C if K_b for CH_3COO^- at this temperature is 5.025×10^{-10} .

Question 12

- (a) Does temperature affect pH of buffer solution? Explain.
- (b) The solubility benzoic acid in water at 0°C is 2.44gdm^{-3} ; if the freezing point at standard pressure of a saturated solution of benzoic acid is -0.0392°C . Calculate the dissociation constant of the acid (Ebullioscopic constant of water is 1.86°C).

Question 13

- (a) Is it possible for CH_3COONa and HCl to make a buffer? Explain.
- (b) What is the condition for pH and pK_a of ethanoic acid (CH_3COOH) solution to be equal?

Question 14

- (a) Explain briefly how do the buffer solutions resist the change in pH?
- (b) Prove that $[\text{H}_3\text{O}^+]$ for any weak acid, H_nA is given by;
$$[\text{H}_3\text{O}^+] = \sqrt[n+1]{nCK_a}$$
 where C is concentration of the acid.

Question 15

- (a) The solubility product, K_{sp} , of AgCl has a value of 1.56×10^{-10} at 25°C and this value increases to 2.15×10^{-8} at 100°C. Explain why K_{sp} is higher at 100°C. Include reference to the relevant equilibrium equation in your answer.
- (b) The dissociation constant of acetic (ethanoic acid) is 1.8×10^{-5} . Show that the pH of a solution containing 0.02 of a mole ethanoic acid and 0.2mole of a mole of sodium ethanoate per dm^3 is 5.7.

Question 16

- (a) Explain clearly what is wrong with the following definition:
 - (i) **Buffer solution:** *Is the solution which can maintain its pH value on addition of any amount of acid or base.*
 - (ii) **Common ion effect:** *Is the depression in solubility of sparingly soluble substance after introducing strong electrolyte with the same ion as that present in sparingly soluble substance.*
- (b) How many cm^3 of 0.1M HCOONa that must be added to 100 cm^3 of 0.01M HCOOH to make a buffer solution of pH 5? (K_a value of HCOOH is 1.6×10^{-4}).

Question 17

- (a) State Bronsted – Lowry theory of acids and bases and hence list down at least four advantages of the Bronsted – Lowry concept over the Arrhenius concept.
- (b) What is the pH of a buffer solution by adding 100cm^3 of chloroethanoic acid (CH_2ClCOOH) of concentration 0.5M to 100cm^3 of 0.25MNaOH . (pK_a of CH_2ClCOOH is 2.86).

Question 18

- (a) What is the concentration hydronium ion (H_3O^+), of a dm^3 buffer solution that contains 0.1mole of hydrocyanic acid (HCN) and 0.8mole of sodium cyanide?
- (b) If 0.1 mole of hydrochloric acid, HCl, is added to the buffer solution in (a) above, what will be the new $[\text{H}_3\text{O}^+]$.
- (c) Calculate the pH of the buffer solution in (a) above if 0.02mole of sodium hydroxide (NaOH) is added to it. $\text{K}_a(\text{HCN}) = 4.93 \times 10^{-10}$.

Question 19

The K_{sp} of $\text{Mg}(\text{OH})_2$ at 25°C is $1.1 \times 10^{-11}\text{mol}^3\text{dm}^{-9}$

Calculate the solubility (in gdm^{-3}) of $\text{Mg}(\text{OH})_2$

- (i) In water
(ii) In 0.1MNaOH

Question 20

The solubility of Lead (II) sulphate at 20°C is 0.4gdm^{-3} :

- (i) What is the solubility product?
(ii) Calculate the solubility in gdm^{-3} in a 0.01M of Na_2SO_4 solution. ($\text{Pb} = 207, \text{S} = 32, \text{O} = 16$).

Question 21

The solubility product of silver chloride at room temperature is $1 \times 10^{-10}\text{mol}^2\text{dm}^{-6}$. What is the maximum loss from a precipitate of silver chloride if it is washed with:

- (a) One dm^3 of distilled water
(b) One dm^3 of 0.01MHCl ($\text{Ag} = 108$ and $\text{Cl} = 35.5$)

Question 22

- (a) Anhydrous aluminium chloride does not conduct electricity but in aqueous solution conducts. Explain.
- (b) How many grams of silver chloride will be precipitated if 5.85g of NaCl are added to a litre of saturated silver chloride solution? ($\text{K}_{\text{sp}}(\text{AgCl}) = 1.69 \times 10^{-10}\text{mol}^2\text{dm}^{-6}$)

Question 23

If the dissociation constant for NaF and NH_3 are 1.5×10^{-11} and 1.77×10^{-5} respectively. Find the pH of:

- (i) A 0.25M solution of NaF
(ii) A 0.01M solution of NH_3

Question 24

The solubility of $\text{Fe}(\text{OH})_2$ in water at 25°C is 0.6mgdm^{-3} ; calculate:

- (a) The K_{sp} value of $\text{Fe}(\text{OH})_2$
(b) The minimum pH required to precipitate Fe^{2+} so completely that no more than 1microgram (10^{-6}g) of Fe^{2+} remains in solution.

Question 25

To a solution containing $0.1\text{M}\text{Ca}^{2+}$ and $0.1\text{M}\text{Ba}^{2+}$, Na_2SO_4 is added slowly. The solubility product of CaSO_4 and BaSO_4 are 2.4×10^{-5} and 1.1×10^{-10} respectively;

- (a) Which will precipitate first, CaSO_4 or BaSO_4 ? Explain
(b) What is the $[\text{SO}_4^{2-}]$ at the instant the first solid precipitates
(c) Neglect dilution and calculate the $[\text{Ba}^{2+}]$ present when the first precipitate of CaSO_4 occurs

Question 26

- (a) Give the meaning of the following terms:
- Solubility
 - Saturated solution
 - Saturated point
 - Supersaturated solution
 - Fractional precipitation
- (b) At room temperature, the solubility products of silver chloride and silver chromate are respectively $1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ and $1 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$. What is the concentration in mol dm^{-3} of potassium chromate at the end point when used as indicator in titrating a chloride by silver nitrate?

Question 27

The following data are values for K_w at different temperature, in units of $\text{mol}^2 \text{ dm}^{-6}$

Temperature ($^{\circ}\text{C}$)	10	20	30
$K_w \times 10^{-14}$	0.293	0.681	1.471

- What is the pH of pure water at 30°C
- What is the pH at equivalent point of titration of aqueous hydrochloric acid with potassium hydroxide at 10°C ?

Question 28

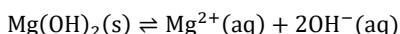
For weak acid HA, $K_a = 1.0 \times 10^{-6} \text{ mol dm}^{-3}$. Given two solutions, one containing 0.1 mol dm^{-3} of HA and other 0.1 mol dm^{-3} of sodium hydroxide. Explain how would you make:

- A solution with pH = 6
- A solution with pH = 5

Which of these solution would constitute the best buffer solution?

Question 29

- (a) When excess magnesium hydroxide is added to water and shaken, a saturated solution is formed and the mixture reaches equilibrium;



The solubility product, K_{sp} for this process is;

$$K_{sp} = [\text{Mg}^{2+}(\text{aq})][\text{OH}^{-}(\text{aq})]^2$$

- Give a reason why the magnesium hydroxide is not included in the expression for K_{sp} .
 - Derive units of K_{sp}
- (b) Calculate concentration of calcium carbonate precipitate in g dm^{-3} if 0.1 M of calcium chloride is added to equal volume of 0.1 M of sodium carbonate solution. Given that: K_{sp} of $\text{CaCO}_3 = 1.69 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$

Question 30

- Explain how the value of solubility product of sparingly soluble substance varies with temperature change.
- Calculate the pH of $1 \times 10^{-9} \text{ M HCl}$.

Question 31

- Is it possible for neutral solution to have pH of less than 7? Explain your answer.
- The pH of a solution A, 0.15 M solution of weak monoprotic acid, Hx is 2.69
 - Calculate $[\text{H}^{+}]$ in solution A and hence determine the value of K_a for Hx
 - A 25 cm^3 sample of A is titrated with 0.25 M NaOH . Calculate the pH of the titrated solution when Hx is exactly half neutralized and $[\text{Hx}] = [\text{x}^{-}]$

Question 32

- (a) Classify the following species as Bronsted acid/Base. S^{2-} , HCO_3^- , H_2O , NH_3 .
- (b) The ionisation constant of NH_4^+ in water is $5.6 \times 10^{-10} \text{ mol dm}^{-3}$ at 25°C . The rate constant for the reaction of NH_4^+ ions and OH^- ions to form NH_3 and water at 25°C is $3.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$. Calculate the rate constant for the proton transfer from water to NH_3 .

Question 33

- (a) Explain the two components of the buffer solution.
- (b) An unknown student taken an unknown weight of an unknown weak monobasic acid, dissolves it in an unknown amount of water, and titrates it with a strong monoacid base of unknown concentration. When he has added 10.00mL of base, he noticed that the concentration of H_3O^+ is $1.0 \times 10^{-5} \text{ M}$. He continues the titration until he reaches the equivalent point. At this time burette reads 22.22mL. What is the dissociation constant of acid?

PART SIX

ELECTROCHEMISTRY

Is the study of chemical changes produced by electrical current and the production of electricity by chemical reactions. It is the scientific study of the chemical species and reactions that take place at the interface between an electron conductor and an ion conductor (electrolyte) in which an electron transfer occurs between the electrode and the electrolyte in solution.

Chapter 20

REDOX REACTIONS

INTRODUCTION

Redox reactions occur every day and are vital to some of the basic functions of life. Some examples include photosynthesis, respiration, combustion and rusting. In these redox reactions electrons are transferred between two species. The transfer of electrons leads to a change in oxidation number of the species involved in the redox reactions.

The modern definition of redox reaction is based on this concept of electron transfer or electron flow. In this perspective, redox reactions can simply be defined as *chemical reactions which involve transfer of electrons*.

Oxidation and reduction

We have seen that, in the redox reactions there is a transfer of electrons. The transfer of electrons means that one specie is losing electrons while another specie is gaining electrons simultaneously. The action of losing electrons is known as **oxidation** while that of gaining electrons is known as **reduction**. Actually even the term **redox** itself originated from these two terms, **reduction** and **oxidation**.

In the order of their discovery (according to development of study of chemistry) starting with the oldest one to the latest one, **oxidation** can be defined in the following ways:

Oxidation can be defined as *the loss of electron(s) by an atom, ion or a molecule* whereas **reduction** is *the gain of electrons by an atom, ion or a molecule*.

When electrons are removed from an atom or ion, the **oxidation state** of the atom or ion **increases**. So oxidation may also be defined as *an increase of oxidation state of an atom, ion or a molecule*.

On another hand when electrons are added to an atom or ion, the **oxidation state** of the atom **decreases**. So reduction may also be defined as *the decrease of oxidation state of an atom, ion or a molecule*.

Therefore, in redox reactions, *oxidation number of a molecule, atom or ion changes by gaining or losing electron(s)*.

Oxidising agent and reducing agent

An **oxidising agent** (or **oxidant**) is *the specie which gains electrons from the electron donating specie during redox reaction*.

- Oxidising agents are **reduced** during redox reaction and their **oxidation states decrease** during the reaction.

On another hand, reducing agent (or **reductant**) is *the specie which donates electrons to the electron deficient specie during redox reaction*.

- Reducing agents are **oxidised** during redox reactions and their **oxidation states increase** during the reaction

It should be noted that:

$$\text{Number of electrons lost by reductant} = \text{Number of electrons gained by oxidant}$$

So it can be concluded that **the reaction will be redox if and only if it involves the change in oxidation state of species involved in the reaction. Otherwise the reaction is not redox.**

So the ability to determine oxidation states of species involved in the reaction is very important to determine whether the reaction is redox or not. Rules of determining oxidation states are going to be discussed in the next section.

Oxidation state

Oxidation state (also termed as **oxidation number**) is the number of electrons gained or lost by an atom in combining with another atom by assumption that the bond formed between the atoms is ionic.

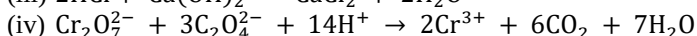
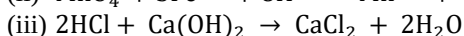
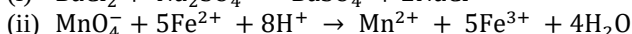
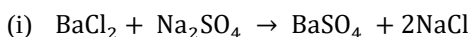
- Oxidation number (**O.N**) gives the relative electron electronegativity of the two combining atoms; whereby the more electronegative atom has negative oxidation number while the more electropositive (less electronegative) has positive oxidation number.

Rules of assigning oxidation numbers

- The oxidation number of neutral element is zero.
- The total oxidation number of atoms in a neutral compound is zero.
- The oxidation number of an ion (charged atom) is equal to the charge of the ion.
- The total oxidation number of atoms in a charged radical is equal to the amount of the charge of the radical.
- Some atoms of elements have fixed oxidation number in their compounds. For example:
 - Atoms of all group I elements have oxidation number +1 in their compounds.
 - Atoms of all group II elements have oxidation number of +2 in their compounds.
 - Fluorine atom has oxidation number of -1 in its compounds.
- Oxidation number oxygen atom is -2 except in:
 - Peroxides (e.g. H_2O_2 , Na_2O_2) where its oxidation number is -1.
 - F_2O where its oxidation number is +2
 - Superoxides like KO_2 where is $-1/2$.
- Oxidation number of hydrogen atom is +1 except in ionic hydrides (e.g. NaH) where its oxidation number is -1.

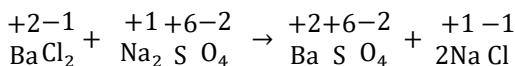
Example 1

In the following reactions determine whether the reaction is redox or not and state the oxidising and reducing agent for redox ones.



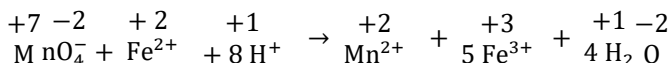
Solution

- (i) Assigning oxidation numbers of each atom involved in the reaction.



Hence the reaction is not redox because oxidation states of all species involved in the reaction have remained the same

- (ii) Assigning oxidation numbers of each atom or ion involved in the reaction.



The reaction is redox because:

- The oxidation number of manganese decreased from +7 to +2
- The oxidation number of iron increased from +2 to +3

Hence:

- The oxidising agent is MnO_4^-
- The reducing agent is Fe^{2+}

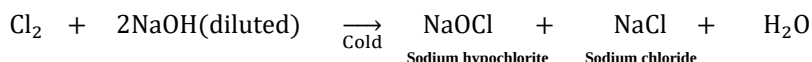
(On your own follow the same procedures to attempt solving (iii) and (iv))

Disproportionation reactions

Disproportionation reaction is the redox reaction whereby both reduction and oxidation occurs in the **same element** contained in a particular molecule or compound. It is also known as **dismutation reaction**.

- Examples of disproportionation reaction are:

- 1) Chlorine gas disproportionate in cold and dilute sodium hydroxide (NaOH) yielding hypochlorite and chloride and its **yellowish colouration disappears**.



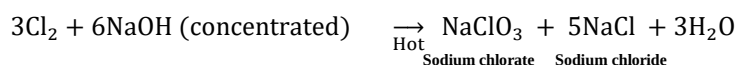
Where: Oxidation number of Cl atom in Cl_2 is 0

Oxidation number of Cl atom in NaOCl is +1

Oxidation number of Cl atom in NaCl is -1

From above example, it is clearly understood that chlorine atom has been oxidised to hypochlorite in which its oxidation number increases from 0 to +1 while another chlorine atom from the same chlorine element has been reduced to chloride in which its oxidation number has been decreased from 0 to -1.

- 2) Chlorine gas disproportionate in hot concentrated NaOH yielding chlorate and chloride and its yellowish colouration disappears.



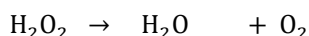
Where: Oxidation number of Cl atom in Cl_2 is 0

Oxidation number of Cl atom in NaClO_3 is +5

Oxidation number of Cl atom in NaCl is -1

Again, it is clearly understood that chlorine atom has been oxidised to chlorate in which its oxidation number increases from 0 to +5 while another chlorine atom from the same chlorine element has been reduced to chloride in which its oxidation number has been decreased from 0 to -1.

- 3) Decomposition of hydrogen peroxide, disproportionates the peroxide into water and oxygen gas which is observed as effervescence of colourless gas which relight glowing splint.



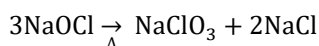
Where:

Oxidation number of oxygen in O_2 is 0

Oxidation number of oxygen in H_2O_2 is -1 (Decreases from 0 hence reduction)

Oxidation number of oxygen in H_2O is +1 (Increases from 0 hence oxidation)

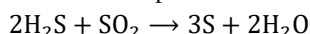
- 4) Heating of NaOCl, disproportionates the hypochlorite into chlorate and chloride.



The reader should understand that:

In some cases, the opposite of disproportionation may happen whereby two reactants containing the same element in different oxidation states react to give a product in which the element's oxidation state is different to either of the original oxidation state. Reactions of this kind are known as **comproportionation** or **synproportionation reactions**.

A good example of this is the reaction between hydrogen sulphide and sulphur dioxide whereby the two compounds comproportionate to elemental sulphur.



Where:

Oxidation number of sulphur in H_2S increases from -2 to 0 in S (oxidation).

Oxidation number of sulphur in SO_2 decreases from +4 to 0 in S (reduction).

By definition, **comproportionation reaction** is the redox reaction in which two reactants containing the same element in different oxidation states react to give a product containing the element in an intermediate oxidation state.

BALANCING REDOX REACTIONS IN ACIDIC AND BASIC MEDIUM

Like **acid – base reactions**, redox reactions are matched set, that is, there cannot be an oxidation reaction without a reduction reaction happening simultaneously. The oxidation alone and the reduction alone are each called a **half – reaction**, because two half – reactions always occur together to form a whole reaction. When writing half – reaction the gained or lost electrons are typically included explicitly in order that the half – reaction be balanced with respect to electric charge.

Balancing in acidic medium

Redox reactions are balanced by using the following procedures:

1. Balancing material

This involves balancing all other atoms present leaving oxygen and hydrogen atoms. This is done by trial and error method.

2. Balancing oxygen atoms

This is done by adding suitable number of water molecules to the side of fewer oxygen atoms

3. Balancing hydrogen atoms

This is done by adding suitable number of hydrogen protons (H^+) to the side of fewer hydrogen atoms.

4. Balancing charges

This is done by adding suitable number of electrons to the side of higher charge.

It should be noted that:

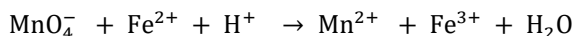
The above four procedures are done after splitting the overall reaction equation into **two half reactions** (hence the name '**half reaction method**' of balancing redox reactions). The two half reactions are **oxidation half reaction** and **reduction half reaction**

5. Conservation of electrons (Balancing of electrons)

This is done in writing overall reaction equation by making sure that number of electrons lost in oxidation half reaction is equal to the number of electrons gained in reduction half reaction. This may require multiplication of number(s) to all terms of half reaction(s)

Example 2

By using half reaction method, balance the following redox reaction:



Solution

Oxidation half reaction: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ (Not balanced)

Balancing charges: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^- \dots\dots\dots$ (i)

(The equation (i) above is the balanced oxidation half reaction equation)

Reduction half reaction: $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$

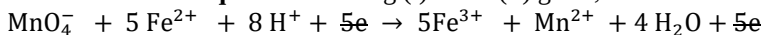
Balancing oxygen atoms: $\text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

Balancing hydrogen atoms: $\text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

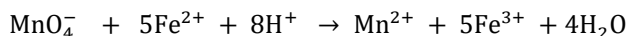
Balancing charges: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \dots\dots\dots$ (ii)

(The equation (ii) above is the balanced reduction half reaction equation)

Overall reaction equation: Taking (i) $\times 5$ + (ii) gives;



Hence the overall balanced reaction equation is:

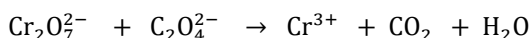


It should be noted that:

Presence of H^+ at the left hand side confirms that the reaction took place under acidic medium (**The medium should be present at the start of the chemical reaction i.e. it must appear at left hand side of the reaction equation**).

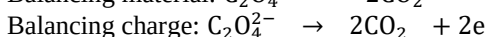
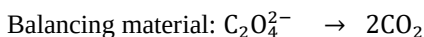
Example 3

By using half reaction method, balance the following redox reaction under acidic medium.

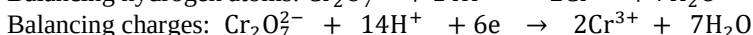
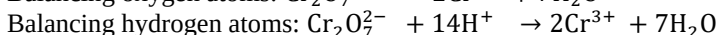
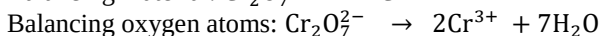
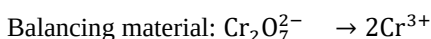


Solution

Oxidation half reaction

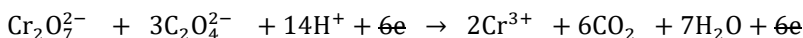


Reduction half reaction

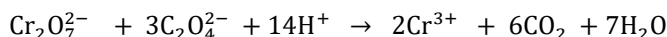


Overall reaction equation

Taking (i) $\times 3$ + (ii) gives;

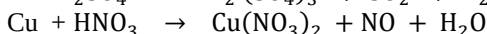
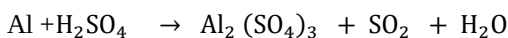


Hence the overall reaction equation is:

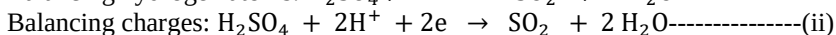
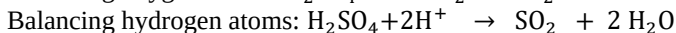
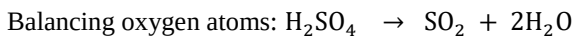
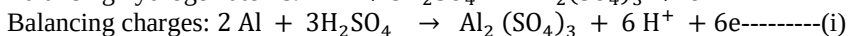
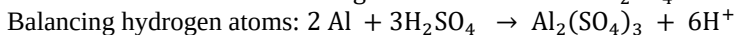
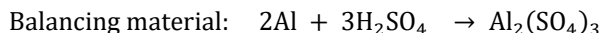


Example 4

By using half reaction method, balance the following redox reactions:



Solution

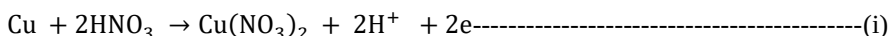


Writing overall reaction equation by taking (i) + $3 \times$ (ii):



Oxidation half reaction

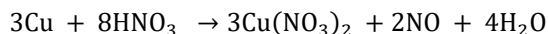
Following the same procedures as in (i), it gives the following oxidation half reaction equation:



Reduction half reaction

In this case the equation is: $\text{HNO}_3 + 3\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$ -----(ii)

Writing overall reaction equation by taking (i) $\times 3$ + (ii) $\times 2$

**Balancing in basic medium**

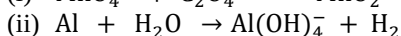
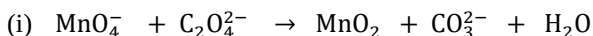
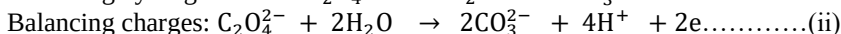
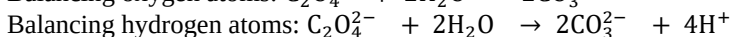
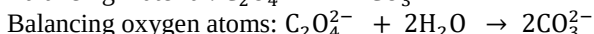
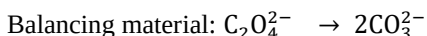
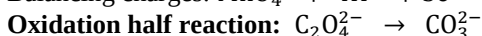
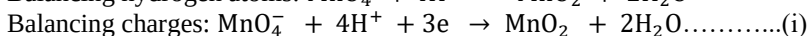
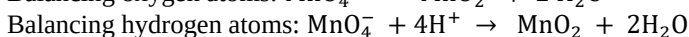
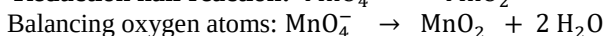
Balancing the redox reaction equation under basic medium is simply done by eliminating H^+ from the overall balanced equation by adding suitable number of OH^- to obtain OH^- on one side and H_2O on the other side.

However **it should be noted that**, H_2O and OH^- may be on one side if:

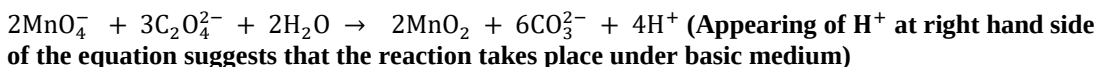
- The reaction is between amphoteric metal with $\text{NaOH}(\text{aq})$ or
- The reaction is a disproportionation one.

Example 5

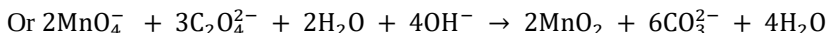
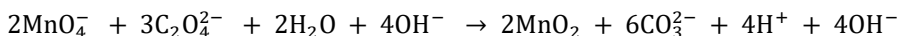
Balance the following redox reactions in basic medium

**Solution**

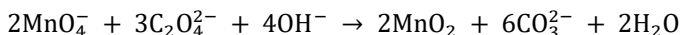
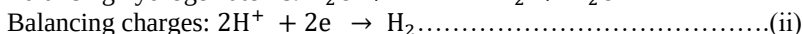
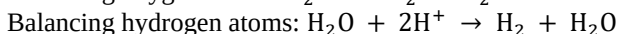
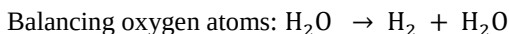
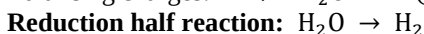
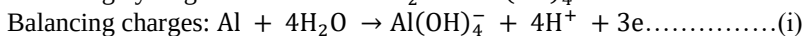
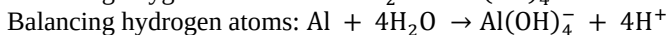
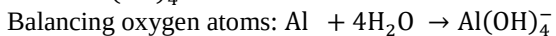
Taking (i) $\times 2$ + (ii) $\times 3$ gives



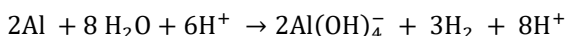
Adding 4OH^- both sides gives



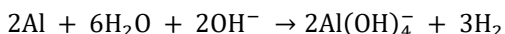
Hence the balanced overall reaction equation is:

**Oxidation half reaction**

Taking (i) $\times 2$ + (ii) $\times 3$ gives:



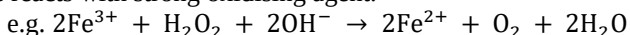
Adding 2OH^- both sides gives overall reaction equation as follows:



ACTION OF HYDROGEN PEROXIDE

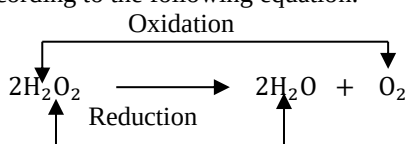
In redox reactions, hydrogen peroxide can undergo oxidation, reduction or disproportionation depending on reacting conditions.

Oxidation: It can be oxidised to oxygen gas thus acting as reducing agent. This happens when the peroxide reacts with strong oxidising agent.



Reduction: It can be reduced to water thus acting as oxidising agent. This happens when the peroxide reacts with strong reducing agent. e.g. $\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{I}_2$

Disproportionation: It can disproportionate to water and hydrogen gas. This occurs in its decomposition according to the following equation:

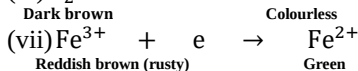
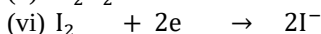
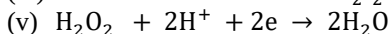
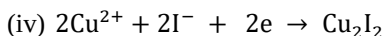
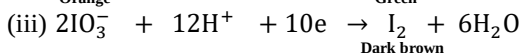
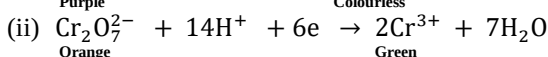
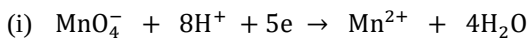


Note: The volume in cm^3 of oxygen gas produced when 1cm^3 of H_2O_2 (hydrogen peroxide) is decomposed at given conditions of temperature and pressure (normally at s.t.p) is known as **volume strength** or **volume rating**. It answers the question: *the volume of oxygen gas produced (on decomposition of the peroxide) is how many times the volume of hydrogen peroxide?*

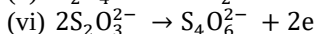
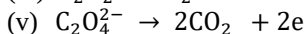
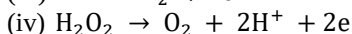
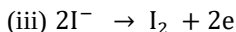
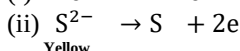
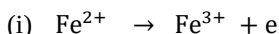
COMMON REDUCTION AND OXIDATION HALF REACTIONS

To make the work of dealing with problems which involve knowledge of redox reactions easier, a student should be able to memorise the following common reduction and oxidation half reactions.

Common reduction half reactions (oxidising agents are on left hand side)



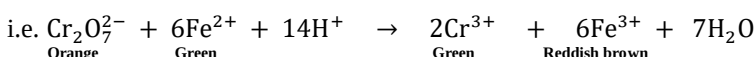
The reader should not confuse the formation of colourless solution in (i) above after reduction of MnO_4^- to Mn^{2+} and the pink colouration which is obtained at the end point of redox titration which employ KMnO_4 as an oxidising agent. The pink colouration is explained by presence of excess (very small unreacted amount) KMnO_4 just after the equivalence point.

Common oxidation half reaction (reducing agents are on left hand side)**Example 6**

With help of balance chemical equation state what will you observe when solution of Iron (II) sulphate is added into a beaker containing acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$.

Solution

A colour mixture of reddish brown and green colouration is observed

**Example 7**

What happen when hydrogen sulphide is added into a beaker containing acidified solution of potassium permanganate?

Solution

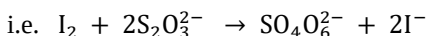
KMnO_4 is reduced to Mn^{2+} while H_2S is oxidised to sulphur which is recognised by its yellow colouration precipitate. i.e. $2\text{MnO}_4^- + 5\text{S}^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{S} + 8\text{H}_2\text{O}$

Example 8

Explain what happens when a solution of sodium thiosulphate is added into a beaker containing iodine solution.

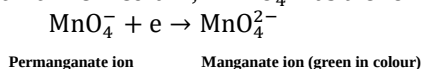
Solution

Sodium thiosulphate being a reducing agent, reduces I_2 which is an oxidising agent to I^- and itself become oxidised to $\text{S}_4\text{O}_6^{2-}$ and dark brown colouration of I_2 disappears.

**ACTION OF KMnO_4 IN DIFFERENT MEDIUM**

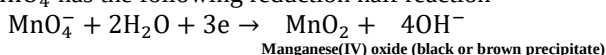
Most of common redox reactions take place under acidic medium. In most cases, basic medium lowers actions (power) of oxidising agent while acidic medium increases the power of oxidising agents to oxidize reducing agents. Some oxidising agents like **$\text{K}_2\text{Cr}_2\text{O}_7$ and KIO_3 needs acidic medium to show their oxidising power, they cannot show oxidation characters in basic or neutral medium.** However KMnO_4 being strongest oxidising agent can show oxidising properties in all three conditions (acidic, basic and neutral medium).

Under strongly alkaline medium, KMnO_4 has the following reduction half reaction:



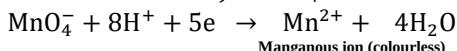
Whereby permanganate gains 1 electron only and its O.N decreases by 1 from +7 (in MnO_4^-) to +6 (in MnO_4^{2-}). Apart from the medium being strong alkali like KOH , the reaction is more predominant when the permanganate is in excess.

Under neutral medium, KMnO_4 has the following reduction half reaction



Whereby the permanganate gains 3 electrons and its oxidation number decreases by 3 from +7 to +4 (in MnO_2) and hence it is stronger oxidising agent under neutral medium than in alkaline (basic) medium. However, the reaction can also occur in basic medium if the base is not very strong.

Under acidic medium, KMnO_4 has the following reduction half reaction:

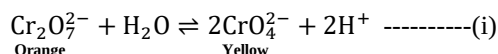


Whereby the permanganate gains 5 electrons and its oxidation number decreases by 5 from +7 to +2 and hence of the three media, the permanganate is strongest oxidising agent in acidic medium.

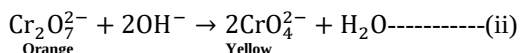
ACTION OF POTASSIUM DICHROMATE (VI)

Potassium dichromate (VI), $\text{K}_2\text{Cr}_2\text{O}_7$ is very strong reducing agent. However, it is not strong oxidising agent as potassium permanganate, KMnO_4 .

- It acts as an oxidising agent in acidic medium only.
- The neutral aqueous solution of dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is equilibrium mixture which contains equal amount of dichromate and chromate (K_2CrO_4) as result of hydrolysis of dichromate according to the following equation:



- Whereby chromate is weak oxidising agent and hence the oxidising strength of dichromate is decreased in the neutral solution. ***What is the effect of adding acid like dilute H_2SO_4 to the above equilibrium?***
- Addition of acidic solution like sulphuric acid which ionises completely to give H^+ thus increasing concentration of H^+ to above equilibrium, shifts position of equilibrium to the left hand side by forming more dichromate which is strong oxidising agent. Hence the dichromate is stronger oxidising agent in acidic solution. We have seen the effect of acidic medium. Then ***what is the effect of adding strong alkaline solution like NaOH (aq) to the above equilibrium?***
- Addition of basic solution like sodium hydroxide which ionises completely to give OH^- , eliminate H^+ from the above equilibrium thus decreasing its concentration, ***how?*** This is because the hydroxyl ions (OH^-) combine with hydrogen proton (H^+) to form water (H_2O). This shifts the position of equilibrium to the right hand side by forming more chromate which is weak oxidising agent according to the following equation of the reaction which is irreversible:



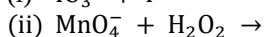
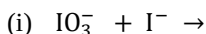
(The equation is simply derived from the above equilibrium by adding 2OH^- to both sides of the equation (i) above).

Hence dichromate is very weak oxidising agent under basic medium.

It should be noted that: KMnO_4 Being stronger oxidising agent than $\text{K}_2\text{Cr}_2\text{O}_7$ and KIO_3 , has the following disadvantage: It cannot be used in redox titration which involve Cl^- because the permanganate is capable of oxidising Cl^- to Cl_2 unlike other oxidising agents which are not strong oxidising agents enough to oxidize the chloride ions.

Example 9

Complete and balance the following redox reactions:



Solution

(i) $\text{IO}_3^- + \text{I}^- \rightarrow \text{No reaction}$

Under neutral medium (no medium is shown in the reaction equation), IO_3^- is incapable of showing oxidising character; it needs acidic medium to exhibit oxidising characters.

(ii) $3\text{H}_2\text{O}_2 + 2\text{MnO}_4^- \rightarrow 2\text{MnO}_2 + 3\text{O}_2 + 2\text{H}_2\text{O} + 2\text{OH}^-$

Under neutral medium; MnO_4^- is reduced to MnO_2 .

Thus **reduction half reaction** can be written as follows: $\text{MnO}_4^- \rightarrow \text{MnO}_2$;

Balancing oxygen atoms: $\text{MnO}_4^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$;

Balancing hydrogen atoms: $\text{MnO}_4^- + 4\text{H}^+ \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$;

Balancing charges: $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$;

Adding 4OH^- both sides: $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- + 4\text{OH}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} + 4\text{OH}^-$;

Simplifying the equation: $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$;

Thus: the balanced reduction half reaction: $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$ -----(i)

The balanced oxidation half reaction equation: $\text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + \text{O}_2 + 2\text{e}^-$ -----(ii)

Taking (i) $\times 2$ + (ii) $\times 3$: $2\text{MnO}_4^- + 4\text{H}_2\text{O} + 3\text{H}_2\text{O}_2 \rightarrow 2\text{MnO}_2 + 8\text{OH}^- + 6\text{H}^+ + 3\text{O}_2$;

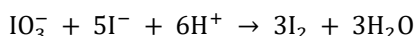
Simplifying the equation gives: $2\text{MnO}_4^- + 3\text{H}_2\text{O}_2 \rightarrow 2\text{MnO}_2 + 2\text{OH}^- + 3\text{O}_2 + 2\text{H}_2\text{O}$

Example 10

Dark brown colouration is observed when dilute hydrochloric acid is added to a beaker containing solution mixture of potassium iodate and potassium iodide. Explain.

Solution

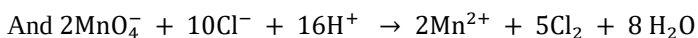
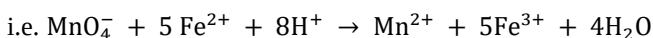
Hydrochloric acid acts as an acidic medium to allow redox reaction between KIO_3 and KI so as to liberate iodine which appears in dark brown colouration

**Example 11**

Explain why acidified KMnO_4 cannot be used in redox titration of the permanganate against iron (II) chloride.

Solution

KMnO_4 being very strong oxidising agent, oxidizes both Fe^{2+} and Cl^- (from FeCl_2) to Fe^{3+} and Cl_2 respectively thus interfering measurement of correct volume of KMnO_4 solution which is exactly used to oxidize Fe^{2+} and Fe^{3+} .

**Example 12**

Hydrochloric acid can be used as an acidic medium in redox titration of potassium dichromate (VI) against potassium iodide while the same acid cannot be applied as an acidic medium in redox titration of potassium manganate (VII) against potassium iodide. Explain

Solution

$\text{K}_2\text{Cr}_2\text{O}_7$ being weaker oxidising agent (than KMnO_4) is unable to oxidize Cl^- (from HCl) to Cl_2 while KMnO_4 being stronger oxidising agent, oxidizes Cl^- (From HCl (aq)) to Cl_2 thus interfering measurement of correct volume of KMnO_4 which is exactly used to oxidize Cl^- to Cl_2 .

i.e. $\text{Cr}_2\text{O}_7^{2-} + \text{Cl}^- + \text{H}^+ \rightarrow \text{No reaction}$

While $2\text{MnO}_4^- + 10\text{Cl}^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O}$

To close the discussion about oxidising characters of oxidising agents in different media.....!

- Concentrated sulphuric acid has oxidising properties, so it should not be used as an acidic medium for redox titration in its concentrated form.
- Sulphuric acid is always used as an acidic medium in its diluted form.
- The oxidising character of nitric acid (HNO_3) also explains why the acid should not be used as an acidic medium for redox titration in its either dilute or concentrated form.

Example 13

Concentrated sulphuric acid should not be used in redox titration of potassium permanganate against FeSO_4 . Explain

Solution

Concentrated H_2SO_4 is good oxidising agent so it tends to oxidize Fe^{2+} (from FeSO_4) to Fe^{3+} as KMnO_4 does thus interfering measurement of correct volume of KMnO_4 which is exactly used to oxidize Fe^{2+} to Fe^{3+} .

EQUIVALENT WEIGHT AND NORMALITY IN REDOX REACTION

Equivalent weight

Generally; **Equivalent weight** can be defined as *the mass of a compound required to give (or react with) one mole (Avogadro's number) of fundamental entity in a reaction we might consider.*

In redox reaction, the fundamental entity is **electron**.

Thus, **for an oxidising agent:** equivalent weight is *the mass of the oxidising agent required to gain one mole of electrons from reducing agent in the redox reaction.*

Equivalent weight

$$= \frac{\text{Molar mass of the oxidising agent}}{\text{Number of moles electrons gained by one mole of the oxidising agent}}$$

But **Number of mole of electrons gained by one of the compound = Number of electrons gained by one molecule of the compound**

$$\text{So, Equivalent weight} = \frac{\text{Molar mass of the oxidising agent}}{\text{Number of electrons gained by one molecule of the oxidising agent}}$$

And **for a reducing agent:** equivalent weight is *the mass of the reducing agent required to donate one mole of electrons to oxidising agent during redox reaction.*

Equivalent weight

$$= \frac{\text{Molar mass of the reducing agent}}{\text{Number of moles electrons gained by one mole of the oxidising agent}}$$

$$\text{Or Equivalent weight} = \frac{\text{Molar mass of the reducing agent}}{\text{Number of electrons gained by one molecule of the reducing agent}}$$

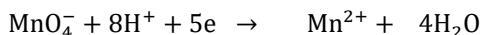
Whence the two results for reducing and oxidising agent may be combined to get the following result:

For redox reaction:

$$\text{Equivalent weight} = \frac{\text{Molar mass}}{\text{Number of electrons transferred by one molecule of the reactant}}$$

Examples:

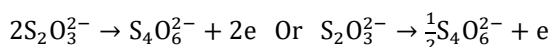
1) Acidified KMnO_4 has the following reduction half reaction:



Whereby one molecule of the permanganate gains five electrons (or five moles of the permanganate gains five moles of electrons) and hence:

$$\text{Equivalent weight of KMnO}_4 \text{ in acidic medium} = \frac{\text{Molar mass of KMnO}_4}{5}$$

2) Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) has the following oxidation half reaction:



(Dividing by two throughout the first equation so as to get **one molecule** of the reactant)

Whereby one molecule of the thiosulphate donates one electron and hence:

$$\text{Equivalent weight of Na}_2\text{S}_2\text{O}_3 = \frac{\text{Molar mass of Na}_2\text{S}_2\text{O}_3}{1}$$

Normality

Generally; **Normality** is the number of equivalents of solute dissolved in one litre of the solution

$$\text{Thus: Normality} = \frac{\text{number of equivalents of solute}}{\text{volume of solution in litres (or dm}^3\text{)}}$$

Its unit is N

$$\text{But number of equivalents of solute} = \frac{\text{mass of solute}}{\text{Equivalent weight of solute}}$$

$$\text{Then: Normality} = \frac{\text{mass of solute}}{\text{volume of solution in dm}^3 \times \text{equivalent weight of solute}}$$

$$\text{But } \frac{\text{mass of solute}}{\text{volume of solution in dm}^3} = \text{mass concentration of solute in g/dm}^3$$

$$\text{Thus: Normality} = \frac{\text{mass concentration in g/dm}^3}{\text{equivalent weight of solute}}$$

For redox reactions:

$$\text{Equivalent weight} = \frac{\text{molar mass}}{\text{number of electrons transferred by one molecule of the reactant}}$$

$$\text{Then from Normality} = \frac{\text{mass concentration in g/dm}^3}{\text{equivalent weight of solute}};$$

$$\text{It becomes; Normality} = \frac{\text{mass concentration in g/dm}^3 \times \text{number of electrons transferred by one molecule of the reactant}}{\text{Molar mass of solute}}$$

$$\text{But } \frac{\text{mass concentration in g/dm}^3}{\text{molar mass of solute}} = \text{Molarity}$$

Hence **for redox reactions:**

Normality

= **Molarity** $\times$ **Number of electrons transferred by one molecule of oxidising or reducing agent**

The term '**A normal solution**' is used to express the solution of 1N

Note: Normality of oxidising and reducing agent are connected by the following equation:

$$\mathbf{N_o V_o = N_r V_r}$$

Where $\mathbf{N_o}$ and $\mathbf{N_r}$ is the normality of oxidising and reducing agent respectively

V_o and V_r is the volume of oxidising and reducing agent respectively.

Proof:

Recall: Normality = $\frac{\text{number of equivalents of solute}}{\text{volume of solution in litres (or dm}^3\text{)}}$

From which; Number of equivalents = Normality $\times$ Volume = NV

But at equivalence point;

Number of equivalents of oxidizing agent = Number of equivalents of reducing agent

Where Number of equivalents of oxidising agent = $N_o V_o$

And Number of equivalents of reducing agent = $N_r V_r$

Hence $N_o V_o = N_r V_r$

REDOX TITRATION

Redox titration involves titration of an oxidant with reductant or vice-versa. There must be a sufficiently large difference between oxidising and reducing capabilities of these agents for the reaction to undergo completion with sharp end point.

Types of redox indicators

There are three common types of redox indicator, namely:

- Self-indicators
- Internal indicators
- External indicators

Self-indicators

When the titrant itself is **strongly coloured** that after equivalence point, a single drop of the titrant (of negligible volume) produces an intense colour in the reaction mixture thus acting as an indicator; such indicators are known as self-indicators. A good example of self-indicator is potassium permanganate (KMnO_4) which is deep purple coloured and it is reduced by reductant to form Mn^{2+} which is colourless. After complete reduction of the analyte, the solution mixture is colourless at the equivalence point; and since the permanganate is strongly coloured, its single drop of negligible volume can change the colour of solution into pink thus detecting end point. **However, although $\text{K}_2\text{Cr}_2\text{O}_7$ solution is strongly coloured and its single drop change the colour of colourless solution into yellow, it is not used as self-indicator like KMnO_4 , why?**

This is because its reduction product, Cr^{3+} , it is green in colour and not colourless like Mn^{2+} which is reduction product of acidified KMnO_4 . This hinders visual detection of the end point by observing the dichromate colour. Hence indicator must be used in titrations of dichromate solutions.

Internal indicators

Such indicators are added to the reaction mixture and they show their action through redox reaction. The indicators are always weaker reducing agent than the analyte so that they react with titrant only when whole of the analyte has consumed, producing a readily detectable colour change. A good example of internal indicator is diphenylamine which is used in titrations of potassium dichromate (VI).

External indicators

In case a suitable redox indicator is not available for given system; an indicator may be employed which will indicate the completion of reaction by physically or chemically reacting with analyte (**not through redox reaction**). Such indicators are called external indicators. A good example of external indicator is **starch indicator** which is commonly used in titrations which involve iodine. With iodine,

starch gives blue colouration which disappears after complete reduction of the iodine i.e. when the iodine is absent. Thus iodine is used to detect presence of iodine. **However, when iodine is an analyte, the starch must be added just close to the end point, why?**

This is because in large amount of iodine (at the beginning of titration), starch form a complex with the iodine. The iodine in the complex resists reduction of reducing agents like sodium thiosulphate and therefore blue colouration cannot disappear and hence end point can never be reached.

Iodometry and iodimetry titration

Iodometry and **iodimetry** are similar in a manner that both are redox titrations which involve iodine as an oxidising agent. The titration of iodine may be done directly or indirectly.

Iodimetry is the redox titration whereby an analyte which is reducing agent is titrated directly with standard iodine solution.

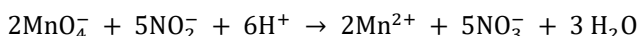
Iodometry is the redox titration whereby an analyte which is an oxidising agent is added to excess iodide solution to liberate iodine whose amount is determined by titration with sodium thiosulphate

Calculations on redox titrations

Example 14

52.3cm³ of sodium nitrite solution, added from a burette were needed to discharge the colour of 25cm³ of an acidified 0.02M KMnO₄ solution.

- What was the concentration of the nitrite solution in grams of anhydrous salt per dm³?
- Why was nitrite in the burette?

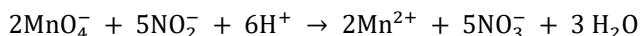


Solution

- Number of moles KMnO₄ in 25cm³ of its solution

$$= \frac{25}{1000} \times 0.02\text{mol} = 5 \times 10^{-4}\text{mol} = \text{Number of moles of MnO}_4^-$$

MnO₄⁻ reacts with NO₂⁻ (from NaNO₂) according to the following equation:



From which mole ratio of MnO₄⁻ to NO₂⁻ is 2: 5

Thus number of moles of NO₂⁻ in 52.3cm³ of its solution

$$= \frac{5}{2} \times 5 \times 10^{-4}\text{mol} = 1.25 \times 10^{-3}\text{mol} = \text{Number of moles of NaNO}_2$$

Mass concentration of NaNO₂ = [NaNO₂]M_{NaNO₂}

$$\text{But } [\text{NaNO}_2] = \frac{1.25 \times 10^{-3}}{0.0523}\text{M and } M_{\text{NaNO}_2} = 69\text{g mol}^{-1}$$

$$\text{Thus mass concentration of NaNO}_2 \text{ in g dm}^{-3} = \frac{1.25 \times 10^{-3} \times 69}{0.0523}\text{g dm}^{-3}$$

Hence mass concentration of sodium nitrite is 1.649gdm⁻³

- If a solution of a nitrite is titrated in the ordinary way with potassium permanganate by putting the permanganate in the burette, poor results are obtained, because the nitrite solution has first to be acidified with dilute sulphuric acid which reacts with the nitrite to give nitrous acid. The liberated nitrous acid being volatile and unstable is partially lost.

Example 15

1.6g of ethanedioic acid crystals, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, was made up to 250cm^3 of aqueous solution and 25cm^3 of this solution heated to temperature of about 70°C , needed 26.2cm^3 of a manganate (VII) for oxidation in titration.

- Calculate the molarity of the manganate (VII).
- Concentration of the manganate solution in gdm^{-3}
- Why in that particular experiment, ethanedioic must be heated?

Solution

(a) Molar mass of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is 126g mol^{-1}

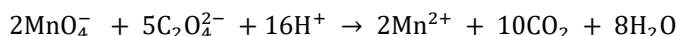
Using; $[\quad] = \frac{m}{M_r V}$

$$\text{Then } [\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}] = \frac{1.6}{126 \times 0.25} \text{M} = 0.05\text{M}$$

Number of moles of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 25cm^3 of its solution

$$= \frac{25}{1000} \times 0.05\text{mol} = 1.25 \times 10^{-3}\text{mol} = \text{number of moles of } \text{C}_2\text{O}_4^{2-}$$

$\text{C}_2\text{O}_4^{2-}$ reacts with MnO_4^- according to the following equation:



From which mole ratio of MnO_4^- to $\text{C}_2\text{O}_4^{2-}$ is 2: 5

Thus number of moles of manganate (VII) solution

$$= \frac{2}{5} \times 1.25 \times 10^{-3}\text{mol} = 5 \times 10^{-4}\text{mol}$$

$$\text{Then } [\text{MnO}_4^-] = \frac{5 \times 10^{-4} \times 10^3}{26.2} \text{M} = 0.019\text{M}$$

Hence Molarity manganate (VII) solution is 0.019M

(b) Molar mass of KMnO_4 is 158g mol^{-1}

Using mass concentration in $\text{gdm}^{-3} = [\quad] \text{Mr}$

$$\text{Mass concentration of } \text{KMnO}_4 = 0.019 \times 158\text{gdm}^{-3} = 3.002\text{gdm}^{-3}$$

Hence mass concentration of manganate (VII) solution is 3.002gdm^{-3}

(c) The reaction at room reaction is slow because of the equilibrium nature of the reaction. furthermore:

- CO_2 is soluble in water, thus heating removes all dissolved CO_2 out of the solution, driving the reaction in forward direction.
- Also at low temperature, the reduction of MnO_4^- may not be complete producing Mn (III) instead of Mn (II).

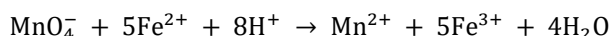
Example 16

Calculate X in the formula $\text{FeSO}_4 \cdot \text{XH}_2\text{O}$ from the following data: 24.400g of iron (II) sulphate crystals were made up to 1dm^3 of aqueous solution acidified with sulphuric acid. 25cm^3 of this solution required 20cm^3 of 0.022M KMnO_4 .

Solution

$$\text{Number of moles of } \text{KMnO}_4 = \frac{20}{1000} \times 0.022\text{mol} = 4.4 \times 10^{-4}\text{mol}$$

KMnO_4 reacts with $\text{FeSO}_4 \cdot \text{XH}_2\text{O}$ according to the following equation:



From which mole ratio of MnO_4^- to Fe^{2+} is 1:5

Then number of moles of Fe^{2+} (from $\text{FeSO}_4 \cdot \text{XH}_2\text{O}$)

$$= 5 \times 4.4 \times 10^{-4} \text{ mol} = 2.2 \times 10^{-3} \text{ mol in } 25 \text{ cm}^3 \text{ of its solution}$$

Number of moles of $\text{FeSO}_4 \cdot \text{XH}_2\text{O}$ in 1 dm^3 (1000 cm^3) of its solution

$$= \frac{2.2 \times 10^{-3} \times 1000}{25} \text{ mol} = 0.088 \text{ mol}$$

Using $M_r = \frac{m}{n}$;

$$\text{Molar mass of } \text{FeSO}_4 \cdot \text{XH}_2\text{O} = \frac{24.4}{0.088} \text{ g mol}^{-1} = 277.3 \text{ g mol}^{-1}$$

It follows that; $56 + 32 + 64 + 18x = 277.3$; $x = 7$

The value of x is 7

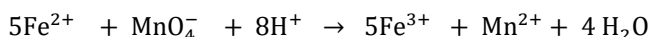
Example 17

Calculate the percentage of iron in a sample of iron wire from the following data: 1.400g of the wire dissolved in excess of dilute sulphuric acid and the solution made up to 250 cm^3 . 25 cm^3 of this solution needed 25.37 cm^3 of 0.0196 M KMnO_4 for oxidation.

Solution

With dilute sulphuric acid, Fe gives Fe^{2+} which will further be oxidised by KMnO_4 to Fe^{3+} .

Fe^{2+} reacts with MnO_4^- (from KMnO_4) according to the following equation:



Number of moles of KMnO_4 in 25.37 cm^3 of its solution

$$= \frac{25.37}{1000} \times 0.0196 \text{ mol} = 4.97252 \times 10^{-4} \text{ mol}$$

Number of moles Fe^{2+} (from FeSO_4) $= 5 \times 4.97252 \times 10^{-4} \text{ mol}$

$$= 2.48626 \times 10^{-3} \text{ mol in } 25 \text{ cm}^3 \text{ of its solution}$$

Number of moles of Fe^{2+} in 250 cm^3 of its solution

$$= \frac{2.48626 \times 10^{-3} \times 250}{25} \text{ mol} = 2.48626 \times 10^{-2} \text{ mol}$$

Fe reacts with dilute H_2SO_4 to give Fe^{2+} [from FeSO_4] according to the following ionic equation: $\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$

From which mole ratio of Fe to Fe^{2+} is 1:1

Thus number of moles of Fe in 1.4g of iron wire was also $2.48626 \times 10^{-2} \text{ mol}$

Using $m = nM_r$;

$$\text{Mass of iron was } 2.48626 \times 10^{-2} \times 56 \text{ g} = 1.3923056 \text{ g}$$

$$\text{Then \% Fe} = \frac{1.3923056}{1.4} \times 100\% = 99.4504\%$$

Hence the percentage of iron was 99.4504%.

Example 18

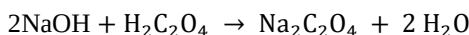
25 cm^3 of a solution containing ethanedioic acid and sodium ethanedioate required 14.75 cm^3 of 0.1 M sodium hydroxide solution for neutralisation, and 30.5 cm^3 of 0.0205 M potassium manganate (VII) solution for oxidation in acidic condition at about 70°C . Calculate the number of grams of each (anhydrous) constituent per dm^3 of the solution.

Solution

Number of moles of NaOH (aq) reacted with $\text{H}_2\text{C}_2\text{O}_4$ (ethanedioic acid)

$$= \frac{14.75}{1000} \times 0.1 \text{ mol} = 1.475 \times 10^{-3} \text{ mol}$$

NaOH reacts with $\text{H}_2\text{C}_2\text{O}_4$ according to the following equation:



From which mole ratio of NaOH to $\text{H}_2\text{C}_2\text{O}_4$ is 2: 1

Then number of moles of $\text{H}_2\text{C}_2\text{O}_4$ in 25cm^3 of the solution

$$= \frac{1}{2} \times 1.475 \times 10^{-3} \text{ mol} = 7.375 \times 10^{-4} \text{ mol}$$

Using $m = nM_r$;

Mass of $\text{H}_2\text{C}_2\text{O}_4$ in 25cm^3 of the solution $= 7.375 \times 10^{-4} \times 90\text{g} = 0.066375\text{g}$

Thus mass of ethanedioic acid in 1000cm^3 of the solution

$$= \frac{0.066375 \times 1000}{25} \text{ g} = 2.655\text{g}$$

Number of moles of KMnO_4 (Potassium manganate (VII))

$$= \frac{30.5}{1000} \times 0.0205 \text{ mol} = 6.2525 \times 10^{-4} \text{ mol}$$

$\text{C}_2\text{O}_4^{2-}$ (from $\text{H}_2\text{C}_2\text{O}_4$ and $\text{Na}_2\text{C}_2\text{O}_4$) reacts with MnO_4^- (From KMnO_4) according to the following equation: $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$

From which mole ratio of MnO_4^- to $\text{C}_2\text{O}_4^{2-}$ is 2: 5

Thus total number of moles of $\text{C}_2\text{O}_4^{2-}$ in 25cm^3 of the solution

$$= \frac{5}{2} \times 6.2525 \times 10^{-4} \text{ mol} = 1.563125 \times 10^{-3} \text{ mol}$$

But the number of moles of $\text{C}_2\text{O}_4^{2-}$ from $\text{H}_2\text{C}_2\text{O}_4$ in $25\text{cm}^3 = 7.375 \times 10^{-4} \text{ mol}$

Thus number of moles of $\text{C}_2\text{O}_4^{2-}$ from $\text{Na}_2\text{C}_2\text{O}_4$ in 25cm^3

$$= (1.563125 \times 10^{-3} - 7.375 \times 10^{-4}) \text{ mol} = 8.25625 \times 10^{-4} \text{ mol}$$

= Number of moles of $\text{Na}_2\text{C}_2\text{O}_4$ in 25cm^3 of the solution

Mass of $\text{Na}_2\text{C}_2\text{O}_4$ in $25\text{cm}^3 = 8.25625 \times 10^{-4} \times 134\text{g}$

Mass of $\text{Na}_2\text{C}_2\text{O}_4$ in $1000\text{cm}^3 = \frac{8.25625 \times 10^{-4} \times 134 \times 1000}{25} \text{ g} = 4.42535\text{g}$

Hence: Mass of ethanedioic acid in 1000cm^3 is 2.655g

Mass of sodium ethanedioate in 1000cm^3 is 4.42535g.

Example 19

25cm^3 of a solution containing iron (II) and iron (III) sulphates required 18.50cm^3 of 0.02M potassium manganate (VII) solution for oxidation in acidic condition. After complete reduction by zinc amalgam, 25cm^3 of the solution required 32.6cm^3 of the same manganate (VII) solution. Calculate the number of grams of each anhydrous sulphate per dm^3 of the solution.

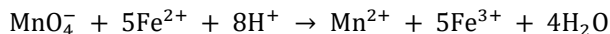
Solution**First titration:**

In this titration, KMnO_4 will oxidize Fe^{2+} from FeSO_4 . Fe^{3+} does not undergo oxidation.

Number of moles of KMnO_4 in 18.5cm^3 of its solution

$$= \frac{18.5}{1000} \times 0.02 \text{ mol} = 3.7 \times 10^{-4} \text{ mol} = \text{number of moles of } \text{MnO}_4^-$$

Fe^{2+} reacts with MnO_4^- according to the following equation:



From which, mole ratio of Fe^{2+} to MnO_4^- is 5: 1

Thus number of moles of Fe^{2+} in 25cm^3 of the solution

$= 5 \times 3.7 \times 10^{-4} = 1.85 \times 10^{-3} \text{ mol} = \text{Number of moles of Iron (II) sulphate in } 25\text{cm}^3 \text{ the mixture of iron (II) sulphate and iron (III) sulphate}$

Then mass of iron (II) sulphate in 25cm^3 of the solution $= 1.85 \times 10^{-3} \times 152\text{g} = 0.2812\text{g}$

Whence mass of iron (II) sulphate in 1dm^3 (1000cm^3) of the solution

$$= \frac{0.2812 \times 1000}{25} \text{ g} = 11.248\text{g}$$

Second titration:

After complete reduction, the iron (II) ions derived from the original iron (III) are also oxidised by the manganate (VII) solution. Thus the increase in volume of KMnO_4 solution used in second titration is what used to oxidize these iron (II) ions

i.e. $(32.6 - 18.5)\text{cm}^3$ or 14.1cm^3 of 0.02M KMnO_4 solution was used.

Number of moles of KMnO_4 used to oxidize the reduced ions

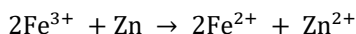
$$= \frac{14.1}{1000} \times 0.02 \text{ mol} = 2.82 \times 10^{-4} \text{ mol}$$

From the mole ratio;

Number of moles of Fe^{2+} from reduction of Fe^{3+}

$$= 5 \times 2.82 \times 10^{-4} \text{ mol} = 1.41 \times 10^{-3} \text{ mol}$$

Equation of reduction of Fe^{3+} by Zn



From which mole ratio of Fe^{3+} to Fe^{2+} is 1: 1

Thus number of moles of Fe^{3+} was also $1.41 \times 10^{-3} \text{ mol}$

But one mole of iron (III) sulphate ($\text{Fe}_2(\text{SO}_4)_3$) produces 2moles of Fe^{3+} according to equation:
 $\text{Fe}_2(\text{SO}_4)_3 \rightarrow 2\text{Fe}^{3+} + 3\text{SO}_4^{2-}$

It follows that, number of moles of $\text{Fe}_2(\text{SO}_4)_3 = \frac{1.41 \times 10^{-3}}{2} \text{ mol} = 7.05 \times 10^{-4} \text{ mol}$

Then mass of $\text{Fe}_2(\text{SO}_4)_3$ in 25cm^3 of the solution $= 7.05 \times 10^{-4} \times 400\text{g} = 0.282\text{g}$

Whence mass of iron (III) sulphate in 1dm^3 (1000cm^3) of the solution

$$= \frac{0.282 \times 1000}{25} \text{ g} = 11.28\text{g}$$

Hence: Mass of iron (II) sulphate in 1dm^3 is 11.25g

Mass of iron (III) sulphate in 1dm^3 is 11.28g

Example 20

12.5cm³ of a given solution of hydrogen peroxide were diluted to 500cm³ with distilled water. 25cm³ of this diluted solution then required 22.5cm³ of 0.02M potassium manganate (VII) solution for titration in acidic conditions. Calculate:

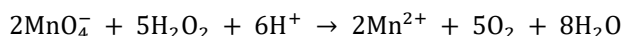
- The concentration of the original hydrogen peroxide solution.
- The volume strength of the hydrogen peroxide solution, assuming s.t.p conditions.

Solution

- Number of moles of KMnO₄ in 22.5cm³ of its solution

$$= \frac{22.5}{1000} \times 0.02 \text{ mol} = 4.5 \times 10^{-4} \text{ mol} = \text{number of moles of MnO}_4^-$$

MnO₄⁻ reacts with H₂O₂ according to the following equation:



From which mole ratio of MnO₄⁻ to H₂O₂ is 2: 5

Number of moles of H₂O₂ in 25cm³ of diluted solution

$$= \frac{5}{2} \times 4.5 \times 10^{-4} \text{ mol} = 1.125 \times 10^{-3} \text{ mol}$$

$$\text{Molarity of diluted solution of H}_2\text{O}_2 = \frac{1.125 \times 10^{-3} \times 10^3}{25} \text{ M} = 0.045 \text{ M}$$

Using dilution principle: M_cV_c = M_dV_d

Where:

M_c is the molarity of concentrated H₂O₂ solution

M_d is the molarity of diluted H₂O₂ solution = 0.045M

V_c is the volume of concentrated H₂O₂ solution = 12.5cm³

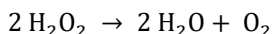
V_d is the volume of diluted H₂O₂ solution = 500cm³

$$\text{Then } M_c = \frac{M_d V_d}{V_c} = \frac{0.045 \times 500}{12.5} \text{ M} = 1.8 \text{ M}$$

Mass concentration of the original H₂O₂ solution = 1.8 × 34gdm⁻³ = 61.2gdm⁻³

Hence the concentration of original hydrogen peroxide is 61.2gdm⁻³

- Hydrogen peroxide decomposes to give oxygen gas according to the following equation:



From which mole ratio of H₂O₂ to O₂ is 2: 1

Number of moles of H₂O₂ in 12.5cm³ of its solution

$$= \frac{12.5}{1000} \times 1.8 \text{ mol} = 0.0225 \text{ mol}$$

Thus 0.0225mol of H₂O₂ produces $\frac{0.0225}{2}$ mol or 0.01125mol of oxygen

But 0.0225mol of H₂O₂ is contained in 12.5cm³ of its volume

And 1mol of O₂ is contained in 22.4dm³ or 22400cm³ of its volume

It follows that: 12.5cm³ of H₂O₂ produces 0.01125 × 22400cm³ or 252cm³ of O₂

Whence 1cm³ of H₂O₂ produces $\frac{252}{12.5}$ cm³ or 20.16cm³ of O₂

Hence the volume strength of H₂O₂ solution is 20.16 (The hydrogen peroxide solution produces 20.16 times its own volume of oxygen gas when heated)

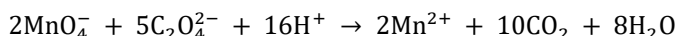
Example 21

Calculate the percentage of calcium in calspar from the following data: 1.25g of calspar was dissolved in dilute hydrochloric acid and calcium ethanedioate was precipitated from neutralised solution by ammonium ethanedioate. Then washed precipitate was dissolved by addition of hot dilute sulphuric acid and made up to 250cm³. 25cm³ of this solution needed 24cm³ of 0.0208MKMnO₄ for oxidation.

Solution

Number of moles of KMnO₄ in 24cm³ of its solution = $\frac{24}{1000} \times 0.0208 \text{ mol} = 4.992 \times 10^{-4} \text{ mol}$

MnO₄⁻ (from KMnO₄) reacts with C₂O₄²⁻ (from CaC₂O₄) according to the following equation



From which mole ratio of MnO₄⁻ to C₂O₄²⁻ is 2: 5

Thus number of moles of C₂O₄²⁻ was $\frac{5}{2} \times 4.992 \times 10^{-4} \text{ mol}$

= $1.248 \times 10^{-3} \text{ mol}$ in 25cm³ of the solution.

Then number of moles of C₂O₄²⁻ in 250cm³ of its solution = $\frac{1.248 \times 10^{-3} \times 250}{25} \text{ mol} = 0.01248 \text{ mol}$ = number of moles of Ca in CaC₂O₄ (**In one mole of CaC₂O₄, there is one mole of Ca and whence their mole ratio is 1:1**)

Mass of calcium in CaC₂O₄ = $0.01248 \times 40 \text{ g} = 0.4992 \text{ g}$ = mass of calcium (Ca) in 1.25g of calspar

Whence % Ca = $\frac{0.4992}{1.25} \times 100\% = 39.936\%$

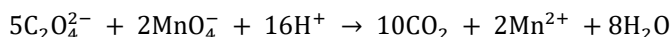
Hence the percentage of calcium in calspar is 39.936%

Example 22

A solution of ethanedioic acid was made up and it was calculated that 22.5cm³ of certain potassium manganate (VII) solution would oxidize 25cm³ of the ethanedioic acid solution. In practice it was found that only 16.1cm³ of the manganate (VII) solution were needed. The error lay in fact that the calculation was based on formula of anhydrous acid where the crystalline acid was actually weighed out. What is the value of X in the formula: H₂C₂O₄.XH₂O.

Solution

MnO₄⁻ reacts with C₂O₄²⁻ according to the following equation:



Let mass of ethanedioic acid in 25cm³ of its solution be m in grams

First case: If the acid is considered to be anhydrous

Number of moles of anhydrous H₂C₂O₄ = $\frac{m}{90}$

But number of moles of KMnO₄ = $\frac{22.5}{1000} M_0$

Where M₀ is the Molarity of oxidising agent (KMnO₄)

Then from above equation, mole ratio of C₂O₄²⁻ (from H₂C₂O₄) to MnO₄ is 5: 2;

Thus $\frac{5 \times 22.5}{2 \times 1000} M_0 = \frac{m}{90}$ or $5.0625 M_0 = m$ ----- (i)

Second case: If the acid is considered to be crystalline

Number of moles of H₂C₂O₄.XH₂O = $\frac{m}{90 + 18x}$

And number of moles of $\text{KMnO}_4 = \frac{16.1}{1000} \text{ M}_0$

$$\text{Then } \frac{5 \times 16.1}{2 \times 1000} \text{ M}_0 = \frac{m}{90 + 18x}$$

$$\text{Or } 0.04025 \text{ M}_0 = \frac{m}{90 + 18x} \text{ -----(ii)}$$

$$\frac{\text{(i)}}{\text{(ii)}} \text{ gives } \frac{5.0625}{0.04025} = 90 + 18x \text{ or } 1.44 = 0.7245x \text{ or } x = 2$$

Hence the value of x in the given formula is 2

Example 23

3g of a sample of haematite (Fe_2O_3) were dissolved in concentrated hydrochloric acid and the solution diluted to 250cm^3 . 25cm^3 of this solution, after reduction with tin (II) chloride, required 26.6cm^3 of 0.02M potassium dichromate for oxidation. Calculate the percentage of iron (III) oxide in the ore.

Solution

Potassium dichromate (VI), $\text{K}_2\text{Cr}_2\text{O}_7$ reacts with Fe^{2+} according to the following ionic equation:
 $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$

Number of moles $\text{K}_2\text{Cr}_2\text{O}_7$ in 26.6cm^3 of its solution

$$= \frac{26.6}{1000} \times 0.02\text{mol} = 5.32 \times 10^{-4}\text{mol of } \text{Cr}_2\text{O}_7^{2-}$$

From the above equation; 1 mol of $\text{Cr}_2\text{O}_7^{2-}$ reacts with 6 mol of Fe^{2+}

Thus number of moles of Fe^{2+} in 25cm^3 of its solution

$$= 6 \times 5.32 \times 10^{-4}\text{mol} = 3.192 \times 10^{-3}\text{mol}$$

Then number of moles of Fe^{2+} in 250cm^3 of its solution

$$= \frac{3.192 \times 10^{-3} \times 250}{25} \text{mol} = 3.192 \times 10^{-2}\text{mol}$$

But 1 mol of Fe_2O_3 produce 2moles of Fe^{3+} which in turn produce 2 moles of Fe^{2+} after reduction.

$$\text{Thus number of moles of } \text{Fe}_2\text{O}_3 \text{ was } \frac{3.192 \times 10^{-2}}{2} \text{mol} = 1.596 \times 10^{-2}\text{mol}$$

Then using $m = nM_r$;

Mass of Fe_2O_3 is $1.596 \times 10^{-2} \times 160\text{g}$ or 2.5536g

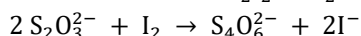
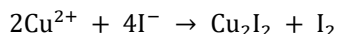
But total mass of the ore (haematite) is 3g

$$\text{It follows that, } \% \text{Fe}_2\text{O}_3 \text{ in the ore} = \frac{2.5536}{3} \times 100\% = 85.12\%$$

Hence the percentage of iron (III) oxide in the ore is 85.12%

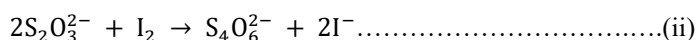
Example 24

25cm^3 of a copper (II) sulphate solution were added to 20cm^3 of potassium iodide solution, i.e. excess potassium iodide. The iodine liberated was titrated by 22.5cm^3 of 0.1080M sodium thiosulphate solution. Calculate the concentration of the solution in grams of the pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per dm^3 of the solution.

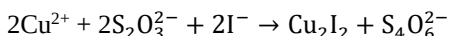


Solution

Equations for reactions:



(i)+(ii) gives the overall reaction equation which is:



From which mole ratio of Cu^{2+} to $\text{S}_2\text{O}_3^{2-}$ is 2: 2 or 1: 1

Number of moles of $\text{Na}_2\text{S}_2\text{O}_3$ in 22.5cm^3 of its solution

$$= \frac{22.5}{1000} \times 0.1080\text{mol} = 2.43 \times 10^{-3}\text{mol of } \text{S}_2\text{O}_3^{2-}$$

Thus number of moles of Cu^{2+} = Number of moles of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was also $2.43 \times 10^{-3}\text{mol}$ in 25cm^3 of its solution.

$$[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}] = \frac{2.43 \times 10^{-3} \times 10^3}{25} \text{M} = 0.0972\text{M}$$

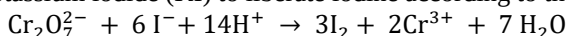
But molar mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is 250gdmol^{-1}

Thus mass concentration of the solution = $0.0972 \times 250\text{gdm}^{-3} = 24.3\text{gdm}^{-3}$

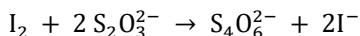
Hence concentration of solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is 24.3gdm^{-3}

Example 25

A standard solution is prepared by dissolving 1.185g of potassium dichromate (VI), $\text{K}_2\text{Cr}_2\text{O}_7$ making up to 250cm^3 of solution. The solution is used to find the concentration of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) solution. A 25cm^3 portion of the potassium dichromate (VI) solution was acidified and added to an excess of potassium iodide (KI) to liberate iodine according to the following equation:



The liberated iodine may be estimated by using sodium thiosulphate solution which is oxidised as follows.



When the solution was titrated against sodium thiosulphate, 17.5cm^3 of sodium thiosulphate were required. Calculate:

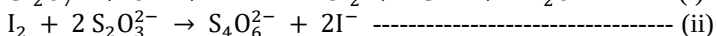
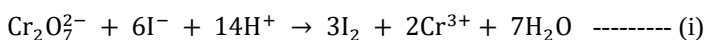
- The concentration mole per litre of potassium dichromate solution.
- The concentration in mole per litre of sodium thiosulphate solution.
- The number of electrons which were accepted by potassium dichromate (VI) during the reaction.
- Normality of potassium dichromate (VI) solution.
- Normality of sodium thiosulphate solution.

Solution

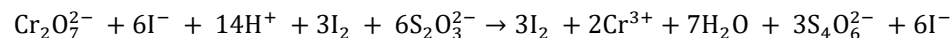
(i) Using $[] = \frac{m}{M_r V}$

$$[\text{K}_2\text{Cr}_2\text{O}_7] = \frac{1.185 \times 1000}{294 \times 250} \text{M} = 0.0161\text{M}$$

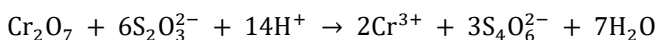
(ii) Given that:



Eliminating I_2 in the two equations (i) and (ii) by taking (i) + $3 \times$ (ii) so as to write overall reaction equation as follows:



Cancelling like terms which appears in both sides of the equation gives overall reaction equation which is:



Number of moles of $\text{K}_2\text{Cr}_2\text{O}_7$ in 25cm^3 of its solution

$$= \frac{25}{1000} \times 0.0161 \text{ mol} = 4.025 \times 10^{-4} \text{ mol of } \text{Cr}_2\text{O}_7^{2-}$$

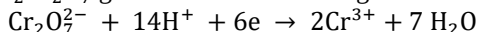
From above overall reaction equation: Mole ratio of $\text{Cr}_2\text{O}_7^{2-}$ to $\text{S}_2\text{O}_3^{2-}$ is 1: 6.

Thus number of moles of $\text{S}_2\text{O}_3^{2-}$

$$= 6 \times 4.025 \times 10^{-4} \text{ mol} = 2.415 \times 10^{-3} \text{ of } \text{Na}_2\text{S}_2\text{O}_3 \text{ in } 17.5 \text{ cm}^3$$

$$[\text{Na}_2\text{S}_2\text{O}_3] = \frac{2.415 \times 10^{-3} \times 10^3}{17.5} = 0.138 \text{ M}$$

(iii) $\text{K}_2\text{Cr}_2\text{O}_7$ gains electrons according to the following equation (reduction half reaction):



From which, one mole of $\text{Cr}_2\text{O}_7^{2-}$ (or $\text{K}_2\text{Cr}_2\text{O}_7$) gains 6 moles of electrons;

But number of moles of $\text{K}_2\text{Cr}_2\text{O}_7$ reacted was $4.025 \times 10^{-4} \text{ mol}$

Thus number of moles of electrons gained was $6 \times 4.025 \times 10^{-4} \text{ mol}$

$$= 2.415 \times 10^{-3} \text{ mol of electrons}$$

Using $N = nN_A$, number of electrons gained = $2.415 \times 10^{-3} \times 6.02 \times 10^{23}$

$$= 1.45383 \times 10^{21} \text{ electrons}$$

Hence number of electrons gained in the reaction was $1.45383 \times 10^{21} \text{ electrons}$

(iv) Normality of $\text{K}_2\text{Cr}_2\text{O}_7 = [\text{K}_2\text{Cr}_2\text{O}_7] \times \text{number of electrons gained by its one molecule.}$

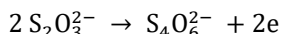
But from (iii) above;

Number of electrons gained by one molecules of $\text{K}_2\text{Cr}_2\text{O}_7$ is six electrons

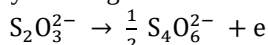
Thus Normality of $\text{K}_2\text{Cr}_2\text{O}_7 = 0.0161 \times 6N = 0.0966N$

Hence normality of potassium dichromate (VI) solution is 0.0966N

(v) $\text{Na}_2\text{S}_2\text{O}_3$ donates electrons according to the following equation (oxidation half reaction):



Dividing by 2 throughout the above equation so as to get one molecule of $\text{Na}_2\text{S}_2\text{O}_3$ (or $\text{S}_2\text{O}_3^{2-}$)



From which one molecule of $\text{S}_2\text{O}_3^{2-}$ donates 1 electron

And normality $\text{Na}_2\text{S}_2\text{O}_3 = [\text{Na}_2\text{S}_2\text{O}_3] \times \text{number of electrons donated by 1 molecule}$

$$= 0.138 \times 1N = 0.138N$$

Hence normality of $\text{Na}_2\text{S}_2\text{O}_3$ is 0.138N

Alternative solution

Using $N_r V_r = N_o V_o$;

Where $N_o = 0.0966N$, $V_o = 25 \text{ cm}^3$, $V_r = 17.5 \text{ cm}^3$

$$\text{Then } N_r = \frac{N_o V_o}{V_r} = \frac{0.0966 \times 25}{17.5} N = 0.138N$$

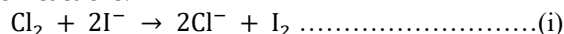
Hence normality of sodium thiosulphate solution is 0.138N.

Example 26

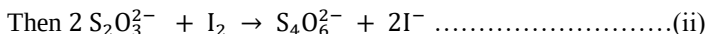
56 dm^3 of air containing a trace of chlorine were passed slowly through an excess of potassium iodide solution at 10°C and 100000 Nm^{-2} (750mmHg). The solution was made up to 250 cm^3 with water and 25 cm^3 of it then required 20.6 cm^3 of 0.1M sodium thiosulphate solution to react with the iodine. What is the percentage by volume of chlorine in the air?

Solution

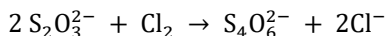
Equations for reactions:



From air



Taking (i) + (ii) gives overall reaction equation which is:



From which mole ratio of $\text{S}_2\text{O}_3^{2-}$ to Cl_2 is 2: 1

Number of moles of $\text{Na}_2\text{S}_2\text{O}_3$ in 20.6cm^3 of its solution

$$= \frac{20.6}{1000} \times 0.1\text{mol} = 2.06 \times 10^{-3}\text{mol of } \text{S}_2\text{O}_3^{2-}$$

Then number of moles of Cl_2 in 25cm^3 of solution $= \frac{2.06 \times 10^{-3}}{2}\text{mol} = 1.03 \times 10^{-3}\text{mol}$

And number of moles of Cl_2 in 250cm^3 of solution

$$= 10 \times 1.03 \times 10^{-3}\text{mol} = 1.03 \times 10^{-2}\text{mol}$$

From ideal gas equation: $PV = nRT$ or $V = \frac{nRT}{P}$

$$\text{Substituting } V = \frac{1.03 \times 10^{-2} \times 0.082 \times 283 \times 760\text{dm}^3}{750} = 0.2422\text{dm}^{-3}$$

$$\% \text{Cl}_2 = \frac{V_{\text{Cl}_2}}{V_{\text{air}}} \times 100\% = \frac{0.2422}{56} \times 100\% = 0.4325\%$$

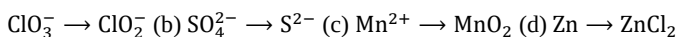
Hence the percentage of chlorine in the air is 0.4325%.

DIGGING EXERCISE 20

EXERCISE 20A: BINDER QUESTIONS

Question 1

Would you use an oxidising agent or reducing agent in order for the following reactions to occur?



Question 2

Chlorate(I) ions are capable of undergoing disproportionation.

- What is meant by the term disproportionation?
- Write an ionic equation for the disproportionation of sodium chlorate(I). Indicate the oxidation numbers of chlorine in each species in which it occurs.
- Write two ionic half equations for this process which illustrate your definition of disproportionation.

Question 3

Given the experimental evidence that $\text{Au}^{3+}(\text{aq})$ will react with $\text{Sn}(\text{s})$, and that $\text{Ag}^+(\text{aq})$ will react with $\text{Sn}(\text{s})$ but not with $\text{Au}(\text{s})$, arrange ions $\text{Ag}^+(\text{aq})$, $\text{Au}^{3+}(\text{aq})$ and $\text{Sn}^{2+}(\text{aq})$ in increasing order of their tendency to gain electrons.

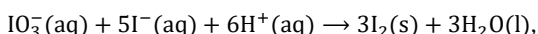
Question 4

Write a balanced ionic equation and identify the oxidants and reductants in each of the following chemical reactions:

- Iron (II) sulphate reacts with an acidified potassium dichromate solution.
- Potassium iodide reacts with an acidified potassium iodate solution.
- Copper (II) sulphate solution and potassium iodide solution react together.
- Chlorine gas and hot concentrated potassium hydroxide react together.

Question 5

- State the oxidation number of iodine in KIO_3 and KIO_4 .
- In the reaction



iodine is simultaneously oxidised and reduced. Explain why this is **not** a disproportionation reaction and hence give the appropriate name for the reaction.

- Describe a chemical test you could carry out to show that iodine was produced in (b) above.
- Suggest, by reference to the ionic equation in (b), the ionic equation for the reduction of KIO_4 to iodine in the presence of excess acid and excess potassium iodide.

EXERCISE 20B: REAL QUESTIONS

Question 6

Potassium manganate (VII) is not used as a primary reagent in volumetric analysis as potassium dichromate (VI) does. Explain.

Question 7

Hydrochloric acid cannot be used as acidic medium during redox titration of potassium permanganate against iron (II) sulphate. Explain.

Question 8

When acidified potassium dichromate reacts with sodium chloride, green colouration is observed. Explain.

Question 9

Why the temperature in the experiment involving reaction between oxalic acid and acidified potassium permanganate, must be above 60°C ?

Question 10

In an experiment done by **Mr. Akilikubwa** in a school's chemistry laboratory: 50cm^3 of solution of hydrogen peroxide were diluted to 1dm^3 with water. 25cm^3 of this solution, when acidified with dilute sulphuric acid, needed 20.25cm^3 of 0.02MKMnO_4 on the titration.

- (i) What is the concentration of the original hydrogen peroxide in mol dm^{-3} ?
- (ii) Why NaMnO_4 should not be used as an oxidant in this experiment? What would be the effect on the value of the obtained titre volume if NaMnO_4 would be used instead of KMnO_4 ?
- (iii) Why concentrated sulphuric acid should not be used as an acidic medium in this experiment? What would be effect on the obtained titre volume if concentrated sulphuric acid would be used instead of dilute sulphuric acid?

EXERCISE 20C: HOT QUESTIONS**Question 11**

50.0cm^3 of solution of hydrogen peroxide were diluted to 1.00dm^3 with water. 25.0cm^3 of this solution, when acidified with dilute sulphuric acid, reacted with 20.25cm^3 of 0.0200mol dm^{-3} KMnO_4 . What is the concentration of the original hydrogen peroxide solution in mol dm^{-3} ?

Question 12

Given the following two half-reactions:

- (i) $\text{S}_4\text{O}_6^{2-}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{S}_2\text{O}_3^{2-}(\text{aq})$
 - (ii) $\text{I}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$
- (a) Construct the full ionic redox equation for the reaction of the thiosulphate ion, $2\text{S}_2\text{O}_3^{2-}$, and iodine.
 - (b) What mass of iodine reacts with 23.5cm^3 of 0.0120mol dm^{-3} sodium thiosulphate solution?
 - (c) 25.0cm^3 of a solution of iodine in potassium iodide solution required 26.5cm^3 of 0.0950mol dm^{-3} sodium thiosulphate solution to titrate the iodine. What is the molarity of the iodine solution and the mass of iodine per dm^3 ? (Atomic masses: I = 126.9, S = 32, O = 16).

Question 13

25.0cm^3 of the potassium iodate solution were added to about 15cm^3 of a 15% solution of potassium iodide (ensures excess iodide ion). On acidification, the liberated iodine needed 24.1cm^3 of 0.0500mol dm^{-3} sodium thiosulphate solution to titrate it.

- (i) Calculate the concentration of potassium iodate(V) in g dm^{-3}
- (ii) What indicator is used for this titration and what is the colour change at the end-point?

Question 14

Calculate the molarities of iron(II) and iron(III) ions in a mixed solution from the following data:

25.0cm^3 of the original mixture was acidified with dilute sulphuric acid and required 22.5cm^3 of 0.0200mol dm^{-3} KMnO_4 for complete oxidation.

A further 25.0cm^3 of the original iron(II)/iron(III) mixture was reduced with zinc and acid and it then required 37.6cm^3 of the KMnO_4 for complete oxidation.

Question 15

2.83g of a sample of haematite iron ore (iron(III) oxide, Fe_2O_3) were dissolved in concentrated hydrochloric acid and the solution diluted to 250cm^3 .

25.0cm^3 of this solution was reduced with tin(II) chloride (which is oxidised to Sn^{4+} in the process) to form a solution of iron(II) ions. This solution required 26.4cm^3 of 0.0200mol dm^{-3} potassium dichromate(VI) for oxidation.

- (a) Calculate the percentage of iron(III) oxide in the ore.
- (b) Why is not potassium manganate(VII) used for this titration?

Question 16

13.2g of iron(III) alum were dissolved in water and reduced to an iron(II) ion solution by zinc and dilute sulphuric acid. The mixture was filtered and the filtrate and washings made up to 500cm³ in a standard volumetric flask.

If 20.0cm³ of this solution required 26.5cm³ of 0.0100mol dm⁻³ KMnO₄ for oxidation. Calculate the percentage by mass of iron in iron alum.

Question 17

1.01g of an impure sample of potassium dichromate(VI), K₂Cr₂O₇, was dissolved in dil. sulphuric acid and made up to 250cm³ in a calibrated volumetric flask. A 25.0cm³ aliquot of this solution pipetted into a conical flask and excess potassium iodide solution and starch indicator were added. The liberated iodine was titrated with 0.100mol dm⁻³ sodium thiosulphate and the starch turned colourless after 20.0cm³ was added.

- Calculate the moles of sodium thiosulphate used in the titration and hence the number of moles of iodine titrated.
- Calculate the moles of dichromate(VI) ion that reacted to give the iodine titrated in the titration.
- Calculate mass of potassium dichromate(VI) in the 25.0cm³ aliquot titrated.
- Calculate the total mass of potassium dichromate(VI) in the original sample and hence its % purity.

Chapter 21

ELECTRODE POTENTIAL

INTRODUCTION

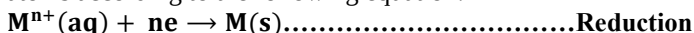
When an electrode is immersed in the solution containing its ions, e.g. $M(s)$ in $M^{n+}(aq)$, two things occur:

Firstly, the electrode starts to dissolve in the solution giving its ions according to the following equation:



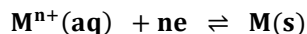
Electrostatic force of attraction between positively charged cations and electrons (released by the electrode in the ionisation process) which are negative, prevent cations from going far away from the electrode. So cations are attracted very close to the electrode.

Secondly, the cations attracted to the electrode gain electrons from the electrode surface to form neutral atoms according to the following equation:



The tendency of a metal in contact with its salt solution to attract metal ions from the solution and convert them into metal atoms by losing electrons is called **deposition pressure**.

Combining oxidation and reduction reaction equations shown above, gives the following reversible reaction equation:



Eventually the equilibrium is established and the electric double layer of oppositely charged ions (positive and negative charges) is formed as shown in the figure below:

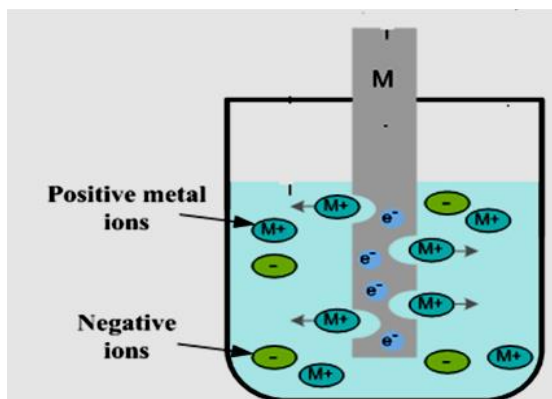


Figure 21.1 Electric double layers in electrode potential formation

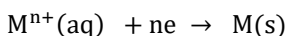
The formation of the electric double layers leads to formation of a potential difference between the electrode and its solution and the potential difference formed under this situation is what we call **electrode potential** denoted by a letter 'E'.

Definition of electrode potential

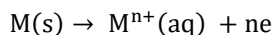
Quantitatively; electrode potential can be defined as *the potential difference between the electric double layers which is formed when an electrode is in contact with solution containing its ions.*

Qualitatively; electrode potential can be defined as *the tendency of a metal when placed in contact with solution of its ions to become positively or negatively charged with respect to the solution.* It can be **reduction** or **oxidation potential**.

Reduction potential is the tendency of a metal in contact with solution of its ions to become positively charged with respect to the solution.



Oxidation potential is the tendency of a metal in contact with a solution of its ions to become negatively charged with respect to the solution.



Thus in the equilibrium: $M^{n+}(aq) + ne \rightleftharpoons M(s)$

If the position of the equilibrium of one reaction lies more to the right hand side than another, then:

- The reduction potential of the reaction is more positive (or less negative).
- The oxidation potential of the reaction is more negative (or less positive).
- The electrode is more positive with respect to the solution containing its ions (when the electrode and the solution are in contact to each other).
- The metal, M, is weaker reducing agent (it undergo reduction more readily).

If the position of the equilibrium of one reaction lies more to the left hand side than another, then:

- The reduction potential of the reaction is more negative (or less positive).
- The oxidation potential of the reaction is more positive (or less negative).
- The electrode is more negative with respect to the solution containing its ions.
- The metal, M, is stronger reducing agent (it undergoes oxidation more readily).

It should be noted that:

Oxidation potential is equal in magnitude and opposite in sign to the reduction potential.

$$E_{\text{oxid}} = -E_{\text{red}}$$

According to IUPAC convention, the term electrode potential means the reduction potential. **Thus electrode potentials are always given as reduction potentials and hence whenever we talk about just electrode potential we always imply reduction potential.**

FACTORS AFFECTING ELECTRODE POTENTIAL

Electrode potential depends upon the following factors:

- Nature of the electrode
- Concentration of metal ions in the solution
- Temperature
- Pressure

Nature of the electrode

No two electrodes have the same standard electrode potential, why? This is because no two electrodes have exactly the same structure and the tendency to gain or lose electrons is also different.

Generally, a solid electrode dissolves to form its ions in aqueous solution according to the following steps:

1. Sublimation (Atomisation)
2. Ionisation
3. Hydration

1. Atomisation (sublimation)

This involves converting solid electrode to its corresponding gaseous atoms. **The process is endothermic.** $M(s) \rightarrow M(g)$ $\Delta H = +ve$

2. Ionisation

This involves converting gaseous atoms to its corresponding gaseous ions. **The process is also endothermic.** $M(s) \rightarrow M^{n+}(g) + ne$ $\Delta H = +ve$

3. Hydration

This involves dissolving gaseous ions in water to form aqueous the ions in the solution. **The process is exothermic.** $M^{n+}(g) + N(aq) \rightarrow M^{n+}(aq)$ $\Delta H = -ve$

The summation of **atomisation energy**, **ionisation energy** and **hydration energy** determine the ability (easiest) of the solid electrode to dissolve in aqueous solution as per forward reaction of the following reaction equation: $M(s) \rightleftharpoons M^{n+}(aq) + ne$

If the summation for one electrode is smaller (more negative or less positive) than another electrode, then:

- The oxidation potential of the electrode will be large (more positive or less negative) and hence forward reaction is more favoured.
- The reduction potential (electrode potential) will be smaller (more negative or less positive) and hence reverse reaction is less favoured.

If the summation of one electrode is larger (more positive or less negative) than another electrode, then:

- The oxidation potential of the electrode will be smaller (more negative or less positive) and hence forward reaction is less favoured.
- The reduction potential (electrode potential) will be larger (more positive or less negative) and hence reverse reaction is more favoured.

Concentration (activity) of metal ions in the solution

Consider the following equilibrium: $M^{n+}(aq) + ne \rightleftharpoons M(s)$

From the above equilibrium it is clearly understood that:

- Increasing **activity (effective concentration)** of $M^{n+}(aq)$ shifts the position of chemical equilibrium to the right hand side thus:
 - Increasing electrode potential (reduction potential)
 - Decreasing oxidation potential
- Decreasing **effective concentration (activity)** of $M^{n+}(aq)$ shifts the position of chemical equilibrium to the left hand side thus:
 - Decreasing electrode (reduction) potential
 - Increasing oxidation potential

So generally we can conclude that, **the electrode potential increases with an increase in concentration of the electrolyte.**

It should s be noted that: The electrode potential does not depend upon the surface area of the electrode because the concentration of the solid metal is taken to be unity (one).

Temperature

The electrode potential decreases with rise in temperature. The variation of electrode potential with change in temperature is given by **Nernst equation** (this will be discussed in detail later).

Pressure

Pressure has effect on electrode potential of gaseous electrode only.

STANDARD ELECTRODE POTENTIAL

Standard electrode potential is the electrode potential which is measured when an electrode is in contact with 1M solution of its ions at 25°C and 1atm (standard conditions). It is denoted as $E^\ominus$.

Measurement of standard electrode potential

The absolute value of a single electrode cannot be measured experimentally, why?

This is because a half-cell reaction cannot take place independently. To measure the potential difference between an electrode and its solution, the electrical connection between two half cells which contain different electrodes must be made. Thus one can measure only the difference between the electrode potential of any two half-cell reaction. **So how the electrode potential is measured?**

The only way out is to use arbitrarily a second electrode which acts as a reference electrode. The common standard reference electrode is standard hydrogen electrode (SHE). Its standard electrode potential is arbitrarily (by convention) taken to be zero at all temperatures so that electrode potentials of all other electrodes are measured against it. **What does standard hydrogen electrode consist of?**

A standard hydrogen electrode consists of a platinum foil coated with platinum black and is dipped in an acid solution with 1M hydrogen ions (H^+) concentration. The platinum foil is in contact with hydrogen gas at 1atm pressure at 25°C.

The reader should not confuse (as many do) the use of two terms: **Normal hydrogen electrode (NHE)** and **standard hydrogen electrode (SHE)**; the former applies when the hydrogen electrode is immersed in a **normal solution (a solution of normality of 1N)** and it is no longer in use; its use has been replaced by the later (SHE) which applies when the hydrogen electrode is immersed to a **molar solution (a solution of molarity of 1M)** at standard conditions (25°C and 1atm).

Construction of electrochemical cell for electrode potential measurement

In order to obtain a cell reaction, one must know the oxidised (reductant) and reduced (oxidant) species to determine the cathode and anode of the cell. In the **electrochemical (galvanic or voltaic) cell**:

- **Anode is negative electrode**, i.e. the oxidised specie (reducing agent) becomes the anode.
- **Cathode is positive electrode**, i.e. the reduced specie (oxidising agent) becomes the cathode.

Conventionally it has been agreed that, **anode (oxidation half-cell) must be kept at the left hand side while cathode (reduction half-cell) must be kept at right hand side.**

- The two half cells are connected by salt bridge and **voltmeter of very high resistance** (so that it does not allow passage of current through it) reads the electrode potential of the electrode.

Measurement of standard electrode potential of a metal which is stronger reducing agent than hydrogen

In this case the electrode (like zinc) is anode while standard hydrogen electrode is cathode.

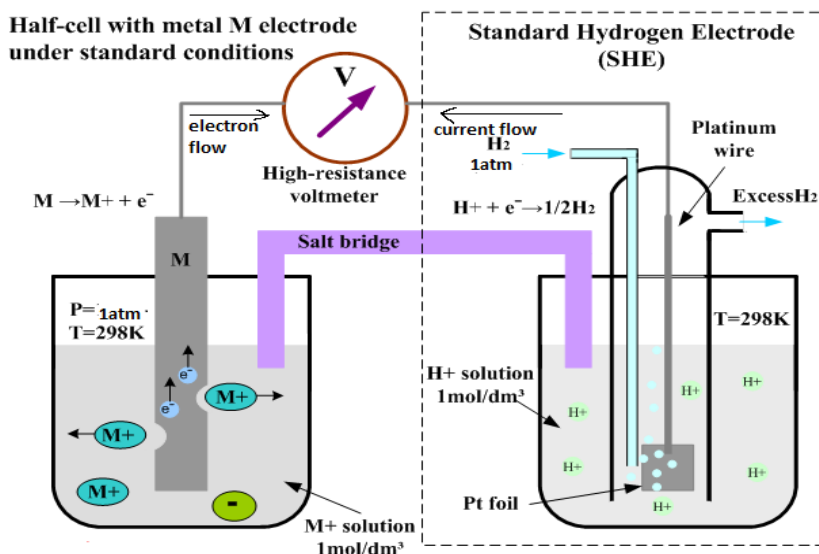


Figure 21.2 Electrochemical cell for standard electrode potential measurement

From zinc electrode, the standard electrode potential is found to be -0.76 V . A negative value means that when Zn/Zn^{2+} half cell is combined with standard hydrogen electrode (SHE); zinc is negative electrode (anode) and the electrons move from the zinc plate to the platinum electrode of SHE though the external circuit. Oxidation takes place at zinc electrode and reduction at the platinum electrode.

At Anode: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

At cathode: $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

Measurement of standard electrode potential of a metal which is weaker reducing agent than hydrogen

In this case, the electrode like copper become cathode while standard hydrogen electrode is anode.

For copper electrode, the standard electrode potential is found to be $+0.34\text{ V}$. The positive value means that when Cu^{2+}/Cu half cell is combined with SHE, copper is positive electrode (cathode) and electrons move from the platinum electrode of SHE to the copper plate through the external circuit. Reduction takes place at copper electrode and oxidation at platinum electrode of SHE.

At anode: $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$

At cathode: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$

Composition of salt bridge

A salt bridge is inverted U – tube containing an inert paste of a strong electrolyte (potassium chloride or sodium sulphate is commonly used) and agar – gel.

Significance of salt bridge

The salt bridge:

- Allows the ions to migrate from cathode half-cell into the anode half-cell so as to complete the circuit
- Prevents the diffusion of the electrolytes from one half – cell to the other thus maintaining the charge balance in the two half cells.

Functions of platinised platinum in the standard hydrogen electrode

The platinised platinum is useful in the following ways:

- It adsorbs hydrogen gas
- It acts as inert electrode by allowing electrons to flow from hydrogen gas (H_2) to platinum (Pt) and from it (Pt) to H^+ .

Electrodes

Electrodes help in the conduction of electrons into and out of the cell as well as provide the surface for electrode reaction.

- They are made up of electric conductors like metals or graphite.
- They may be in the form of rods or as surface coating on the rods of other material or as a coating on the inside surface of the cell.

By definition:

Electrode is a solid electric conductor through which an electric current enters or leaves an electrolytic cell or other medium.

Electrodes may be divided into two types depending on how they are involved in the electrochemical (or electrolytic) process. These are:

- Inert electrodes and
- Active electrodes

Inert electrodes are electrodes which do not enter into the electrolytic chemical reaction.

- The electrodes made up of noble metals like platinum are used as inert electrodes.

Active electrodes are electrodes which take part in the electrolytic reaction.

- These are either dissolved into the electrolyte or a substance is deposited on them.

Electrodes can also be divided into:

- Anode and
- Cathode

Anode is the electrode at which oxidation occurs.

Cathode is the electrode at which reduction occurs.

Don't confuse: Most of students have misconception that 'anode is positive electrode' and 'cathode is negative electrode'. That is not correct because polarity of the electrode depends on the kind of cell; while for electrochemical cell, anode is negative and cathode is positive, for electrolytic cell, anode is positive and cathode is negative. However, in both cells, oxidation occurs at anode and reduction occurs at cathode, the simple fact which provides the basis above definitions.

Electrolyte

The electrolyte is the substances that give free ions either in molten state or in the aqueous solution. They can be **anolyte** or **catholyte**.

Anolyte is an electrolyte at anode half-cell in which the anode is dipped.

Catholyte is an electrolyte at cathode half-cell in which cathode is dipped.

APPLICATIONS OF ELECTRODE POTENTIAL

Electrode potential is useful in:

- Construction of electrochemical cells
- Construction of electrochemical series

Construction of electrochemical cells

What is electrochemical cell?

Electrochemical cell is a device which uses spontaneous chemical reactions to generate electricity which consists of two half cells connected with a salt bridge. Electrochemical cells are also known as **galvanic cell** or **voltaic cell**.

In constructing electrochemical cell from given standard electrode potentials:

The electrode with more negative (or less positive) electrode potential must be anode i.e. must appear in the left handed half-cell.

Reasons for the choice: Oxidation half reaction of cell reaction occurs at anode half-cell. So the anode electrode (negative electrode) must be stronger reducing agent, i.e. it must undergo reduction by difficulty and this is justified by its smaller value (more negative or less positive) of electrode potential which is reduction potential.

The electrode with more positive (or less negative) electrode potential must be cathode, i.e. it must appear at right handed half-cell.

Reason for the choice: Reduction half reaction of cell reaction occurs at cathode half-cell. So the cathode electrode (positive electrode) must be weaker reducing agent i.e. it must undergo reduction more readily and this is justified by its large value (more positive or less negative) of the electrode potential which is reduction potential.

It should be understood that: Since the anode is better electron donor than cathode, electrons flow from the anode to cathode and the conventional current, flow from the cathode to anode (in opposite direction of electron flow).

Example 1

Draw a voltaic cell diagram which consists of copper and zinc electrodes, given that:

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\theta} = -0.76\text{V}; E_{\text{Cu}^{2+}/\text{Cu}}^{\theta} = +0.34\text{V}$$

Solution

Zinc having more negative electrode potential, its electrode is negative electrode (anode) and it must be kept at left handed half cell as shows in the diagram below:

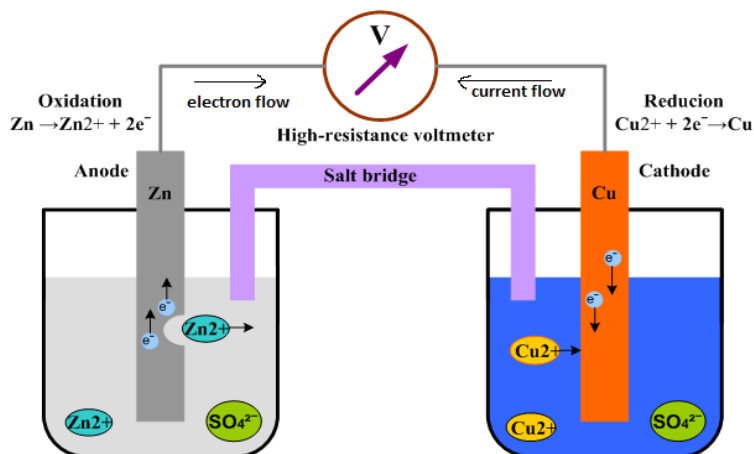


Figure 22.3 Electrochemical cell for example 1

It should be noted that: The galvanic (electrochemical) cell which consists of zinc and copper electrodes immersed in ZnSO_4 and CuSO_4 solutions at anode and cathode respectively is known as **Daniel cell**.

Cell notation

Cell notation express cell reaction of given cell. It also used in writing cell diagram instead of using drawing. For example, cell notation for Daniel cell is;

$\text{Zn(s)} \mid \text{Zn}^{2+}(\text{M}) \parallel \text{Cu}^{2+}(\text{M}) \mid \text{Cu(s)}$ whereby:

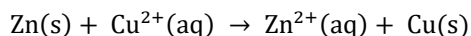
- The anode reaction (negative electrode) must be written on the left hand side and the cathode reaction (positive electrode) on the right hand side.
- A vertical line indicates a contact between two phases. As an example $\text{Zn} \mid \text{Zn}^{2+}$ indicates that zinc electrode is in contact with a solution containing Zn^{2+} ions or $\text{Cu}^{2+} \mid \text{Cu}$ indicates that copper electrode is in contact with a solution containing Cu^{2+}
- In anode reaction, neutral atom is written before its corresponding cation indicating that there is oxidation at the anode while in cathode reaction, the cation is written before its corresponding neutral atom indicating that there is a reduction at the cathode.
- A double line indicates that the solutions in the half cells are separated by a porous barrier or salt bridge
- The molar concentration of the solution is written in brackets after the formula of the ion e.g. $\text{Zn} \mid \text{Zn}^{2+}(0.1\text{M})$ indicates that the zinc plate is in contact with 0.1M Zn^{2+} solution.

Also from above cell notation:

At anode: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

At cathode: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$

Combining anode reaction and cathode reaction, the overall cell reaction is obtained which is



Hence cell diagram can be used to deduce cell reaction. The converse of this is also true, i.e. the cell reactions can be used to deduce the cell diagram.

Example 2

Write cell diagram from the following cell reactions:

- (i) $\text{Zn(s)} + \text{Pb}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Pb(s)}$
 (ii) $\text{Mg(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu(s)}$ E^θ
 (iii) $\text{M(s)} + 2\text{H}^+(\text{aq}) \rightarrow \text{M}^{2+}(\text{aq}) + \text{H}_2(\text{g})$ E^θ
 (iv) $\text{H}_2(\text{g}) + \text{M}^{2+}(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + \text{M(s)}$ E^θ

Solution

- (i) $\text{Zn(s)} \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Pb}^{2+}(\text{aq}) \mid \text{Pb(s)}$
 (ii) $\text{Mg(s)} \mid \text{Mg}^{2+}(1\text{M}) \parallel \text{Cu}^{2+}(1\text{M}) \mid \text{Cu(s)}$ **(With standard electrode potential, E^θ , at the end of the equation means concentration of ions is 1M)**
 (iii) $\text{M(s)} \mid \text{M}^{2+}(1\text{M}) \parallel \text{H}^+(1\text{M}) \parallel \text{H}_2(1\text{atm}), \text{Pt}$ **(With standard electrode potential, E^θ , at the end of the equation means concentration of ions is 1M and partial pressure of the hydrogen gas is 1atm)**
 (iv) $\text{Pt, H}_2(1\text{atm}) \mid \text{H}^+(1\text{M}) \parallel \text{M}^{2+}(1\text{M}) \mid \text{M(s)}$

Note: In writing cell diagram, it is not necessary to include stoichiometric coefficients of species appearing in the cell reaction because multiplying a fixed number to a half-cell reaction does not alter the value of electrode potential.

Calculating standard cell potential (e.m.f)

The **cell potential** of electrochemical cell is the difference in electrode (reduction) potential of the cathode half reaction and that of the anode half reaction.

$$\text{Cell potential, } E_{\text{cell}} = E_{\text{red(cathode)}} - E_{\text{red(anode)}}$$

Since the cathode always appears at right hand side and anode at left hand side, then we can denote:

$$E_{\text{red(cathode)}} \quad \text{as} \quad E_{\text{R}}$$

$$\text{And} \quad E_{\text{red(anode)}} \quad \text{as} \quad E_{\text{L}}$$

$$\text{Then, } E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

The cell potential of a cell, measured at 25°C and 1atm pressure (standard conditions) when concentration of the electrolytes in both half cells is 1M, is known as **standard cell potential, E_{cell}^θ** .

$$\text{Thus } E_{\text{cell}}^\theta = E_{\text{R}}^\theta - E_{\text{L}}^\theta$$

The cell potential of a cell when the circuit draws no current (in zero current flow) is known as **electromotive fore (e.m.f)**.

In order to construct a cell with maximum e.m.f. one must choose the electrode with most negative electrode potential to be anode and that of most positive electrode potential to be the cathode.

It should be noted that: In applying above formulas in calculation of cell potential (or e.m.f), make sure that reduction potentials are used and not otherwise. If the oxidation electrode potential is given instead of reduction electrode potential don't forget to convert it to the reduction potential by using the following relationship: $E_{\text{red}} = -E_{\text{oxid}}$

Example 3

What is the cell potential for the following cell?

$$\text{Zn(s)} \mid \text{Zn}^{2+}(1\text{M}) \parallel \text{Pb}^{2+}(1\text{M}) \mid \text{Pb(s)}$$

$$E_{\text{Pb}^{2+}/\text{Pb}}^\theta = -0.12\text{V}; E_{\text{Zn}^{2+}/\text{Zn}}^\theta = -0.76\text{V}$$

Solution

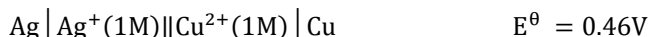
According to the convention, the right hand side electrode is cathode.

So using $E_{\text{cell}}^{\theta} = E_{\text{R}}^{\theta} - E_{\text{L}}^{\theta} = -0.12\text{V} - (-0.76\text{V}) = +0.64\text{V}$

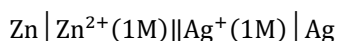
Hence the cell potential for the cell is +0.64V

Example 4

The e.m.f of the following cell is:



Calculate e.m.f of the cell:

**Solution**

Using $E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$

Then:

$$0.46\text{V} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Ag}^+/\text{Ag}} \dots\dots\dots(\text{i})$$

$$\text{And } 1.1\text{V} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}} \dots\dots\dots(\text{ii})$$

(ii) – (i) give;

$$0.64\text{V} = E_{\text{Ag}^+/\text{Ag}} - E_{\text{Zn}^{2+}/\text{Zn}} = \text{e.m.f of the given cell}$$

Hence e.m.f the cell is +0.64V

Example 5

A cell is set up between copper and silver $\text{Cu(s)} \mid \text{Cu}^{2+}(\text{aq}) \parallel \text{Ag}^+(\text{aq}) \mid \text{Ag(s)}$

If two half cells work under standard conditions, calculate e.m.f of the cell

$$E_{\text{Cu}/\text{Cu}^{2+}}^{\theta} = -0.34\text{V}, E_{\text{Ag}^+/\text{Ag}}^{\theta} = 0.8\text{V}$$

Solution

In this problem it is given oxidation electrode potential of copper instead of its reduction electrode potential.

Using $E_{\text{red}}^{\theta} = -E_{\text{oxid}}^{\theta}$

$$E_{\text{Cu}^{2+}/\text{Cu}}^{\theta} = - E_{\text{Cu}/\text{Cu}^{2+}}^{\theta} = -(-0.34\text{V}) = 0.34\text{V}$$

$$\text{Then } E_{\text{cell}}^{\theta} = E_{\text{R}}^{\theta} - E_{\text{L}}^{\theta} = 0.8\text{V} - 0.34\text{V} = 0.46\text{V}$$

Hence the e.m.f of the cell is +0.46V

Example 6

An electrochemical cell is made up of iron rod dipped in 1M solution of Fe^{2+} ions in a beaker and nickel rod dipped in 1M solution of Ni^{2+} in another beaker. A salt bridge is used to connect two half cells;

- In which cell does reduction occur?
- Write half reactions involved
- Which metal is anode
- In which direction are the electrons passing through voltmeter?
- What would be the effect on the voltmeter reading if Fe^{2+} concentration were increased?
- What was the cell potential at the time the cell operation starts?

$$E_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}; E_{\text{Ni}^{2+}/\text{Ni}} = -0.25\text{V}$$

Solution

The electrode potential of iron is more negative than nickel so it is negative electrode (anode)

Thus the cell diagram of the cell is $\text{Fe(s)} \mid \text{Fe}^{2+}(1\text{M}) \parallel \text{Ni}^{2+}(1\text{M}) \mid \text{Ni(s)}$

(a) Reduction occurs at nickel electrode half cell

(b) Half reactions involved are:

At anode: $\text{Fe(s)} \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \dots\dots\dots \text{Oxidation}$

At cathode: $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni(s)} \dots\dots\dots \text{Reduction}$

(c) The anode is iron.

(d) Electrons flow from iron electrode to nickel electrode.

(e) The potential difference will decrease and hence the voltmeter reading will be decreased too.

(f) At the time cell potential starts, e.m.f = cell potential;

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} = -0.25 - (-0.44\text{V}) = 0.19\text{V}$$

Overpotential

In gaseous electrode, the measured e.m.f is greater than the standard (calculated) e.m.f. This is because the accumulation of gaseous molecules on the electrode increases the potential of the ion approaching the electrode hence forming **overpotential**.

Definition of overpotential

This is the potential difference in excess of the potential required to discharge an ion.

Standard e.m.f of galvanic cell and feasibility of reactions

There is important relationship between standard e.m.f and feasibility of the reaction. For the cell reaction of occur the e.m.f must be positive. If the e.m.f is negative, then the reaction occurs in reverse direction. Furthermore:

- The more positive e.m.f the more readily the reaction occurs and vice-versa.
- If there is a factor which increases the easiest for the cell reaction to take place, then the factor is said to increase the e.m.f of the cell in the direction of the reaction.
- If there is a factor which makes more difficulty for the reaction to take place, then the factor is said to decrease the e.m.f of the cell.

Example 7

Given the Daniel cell: $\text{Zn} \mid \text{Zn}^{2+}(1\text{M}) \parallel \text{Cu}^{2+}(1\text{M}) \mid \text{Cu(s)}$

(a) Calculate the e.m.f of the cell at standard condition

(b) Explain how the e.m.f of the cell would be affected by

(i) Increasing concentration of Cu^{2+}

(ii) Increasing concentration of Zn^{2+}

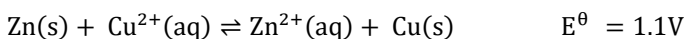
$$(E_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}; E_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V})$$

Solution

$$(a) E_{\text{cell}}^{\theta} = E_{\text{R}}^{\theta} - E_{\text{L}}^{\theta} = 0.34\text{V} - (-0.76\text{V}) = 1.1\text{V}$$

Hence the e.m.f of the cell at standard conditions is 1.1V

(b) From the cell diagram; overall cell reaction is:



(i) Increasing concentration of Cu^{2+} shifts the position of equilibrium to the right hand side and hence e.m.f of the cell is increased.

(ii) Increasing concentration Zn^{2+} shifts the position of equilibrium to the left hand side and hence e.m.f of the cell is decreased.

Example 8

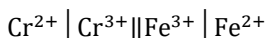
Predict which of the following reactions are favoured and which are not favoured:

- (i) $\text{Fe}^{3+} + \text{Cr}^{2+} \rightarrow \text{Fe}^{2+} + \text{Cr}^{3+}$
 (ii) $\text{Zn}^{2+} + 2\text{Cr}^{2+} \rightarrow \text{Zn(s)} + 2\text{Cr}^{3+}$
 (iii) $\text{Sn}^{2+} + 2\text{Fe}^{3+} \rightarrow \text{Sn}^{4+} + 2\text{Fe}^{2+}$
 (iv) $2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + 2\text{Fe}^{3+}$
 (v) $\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$
 (vi) $\text{I}_2 + 2\text{F}^- \rightarrow 2\text{I}^- + \text{F}_2$

Given that:

**Solution**

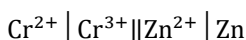
(i) Cell diagram according to given cell reaction



$$\text{Then } E_{\text{cell}}^\theta = E_R^\theta - E_L^\theta = 0.771\text{V} - (-0.408\text{V}) = +1.179\text{V}$$

Since standard e.m.f of the cell is positive, the reaction is spontaneous and hence the reaction is favoured

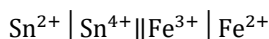
(ii) Cell diagram according to the given cell reaction is:



$$\text{Then } E_{\text{cell}}^\theta = E_R^\theta - E_L^\theta = -0.760\text{V} - (-0.408\text{V}) = -0.352\text{V}$$

Since standard e.m.f. of the cell is negative, the reaction is not spontaneous and hence the reaction is not favoured.

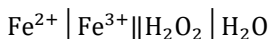
(iii) Cell diagram according to the given cell reaction is;



$$\text{Then } E_{\text{cell}}^\theta = E_R^\theta - E_L^\theta = 0.771\text{V} - 0.150\text{V} = +0.621\text{V}$$

Since the standard e.m.f of the cell is positive, the reaction is favoured

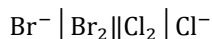
(iv) Cell diagram according to the given cell reaction is;



$$\text{Then } E_{\text{cell}}^\theta = E_R^\theta - E_L^\theta = 1.776\text{V} - 0.771\text{V} = +1.005\text{V}$$

Since the standard e.m.f of the cell is positive, the reaction is favoured

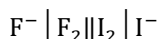
(v) Cell diagram according to the given cell reaction is;



$$\text{Then } E_{\text{cell}}^{\theta} = E_{\text{R}}^{\theta} - E_{\text{L}}^{\theta} = 1.36\text{V} - 1.07\text{V} = +0.29\text{V}$$

Since the standard e.m.f of the cell is positive, the reaction is favoured

(vi) Cell diagram according to the given cell reaction is;



$$\text{Then } E_{\text{cell}}^{\theta} = E_{\text{R}}^{\theta} - E_{\text{L}}^{\theta} = 0.54\text{V} - 2.85\text{V} = -2.31\text{V}$$

Since the standard e.m.f of the cell is negative, the reaction is not favoured.

Variation of electrode potential with concentration

Increasing concentration of an electrolyte, increases electrode potential of an electrode immersed in the electrolyte; the effect of concentration of electrolyte on the electrode potential is well explained by **Nernst equation**.

The **Nernst equation** is used to find out the electrode potential of an electrode in which the concentration of metal ions in solution is not 1M (and of course if temperature is not 25°C).

If the electrode reaction (reduction in forward reaction) is: $\text{M}^{n+}(\text{aq}) + n\text{e} \rightleftharpoons \text{M}(\text{s})$

The reaction quotient for the reaction, Q_c , is given by: $Q_c = \frac{1}{[\text{M}^{n+}]}$

$$\text{Then by Nernst equation: } E = E^{\theta} - \frac{RT}{nF} \ln Q_c$$

$$\text{But } \ln R_Q = 2.303 \log Q_c$$

$$\text{It follows that: } E = E^{\theta} - \frac{2.303RT}{nF} \log Q_c$$

$$\text{Substituting } Q_c = \frac{1}{[\text{M}^{n+}]}, \text{ to the Nernst equation gives: } E = E^{\theta} - \frac{2.303RT}{nF} \log \frac{1}{[\text{M}^{n+}]}$$

Where:

E is the electrode potential of an electrode at any temperature dipped in the solution containing its ions at any concentration.

E^{θ} is the standard electrode potential of the electrode

$[\text{M}^{n+}]$ is the molar concentration of the ions

R is the gas constant = $8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$

T is the absolute temperature in Kelvin, K

F is the Faraday's constant = 96500 Coulombs

n is the number of electrons involved in the balanced equation of the half reaction

If the standard temperature (25°C or 298K) is maintained, the Nernst equation becomes:

$$\begin{aligned} E &= E^{\theta} - \frac{2.303 \times 8.3143 \times 298}{n \times 96500} \log \frac{1}{[\text{M}^{n+}]} \\ &= E^{\theta} - \frac{0.0591}{n} \log \frac{1}{[\text{M}^{n+}]} \end{aligned}$$

Hence if only concentration of ions is altered, the simplified form of Nernst equation become:

$$E = E^{\theta} - \frac{0.0591}{n} \log \frac{1}{[\text{M}^{n+}]} \text{ or } E = E^{\theta} + \frac{0.0591}{n} \log [\text{M}^{n+}]$$

From which it is clearly understood that, when concentration of ions, $[\text{M}^{n+}]$ is increased, the electrode potential also increases as explained earlier.

It should be noted that, in writing reaction quotient, Q_c :

- Concentration of solid metal (electrode) does not appear in Q_c expression. Only liquid (aqueous solution) and gases (if any) species should appear in Q_c expression. This is because effective concentration (activity) of the solid metal is taken to be 1(unity)
- Effective molar concentration (activity) of a gas is taken as its partial pressure in atmosphere.

Example 9

What is the half-cell potential for Fe^{3+}/Fe electrode in which concentration of Fe^{3+} ion is 0.1M at 25°C ?

$$E_{\text{Fe}^{3+}/\text{Fe}}^\theta = +0.771\text{V}$$

Solution

Half-cell reaction: $\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Fe}(\text{s})$

From which: $n = 3$ and $Q_c = \frac{1}{[\text{Fe}^{3+}]} = \frac{1}{0.1} = 10$

From Nernst equation: $E = E^\theta - \frac{0.0591}{n} \log Q_c$

Substituting $E = 0.771 - \frac{0.0591}{3} \log 10 = 0.7513\text{V}$

Hence the cell potential of the half-cell is 0.7513V

Example 10

What is the electrode potential of Mg^{2+}/Mg electrode at which concentration of Mg^{2+} is 0.1M at 25°C ?

$$E_{\text{Mg}^{2+}/\text{Mg}}^\theta = -2.36\text{V}$$

Solution

Half-cell reaction: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$

From which: $n = 2$ and $Q_c = \frac{1}{[\text{Mg}^{2+}]} = \frac{1}{0.1} = 10$

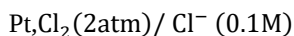
From Nernst equation: $E = E^\theta - \frac{0.0591}{n} \log Q_c$

Substituting $E = -2.36 - \frac{0.0591}{2} \log 10 = -2.38955\text{V}$

Hence the electrode potential is -2.38955V

Example 11

What is the cell potential of the following half-cell at 25°C ?



Given that: $E_{\text{Cl}_2/\text{Cl}^-}^\theta = 1.36\text{V}$

Solution

Half-cell reaction: $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$

From which: $n = 2$ and $Q_c = \frac{[\text{Cl}^-]^2}{P_{\text{Cl}_2}} = \frac{(0.1)^2}{2} = 5 \times 10^{-3}$

From Nernst equation; $E = E^\theta - \frac{0.0591}{n} \log Q_c$

Substituting $E = 1.36 - \frac{0.0591}{2} \log(5 \times 10^{-3}) = 1.428\text{V}$

Hence the cell potential of the half-cell is 1.428V

Example 12

The standard electrode potential of Au^{3+}/Au electrode is +1.42V. At what concentration of Au^{3+} the electrode potential is zero at 25°C?

Solution

Half-cell reaction: $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s})$

From which $n = 3$ and $Q_c = \frac{1}{[\text{Au}^{3+}]}$

Then from Nernst equation; $E = E^\theta - \frac{0.0591}{n} \log Q_c$

Substituting $0 = 1.42 - \frac{0.0591}{3} \log \frac{1}{[\text{Au}^{3+}]}$ or $0.0197 \log [\text{Au}^{3+}] = -1.42$

Or $[\text{Au}^{3+}] = \log^{-1} \left(\frac{-1.42}{0.0197} \right) = 8.29 \times 10^{-73} \text{M}$

Hence at 25°C, the electrode potential is zero when concentration of Au^{3+} is $8.29 \times 10^{-73} \text{M}$.

Variation of cell potential with concentration

Increasing concentration of anolyte of the electrochemical cell, decreases cell potential of the cell, while increasing concentration of catholyte increases the cell potential.

The cell potential of a cell constructed from non – standard electrodes is given by the following modified form of Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^\theta - \frac{0.0591}{n} \log Q_c$ at 25°C

Where:

E_{cell} is the cell potential of the cell

E_{cell}^θ is the standard cell potential of the cell $= E_R^\theta - E_L^\theta$

n is the number of electrons involved in the balanced equation of the **overall cell reaction**

Q_c is the reaction quotient which is derived from the equation of the **overall cell reaction**

Example 13

A galvanic cell consists of metallic zinc plate immersed in 0.1M $\text{Zn}(\text{NO}_3)_2$ solution and metallic plate of lead in 0.02M $\text{Pb}(\text{NO}_3)_2$ solution. Calculate the e.m.f cell at 25°C

$$E_{\text{Zn}^{2+}/\text{Zn}}^\theta = -0.76\text{V}; E_{\text{Pb}^{2+}/\text{Pb}}^\theta = -0.13\text{V}$$

Solution

Cell diagram of given cell: $\text{Zn} | \text{Zn}^{2+}(0.1\text{M}) || \text{Pb}^{2+}(0.02\text{M}) | \text{Pb}$

Oxidation half-cell reaction (at anode):



Reduction half-cell reaction (at cathode):



Writing overall cell reaction by taking (i) + (ii):

Cell reaction: $\text{Zn}(\text{s}) + \text{Pb}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Pb}(\text{s})$

From which $n = 2$ and $Q_c = \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]} = \frac{0.1}{0.02} = 5$

And $E_{\text{cell}}^\theta = E_{\text{cathode}}^\theta - E_{\text{anode}}^\theta = -0.13\text{V} - (-0.76\text{V}) = 0.63\text{V}$

From Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log Q_c$

Substituting $E_{\text{cell}} = 0.63 - \frac{0.0591}{2} \log 5 = 0.6093V$

Hence the e.m.f of the cell is 0.6093V

Example 14

What is potential for the cell at 25°C:



Given that: $E_{\text{Cr}^{3+}/\text{Cr}}^{\theta} = -0.74V$; $E_{\text{Fe}^{2+}/\text{Fe}}^{\theta} = -0.44V$

Solution

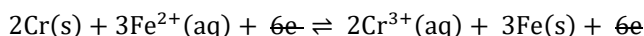
Oxidation half-cell reaction (at anode):



Reduction half-cell reaction (at cathode)

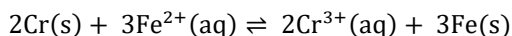


Writing overall cell reaction by taking (i) $\times 2$ + (ii) $\times 3$ to give



Where $n = 6$

Simplifying the above equation by cancelling like terms to give the following cell reaction:



From which $Q_c = \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3} = \frac{(0.1)^2}{(0.01)^3} = 10000$

And $E_{\text{cell}}^{\theta} = E_{\text{cathode}}^{\theta} - E_{\text{anode}}^{\theta} = -0.44V - (-0.74V) = 0.3V$

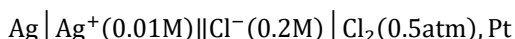
From Nernst equation; $E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log Q_c$

Substituting $E_{\text{cell}} = 0.3 - \frac{0.0591}{6} \log 10000 = 0.2606V$

Hence the cell potential is 0.2606V

Example 15

What is the potential for the cell at 25°C:



Given that: $E_{\text{Ag}^+/\text{Ag}}^{\theta} = 0.8V$; $E_{\text{Cl}_2/\text{Cl}^-}^{\theta} = 1.36V$

Solution

Oxidation half-cell reaction (at anode): $\text{Ag}(s) \rightleftharpoons \text{Ag}^+(\text{aq}) + e \dots\dots\dots(i)$

Reduction half-cell reaction (at cathode): $\text{Cl}_2(\text{g}) + 2e \rightleftharpoons 2\text{Cl}^- \dots\dots\dots(ii)$

Writing overall cell reaction by taking (i) $\times 2$ + (ii)

Cell reaction: $2\text{Ag}(s) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + 2\text{Cl}^-(\text{aq})$

Where $n = 2$ and $Q_c = \frac{[\text{Ag}^+]^2 [\text{Cl}^-]^2}{P_{\text{Cl}_2}} = \frac{(0.01)^2 \times (0.2)^2}{0.5} = 8 \times 10^{-6}$

And $E_{\text{cell}}^{\theta} = E_{\text{cathode}}^{\theta} - E_{\text{anode}}^{\theta} = 1.36V - 0.8V = 0.56V$

From Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log Q_c$

Substituting $E_{\text{cell}} = 0.56 - \frac{0.0591}{2} \log(8 \times 10^{-6}) = 0.7106\text{V}$

Hence the potential for the cell is 0.7106V

Concentration cells

If two plates of the same metal are dipped separately into two solutions of the same electrolyte at different concentration and the solutions are connected with a salt bridge, the whole arrangement is found to act as galvanic (electrochemical) cell, why? This is because at different concentration of the electrolyte, the two half cells have different electrode potential.

The plate in more dilute solution has lower electrode potential and hence it acts as anode (negative electrode) while the plate in more concentrated solution has greater electrode potential thus acting as cathode.

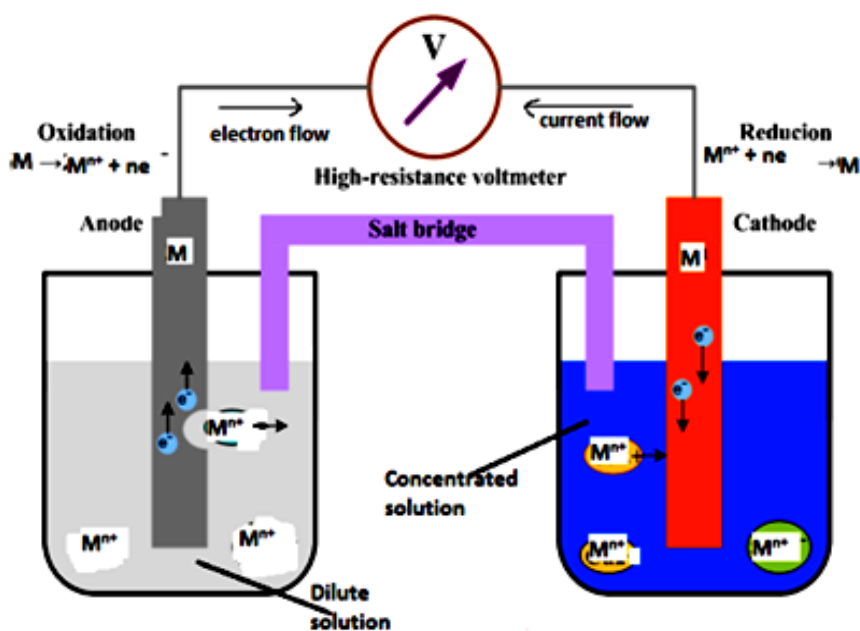


Figure 21.4 Concentration cell

Anode reaction: $M(s) \rightleftharpoons M^{n+}(\text{Dilute}) + ne$ (The solid electrode dissolves in solution at anode half-cell)

Cathode reaction: $M^{n+}(\text{concentrated}) + ne \rightleftharpoons M(s)$ (The solid deposits at cathode half-cell)

Definition of concentration cell

This is the electrochemical cell which consists of the same electrodes and the same electrolytes at different concentration which are connected by a salt bridge.

Calculations of cell potential (e.m.f) of concentration cells

By using Nernst equation:

$$E = E^{\theta} - \frac{0.0591}{n} \log Q_c$$

If M_d represents $[M^{n+}(\text{dilute})]$

M_c represents $[M^{n+}]$ (concentrated)

$$\text{Then } E_{\text{anode}} = E_{M^{n+}/M} - \frac{0.0591}{n} \log \frac{1}{M_d}$$

$$\text{And } E_{\text{cathode}} = E_{M^{n+}/M} - \frac{0.0591}{n} \log \frac{1}{M_c}$$

$$\text{Using } E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$\text{Then } E_{\text{cell}} = \left(E_{M^{n+}/M} - \frac{0.0591}{n} \log \frac{1}{M_c} \right) - \left(E_{M^{n+}/M} - \frac{0.0591}{n} \log \frac{1}{M_d} \right)$$

$$\text{Thus } E_{\text{cell}} = \frac{0.0591}{n} \log \frac{1}{M_d} - \frac{0.0591}{n} \log \frac{1}{M_c}$$

$$\begin{aligned} \text{Or } E_{\text{cell}} &= \frac{0.0591}{n} \left(\log \frac{1}{M_d} - \log \frac{1}{M_c} \right) \\ &= \frac{0.0591}{n} \log \left(\frac{1}{M_d} \div \frac{1}{M_c} \right) = \frac{0.0591}{n} \log \frac{M_c}{M_d} \end{aligned}$$

$$\text{Hence e.m.f of concentration cell is given by: } E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{M_c}{M_d} \right)$$

Where **n** is the number of electrons involved in the cell reaction = oxidation state of the metal ion.

Example 16

What is the cell potential of the cell at 25°C: $\text{Ni} \mid \text{Ni}^{2+}(0.01\text{M}) \parallel \text{Ni}^{2+}(0.1\text{M}) \mid \text{Ni}$

Given that: $E_{\text{Ni}^{2+}/\text{Ni}}^\theta = -0.25\text{V}$

Solution

$$E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{M_c}{M_d} \right)$$

Where: $n = 2$, $M_c = 0.1\text{M}$ and $M_d = 0.01\text{M}$

$$\text{Then } E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{0.1}{0.01} \right) = 0.02955\text{V}$$

Hence the cell potential is 0.02955V

Example 17

A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6}M hydrogen ions. The e.m.f of the cell is a 0.118V. Calculate the concentration of hydrogen ions at the positive electrode

Solution

The positive electrode is the electrode dipped in more concentrated solution. So it is asked to find concentration more concentrated electrolytic solution, M_c

$$\text{Using } E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{M_c}{M_d} \right)$$

But oxidation state of H^+ is 1, i.e. $n = 1$

$$\text{Substituting } 0.118 = \frac{0.0591}{1} \log \left(\frac{M_c}{10^{-6}} \right)$$

$$\frac{M_c}{10^{-6}} = \log^{-1} \left(\frac{0.118}{0.0591} \right) = \log^{-1}(2) = 100$$

$$\text{Or } M_c = 10^{-6} \times 100 = 10^{-4}\text{M}$$

Hence concentration of hydrogen ions at positive electrode is $1 \times 10^{-4}\text{mol dm}^{-3}$

Determination of pH of solution by using electrochemical cells

pH of hydrogen ions (H^+) solution can be determined without using pH meter if the electrochemical cell (concentration electrochemical cell) with the following features is constructed:

- One of the half-cell consists of standard electrode (electrode dipped in 1M solution of its ions at $25^\circ C$).
- Another half-cell which is the hydrogen electrode (adsorbed in platinum at pressures of 1atm) dipped in unknown concentration of its ions, (H^+) whose pH is to be determined.
- The cathode half-cell is the standard electrode if the electrode has positive electrode potential i.e. if the standard electrode has positive E^θ the cell diagram is $Pt, H_2(1atm) | H^+(aq) || M^{n+}(1M) | M(s)$ where M is the standard electrode
- The anode half-cell is the standard electrode if the electrode has negative electrode potential and the cell diagram become $M(s) | M^{n+}(1M) || H^+(aq) | H_2(1atm), Pt$.
- After determination of cell potential of the cell (through voltmeter reading), pH of unknown concentration of H^+ (hydrogen ions) can be calculated.

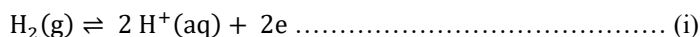
Example 18

The measured voltage of the cell: $Pt(s), H_2(g, 1atm) | H^+(aq) || Ag^+(aq, 1M) | Ag(s)$

is 0.900V at $25^\circ C$. Given $E^\theta_{Ag^+/Ag} = 0.8V$; Calculate the pH of the solution

Solution

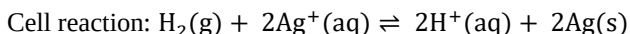
Oxidation half-cell reaction (at anode):



Reduction half-cell reaction (at cathode):



Writing overall cell reaction by taking (i) + 2(ii);



$$\text{From which } n = 2 \text{ and } Q_c = \frac{[H^+]^2}{(P_{H_2}) [Ag^+]^2} = \frac{[H^+]^2}{1 \times 1^2} = [H^+]^2$$

$$\text{And } E^\theta_{\text{cell}} = E^\theta_{\text{cathode}} - E^\theta_{\text{anode}} = 0.8V - 0V = 0.8V$$

$$\text{By Nernst equation; } E_{\text{cell}} = E^\theta_{\text{cell}} - \frac{0.0591}{n} \log Q_c$$

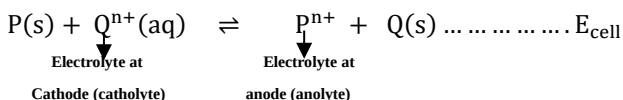
$$\text{Substituting } 0.9 = 0.8 - \frac{0.0591}{2} \log [H^+]^2; 0.1 = -0.0591 \log [H^+]$$

$$-\log [H^+] = \frac{0.1}{0.0591} = 1.69; \text{ but } -\log [H^+] = \text{pH}$$

Hence pH of the solution is 1.69

Equilibrium constant of a cell

An electrochemical (voltaic) cell generates electricity only when the cell potential is positive. The use of the electrochemical cell increases the concentration of the electrolyte in the anodic compartment and decreases the concentration of the electrolyte in the cathodic compartment as the following general cell reaction suggests:



From the above reversible cell reaction, it is clearly understood that: at the start of cell operation, forward reaction is highly favoured thus making the cell potential to be at maximum. As the cell operation proceeds, $[P^{n+}]$ increases and $[Q^{n+}]$ decreases and the backward reaction starts to take place.

What is the effect of this in the cell potential?

This results in a gradual decrease in the cell potential and ultimately an equilibrium reaches where the cell potential is zero and the cell stops producing electricity. When this happens, the cell reaction is said to be in equilibrium.

From the simplified Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log Q_c$

When the cell does not generate e.m.f, its cell potential is zero and the reaction quotient become equal to the equilibrium constant of the cell, K_c .

That is at equilibrium: $E_{\text{cell}} = 0$ and $Q_c = K_c$

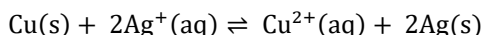
Then $0 = E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log K_c$

Hence $E_{\text{cell}}^{\theta} - \frac{0.0591}{n} \log K_c$

From the above equation, K_c can be easily understood that: If the K_c value of a cell is very large then the cell lasts long (continue operating for long time)

Example 19

Calculate the equilibrium constant for the reaction at 25°C ,



The standard cell potential for the reaction at 25°C is 0.46V

Solution

Anode reaction: $\text{Cu(s)} \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{e}$

Cathode reaction: $(\text{Ag}^+(\text{aq}) + \text{e} \rightleftharpoons \text{Ag(s)}) \times 2$

Cell reaction: $\text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)}$

Thus $n = 2$

Substituting $0.46 = \frac{0.0591}{2} \log K_c$; $\log K_c = 15.567$

$K_c = \log^{-1}(15.567) = 3.69 \times 10^{15}$

Hence the equilibrium constant for the cell is 3.69×10^{15}

(The very large value of K_c implies that the operating time of the cell is large .i.e. the cell lasts long as the cell reaction is far forward)

CONSTRUCTION OF ELECTROCHEMICAL SERIES

This is the another application of electrode potential.

What is the electrochemical series?

This is the arrangement of elements (metal and non – metal) in order of increasing reduction electrode potential.

Electrochemical series is useful determination of:

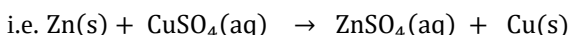
- Reactivity of metal
- Reactivity of non-metals
- Displacement of hydrogen from acids by metal
- Efficiency of zinc and tin as protective against rusting of iron

Reactivity of metals

Metals react by losing electrons. Thus metals are reducing agents and themselves are oxidised in the reaction by losing electrons. So reactivity of metals increases in the same order of their reducing strengths.

- Metals with more negative (or less positive) electrode potential are stronger reducing agents. Thus metals which are found at the top side electrochemical series are stronger reducing agents.
- Being stronger reducing agents, these metals are stronger electropositive and more reactive so that they displace weaker electropositive metals which are found below the electrochemical series from their salt solution.

For example zinc being above copper in the electrochemical series, it is stronger reducing agent and more reactive so that it displaces Cu^{2+} from salt of copper like CuSO_4 .

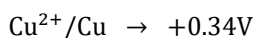
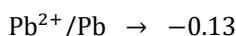
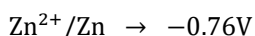
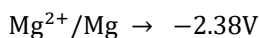


Or ionically $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$ and hence the **coating** of copper metal on the zinc metal is observed.

While $\text{Cu(s)} + \text{Zn}^{2+}(\text{aq}) \rightarrow \text{No reaction}$

Example 20

Below is the part of electrochemical series:



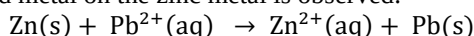
What happen when:

Zinc metal is dipped into Pb^{2+} ?

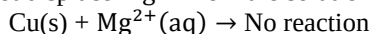
Copper metal is dipped into Mg^{2+} ?

Solution

Having more negative electrode potential, zinc metal displaces Pb^{2+} from the solution (reduces Pb^{2+} to Pb) and the coating of lead metal on the zinc metal is observed.



Nothing happen because copper has greater electrode potential than magnesium (Cu is below Mg electrochemical series) so it cannot displace Mg^{2+} from the solution.

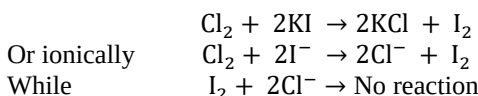


Reactivity of non – metal

In most cases, non-metal reacts by gaining electrons. Gaining of electrons is reduction. So in other words we can say that non - metal are oxidising agents and hence their reactivity increases in the same order to their oxidising strengths. Being oxidising agents, non-metals have positive electrode potential and are found at the bottom side of electrochemical series.

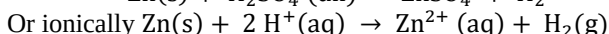
- Non – metals with more positive electrode potential are stronger oxidising agents. Thus non – metals which are found in more bottom side of electrochemical series are stronger oxidising agents.
- Being stronger oxidising agents, these non – metals are more reactive so that they displace weaker electronegative non – metals which are found above them in electrochemical series from their salt solution.

For example chlorine being below iodine in electrochemical series, it is stronger oxidising agent and more reactive so that it displaces I^- from salt of iodine like KI.

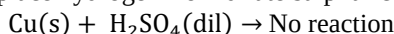


Displacement of hydrogen from acid by metals

Metals which are found above hydrogen in electrochemical series have negative electrode potential. So these metals are stronger reducing agents so that they can displace hydrogen from dilute acids by reducing H^+ of the acids to H_2 and themselves become oxidised. For example, zinc being above hydrogen in electrochemical series, has negative electrode potential and greater reducing strength so that it can displace hydrogen from dilute sulphuric according to the following equation:

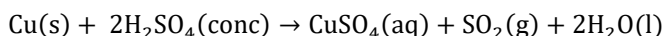


On another hand metals which are found below hydrogen in electrochemical series have positive electrode potential. So these metals are weaker reducing agent so that they cannot displace (reduce) hydrogen from dilute acids. For example, copper being below hydrogen in electro chemical series cannot displace hydrogen from dilute sulphuric acid.

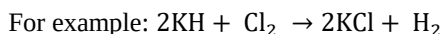


However:

- Concentrated sulphuric acid being good oxidising agent, can oxidize Cu to Cu^{2+} and itself become reduced to SO_2 thus reacting with copper according to the following equation:



- In ionic hydride (a compound which consist of strong electropositive metal and hydrogen only like KH), hydrogen acts as non – metal so that it can be displaced from the salt by any non – metal with positive electrode potential which are stronger oxidising agent than hydrogen.



Efficiency of zinc and tin as protective against rusting of iron

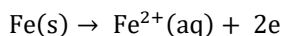
Before comparing the efficiency of zinc and tin in preventing iron rusting, it is important to answer the following two questions firstly:

- What is rusting of iron?
- How rusting process occurs?

Rust is the hydrated iron (III) oxide, $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$. Thus rusting of iron is the formation of hydrated iron (III) oxide, $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ by iron.

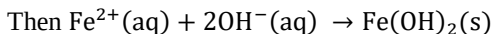
Rusting of iron occurs in the following procedures:

Step 1: Oxidation of Fe into Fe^{2+}

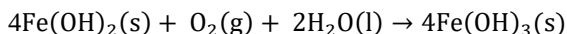


Step 2: Formation of $\text{Fe(OH)}_2(\text{s})$

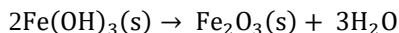
$\text{Fe}^{2+}(\text{aq})$ combines with OH^- from water (H_2O) i.e. $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$



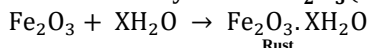
Step 3: Formation of $\text{Fe(OH)}_3(\text{s})$



Step 4: Decomposition of $\text{Fe(OH)}_3(\text{s})$



Step 5: Formation of hydrated $\text{Fe}_2\text{O}_3(\text{s})$ (rust)



Rust is easily recognised by its reddish brown colouration

Comparison:

Electrode potentials for Fe, Sn and Zn are given below:

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\ominus} = -0.76\text{V}$$

$$E_{\text{Fe}^{2+}/\text{Fe}}^{\ominus} = -0.44\text{V}$$

$$E_{\text{Sn}^{2+}/\text{Sn}}^{\ominus} = -0.14\text{V}$$

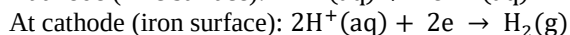
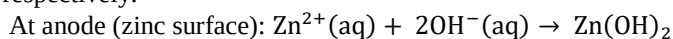
First case: If zinc is used as a protective

Zinc having more negative electrode (reduction) potential, it undergoes oxidation more readily than iron.

- Thus the reaction $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}$ occurs in preference to $\text{Fe(s)} \rightarrow \text{Fe}^{2+} + 2\text{e}$.

This makes electrons to move from zinc surface to iron surface and eventually the zinc surface become the anode and the iron surface become the cathode.

In presence of water (H_2O); OH^- and H^+ from self ionisation of water migrate towards anode and cathode respectively.



Hence zinc is a good protective. Any scratch which exposes the iron surface to the atmosphere does not result into oxidation of the iron.

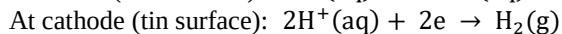
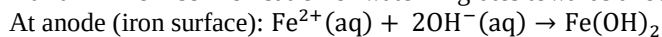
Second case: If tin is used as a protective

Iron having more negative electrode potential, it undergoes oxidation more readily than tin.

- Thus the reaction $\text{Fe(s)} \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}$ occurs in the preference to $\text{Sn(s)} \rightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{e}$.

This makes electron to move from iron surface to tin surface and eventually the iron surface become the anode and the tin surface become the cathode.

Thus OH^- and H^+ from self ionisation of water migrates towards anode and cathode respectively.



Formation of Fe(OH)_2 (**step 2** of the rusting process) at anodic area allows the rusting to continue. So any scratch which expose iron surface to the atmosphere, results into rusting of iron and hence tin is not good protective.

DIGGING DEEPER EXERCISE 21

EXERCISE 21A: BINDER QUESTIONS

Question 1

A cell is formed by dipping Zn rod in 0.01 M Zn^{2+} solution and Ni rod in 0.5M Ni^{2+} solution. The standard electrode potential of Zn and Ni are -0.76 V and -0.25 V respectively.

- Write the cell representation
- Write cell reaction
- Calculate the e.m.f of the cell.

Question 2

- Use the data below to explain why copper(I) ions disproportionate in aqueous solution, but silver(I) ions do not.

	E^θ/V
$\text{Ag}^{2+}(\text{aq}) + \text{e} \rightarrow \text{Ag}^+(\text{aq})$	+1.98
$\text{Ag}^+(\text{aq}) + \text{e} \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Cu}^{2+}(\text{aq}) + \text{e} \rightarrow \text{Cu}^+(\text{aq})$	+0.34
$\text{Cu}^+(\text{aq}) + \text{e} \rightarrow \text{Cu}(\text{s})$	+0.52

- In the light of the information in (a), suggest what you might observe when copper (I) oxide is added to excess dilute sulphuric acid. Write an equation for the reaction.

Question 3

The standard reduction potential of Cu^{2+}/Cu and Ag^+/Ag electrodes are 0.337V and 0.799V respectively. Construct a galvanic cell using these electrodes so that its E_{cell}^θ is positive. For what $[\text{Ag}^+]$ will the e.m.f of cell be zero if $[\text{Cu}^{2+}]$ is 0.01M?

Question 4

Calculate e.m.f of the following cell: $\text{Zn}(\text{s}) \mid \text{Zn}^{2+}(0.1\text{M}) \parallel \text{Sn}^{2+}(0.001\text{M}) \mid \text{Sn}(\text{s})$

Given that: $E_{(\text{Zn}^{2+}/\text{Zn})}^\theta = -0.76\text{V}$; $E_{(\text{Sn}^{2+}/\text{Sn})}^\theta = -0.14\text{V}$

Question 5

Calculate the e.m.f of the cell: $\text{Zn}(\text{s}) \mid \text{Zn}^{2+}(0.024\text{ M}) \parallel \text{Zn}^{2+}(2.4\text{ M}) \mid \text{Zn}(\text{s})$

EXERCISE 21B: REAL QUESTIONS**Question 6**

Predictions from E^θ values concerning the feasibility of a reaction are not always realised in real life. Suggest reasons for this.

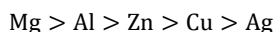
Question 7

Use the data below to explain concisely why zinc is used in preference to tin for coating steel which is used to manufacture cars.

	E^θ / V
$\text{Sn}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Fe}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Zn}^{2+}(\text{s}) + 2\text{e} \rightarrow \text{Zn}(\text{s})$	-0.76

Question 8

The position of some metals in the electrochemical series in the decreasing order of electropositive characters is given:



Can copper spoon be used to stir a solution of aluminium? Explain.

Question 9

Study the following electrode potentials then answer question which follows:

$$E_{\text{Cu}^{2+}/\text{Cu}}^\theta = +0.34\text{V}$$

$$E_{\text{Ni}^{2+}/\text{Ni}}^\theta = -0.25\text{V}$$

$$E_{\text{Fe}^{2+}/\text{Fe}}^\theta = -0.44\text{V}$$

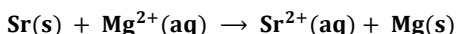
- What would happen if a nickel spatula were used to stir a solution of copper (II) sulphate?
- Can 1M ferrous sulphate solution be stored in a nickel container? Explain your answer.

Question 10

Kipute read the following statement in the chemistry textbook; “A salt bridge is inverted U – tube containing an inert paste of potassium chloride and agar – gel.” Unfortunately, she was unable to understand the use of potassium chloride and agar-gel. If **Kipute** came to you and asked for your help, what would be your explanation?

EXERCISE 21C: HOT QUESTIONS

Question 11



Consider the reaction represented above that occurs at 25°C. All reactants and products are in their standard states. The value of the equilibrium constant, K_c , for the reaction is 4.2×10^{17} at 25°C.

- Predict the sign of the standard cell potential, E^θ , for a cell based on the reaction. Explain your prediction.
- Identify the oxidising agent for the spontaneous reaction.
- If the reaction were carried out at 60°C instead of 25°C, how would the cell potential change? Justify your answer.
- How would the cell potential change if the reaction were carried out at 25°C with a 1.0 M solution of $\text{Mg}(\text{NO}_3)_2$ and a 0.10 M solution of $\text{Sr}(\text{NO}_3)_2$? Explain.
- When the cell reaction in part (d) reaches equilibrium, what is the cell potential?

Question 12

Consider the electrochemical cell below:

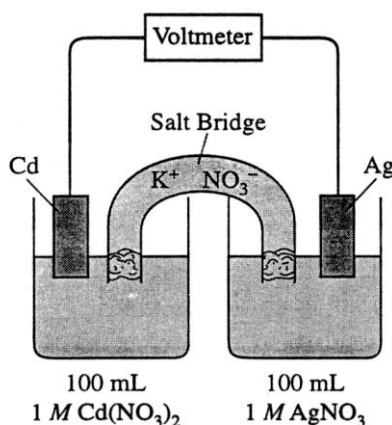
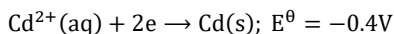


Figure 21.5 Electrochemical cell for question 8

- Write the balanced net-ionic equation for the spontaneous reaction that occurs as the cell operates, and determine the cell voltage.
- In which direction do anions flow in the salt bridge as the cell operates? Justify your answer.
- If 10.0 mL of 3.0-molar AgNO_3 solution is added to the half-cell on the right, what will happen to the cell voltage? Explain.
- If 1.0 grams of solid NaCl is added to each half-cell, what will happen to the cell voltage? Explain.
- If 20.0 mL of distilled water is added to both half-cells, the cell voltage decreases. Explain.

Given that:



Question 13

Calculate the equilibrium constant for the Daniel cell at 25°C, if standard oxidation potential for Zn electrode is +0.765V and for copper electrode is -0.337 V.

Question 14

Calculate equilibrium constant for the reaction of the following cell at 25°C



Given that standard e.m.f of the cell is 1.71V

Question 15

The standard cell potential, E^θ , for the reaction: $\text{Zn}^{2+} + \text{Fe} \rightleftharpoons \text{Zn} + \text{Fe}^{2+}$ is -0.353V . If a piece of iron is placed in a 1M Zn^{2+} solution, what is the equilibrium concentration of Fe^{2+} ?

Question 16

The standard reduction potentials, E^θ , for some electrodes are listed below. This data should be used, where appropriate, to help answer the questions that follow.

	E^θ/V
$\text{Mg}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Mg}(\text{s})$	-2.38
$\text{Fe}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{I}_2(\text{aq}) + 2\text{e} \rightarrow 2\text{I}^-(\text{aq})$	$+0.54$
$\text{Fe}^{3+}(\text{aq}) + \text{e} \rightarrow \text{Fe}^{2+}(\text{aq})$	$+0.77$
$\text{Br}_2(\text{l}) + 2\text{e} \rightarrow 2\text{Br}^-(\text{aq})$	$+1.07$
$\text{Cl}_2(\text{g}) + 2\text{e} \rightarrow 2\text{Cl}^-(\text{aq})$	$+1.36$

- (a) Give the formula of the species given in the data which, under standard conditions, is:
- The most powerful reducing agent;
 - The most powerful oxidising agent.
- (b) Which of the halogens listed would oxidise $\text{Fe}^{2+}(\text{aq})$ to $\text{Fe}^{3+}(\text{aq})$ under standard conditions?
- (c)
- Write an equation to show the reaction that occurs when chlorine is bubbled into a solution containing bromide ions. Give a reason why you would expect the reaction you suggest.
 - Give an industrial application of this reaction.

Chapter 22

ELECTROLYSIS AND ELECTROLYTIC CONDUCTION**ELECTROLYSIS**

The term **electrolysis** comes from two words: **electro** from **electricity** and **lysis** which means dissociation. Electrolysis involves dissociation by using electric current. In this process, electromotive force is used to carry out a non – spontaneous redox chemical reaction. The setup used to serve this purpose is known as **electrolytic cell**.

Electrolytic cell uses electromotive force to produce non – spontaneous redox reaction in contrast to electrochemical cell which use spontaneous redox reaction to produce electromotive force.

By definition; **electrolysis** is the decomposition of an electrolyte or formation of free elements from the electrolytic solution by passage of an electric current through it (the electrolyte).

- Electrolysis takes place inside a device which is known as **electrolytic cell** or **voltameter**.

Definition of electrolytic cell

This is a device (vessel) in which electric current is used to produce chemical reaction.

What electrolytic cells consist of?

An electrolytic cell is a container made of glass, a metal or any other material and contains a substance (compound) called electrolyte either is solution or molten state. Two metallic plates called electrodes (carbon rods can also be used) are dipped in the liquid (solution or molten). One electrode is connected to the positive terminal and the other to the negative terminal of a battery by metallic wire.

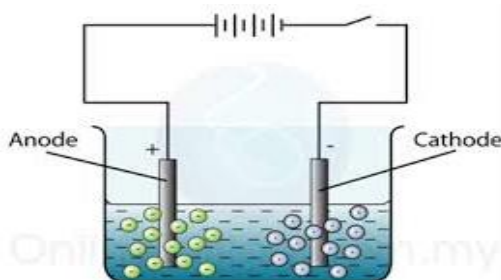


Figure 22.1 Electrolytic cell

Table 22.1 Differences between electrolytic and electrochemical cells

ELECTROCHEMICAL CELL		ELECTROLYTIC CELL	
	Definition		Definition
	Uses chemical reactions to produce electric current.		Uses electric current to produce chemical reactions.
	Anode is negative electrode while cathode is positive electrode.		Anode is positive electrode while cathode is negative electrode.
	Electrons flow from the negative terminal to the positive terminal.		Electrons flow from the negative battery terminal to the negative cathode.
	Chemical reaction is spontaneous.		Chemical reaction is forced by applying a voltage - it is not spontaneous.

Faraday's laws of electrolysis

Faraday's first law of electrolysis

It states that: *The mass of substance liberated by electrolysis is directly proportional to the quantity of electricity which is passed.*

The quantity of electricity, Q , is measured in coulombs (C) such that: $Q = It$

Where: I is current in amperes (A), t is time in seconds (s)

Thus from the law: $m \propto Q$ or $m \propto It$

Introducing the constant for proportionality, the equation become: $m = ZIt$ or $m = ZQ$

Where Z , is the proportionality constant which is known as **electrochemical equivalent of an element (E.C.E)** whose value depends on the nature of a substance

Definition of electrochemical equivalent of an element

This is the mass of the element liberated by the passage of one coulomb of electricity i.e. one ampere for one second.

Thus $Z = \frac{m}{Q}$ or $Z = \frac{m}{It}$

Faraday's second law of electrolysis

It states that: *When the same quantity of electricity is passed through different electrolytes, the masses of the different substances liberated are directly proportional to their equivalent weights.*

Where equivalent weight is given by the following formula:

$$\text{Equivalent weight, } E = \frac{\text{Atomic mass}}{\text{Magnitude of ionic charge}}$$

Warning! The above formula does not give general definition of equivalent weight. Refer to the **chapter 5** of this book to get the general definition.

Relationship between equivalent weight (E) and electrochemical equivalent of an element

Assuming the same amount of electricity Q is passed through two different electrolytes such that:

m_1 is the mass of substance liberated in the first electrolytic cell,

m_2 is the mass of substance liberated in the second electrolytic cell.

Then **from the Faraday's first law of electrolysis:** $m \propto Q$ or $m = ZQ$

Then $m_1 = Z_1Q$ and $m_2 = Z_2Q$

$$\text{Then } \frac{m_1}{m_2} = \frac{Z_1}{Z_2}$$

(Is the form of the Faraday's first law if there is passage of the same quantity of electricity in the two electrolytes).

But **from the Faraday's second law of electrolysis:**

$m \propto E$ or $m = kE$ where k is the proportionality constant

Then $m_1 = kE_1$ and $m_2 = kE_2$

It follows that: $\frac{m_1}{m_2} = \frac{E_1}{E_2}$ (Is another form of the Faraday's second law)

Combining Faraday's first and second law by substituting;

$$\frac{E_1}{E_2} \text{ for } \frac{m_1}{m_2} \text{ in } \frac{m_1}{m_2} = \frac{Z_1}{Z_2} \text{ gives } \frac{E_1}{E_2} = \frac{Z_1}{Z_2}$$

Alternatively the above relationship can be re-written as; $\frac{E_1}{Z_1} = \frac{E_2}{Z_2} = \text{constant}$

That is $\frac{E}{Z}$ is constant and the constant is known as **Faraday's constant, F**

$$\text{Hence } F = \frac{E}{Z}$$

$$\text{But } Z = \frac{m}{Q}$$

$$\text{Then substituting } \frac{m}{Q} \text{ for } Z \text{ in } F = \frac{E}{Z} \text{ gives } F = \frac{EQ}{m}$$

The last equation is the summation of Faraday's first law and Faraday's second law of electrolysis.

Definition of Faradays constant

Faraday constant is the quantity of electricity that passes when one mole of univalent element (or half a mole of a divalent element, etc.) is discharged or dissolved in electrolysis. Its value is 96500C i.e. **1F = 96500C**.

Calculations involving Faraday's laws of electrolysis

Example 1

The electrochemical equivalent of silver is 0.00112gC^{-1} . What mass of silver is deposited by the passage of a steady current of 0.5ampere for 1hour in a silver plating bath.

Solution

$$\text{Using } m = ZIt = 0.00112 \times 0.5 \times 60 \times 60\text{g} = 2.016\text{g}$$

Hence mass of silver deposited is 2.016g

Example 2

0.198g of copper is deposited on a cathode in 40 minutes by passing a steady current of 0.25ampere through copper (II) sulphate solution. Calculate the electrochemical equivalent of copper.

Solution

$$\text{Using } Z = \frac{m}{Q} = \frac{m}{It}$$

$$\text{Where } m = 0.198\text{g}, I = 0.25\text{A and } t = 40\text{min} = 40 \times 60\text{s}$$

$$\text{Substituting } Z = \frac{0.198}{0.25 \times 40 \times 60} \text{gC}^{-1} = 3.3 \times 10^{-4} \text{gC}^{-1}$$

$$\text{Hence the electrochemical equivalent of copper is } 3.3 \times 10^{-4} \text{gC}^{-1}$$

Example 3

A steady current of 0.27A passed for half an hour in a water voltameter liberated 56cm^3 of hydrogen at s.t.p.

- (a) Calculate the electrochemical equivalent of hydrogen
- (b) What are the electrochemical equivalents of:
 - (i) Oxygen
 - (ii) Aluminium

Solution

(a) **At s.t.p:**

Mass of hydrogen gas in 22400cm^3 (22.4dm^3) is 2g

$$\text{Thus mass of hydrogen gas in } 56\text{cm}^3 = \frac{56}{22400} \times 2\text{g} = 5 \times 10^{-3}\text{g}$$

Whence mass of hydrogen liberated in electrolysis is $5 \times 10^{-3} \text{g}$

$$\text{Using } Z = \frac{m}{Q} = \frac{m}{It} = \frac{5 \times 10^{-3}}{0.27 \times 0.5 \times 3600} \text{gC}^{-1} = 1.0288 \times 10^{-5} \text{gC}^{-1}$$

Hence electrochemical equivalent of hydrogen is $1.0288 \times 10^{-5} \text{gC}^{-1}$.

(a) Atomic mass of hydrogen = 1

Magnitude of charge of $\text{H}^+ = 1$

Then equivalent weight of hydrogen, $E_1 = \frac{1}{1} = 1$

Atomic mass of oxygen = 16

Magnitude of charge of $\text{O}^{2-} = 2$

Then equivalent weight of oxygen, $E_2 = \frac{16}{2} = 8$

Atomic mass of aluminium = 27

Magnitude of charge of $\text{Al}^{3+} = 3$

Then equivalent weight of aluminium $E_3 = \frac{27}{3} = 9$

But electrochemical equivalent of hydrogen, $Z_1 = 1.0288 \times 10^{-5} \text{gC}^{-1}$

And $\frac{E}{Z} = \text{constant}$

Then: (i) $\frac{E_1}{Z_1} = \frac{E_2}{Z_2}$; $\frac{1}{1.0288 \times 10^{-5}} = \frac{8}{Z_2}$; $Z_2 = 8.2304 \times 10^{-5} \text{gC}^{-1}$

Hence electrochemical equivalent of oxygen is $8.2304 \times 10^{-5} \text{gC}^{-1}$

(ii) $\frac{E_1}{Z_1} = \frac{E_3}{Z_3}$; $\frac{1}{1.0288 \times 10^{-5}} = \frac{9}{Z_3}$; $Z_3 = 9.2592 \times 10^{-5} \text{gC}^{-1}$

Hence electrochemical equivalent of aluminium is $9.2592 \times 10^{-5} \text{gC}^{-1}$

Example 4

What volume of hydrogen at 15°C and 100700Nm^{-2} (755mmHg) would be liberated in a water voltameter by the passing one ampere for 30minutes?

Solution

Hydrogen is liberated at cathode according to the following equation: $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

From which $2F = 2 \times 96500\text{C}$ or 193000C liberates 2g of H_2

Then $1 \times 30 \times 60\text{C}$ or 1800C liberates $\frac{1800}{193000} \times 2\text{g} = 0.01865\text{g}$ of H_2

From ideal gas equation; $PV = \frac{m}{M_r} RT$

$$\text{Or } V = \frac{mRT}{PM_r} = \frac{0.01865 \times 0.082 \times 288 \times 760}{755 \times 2} \text{dm}^3 = 0.22168 \text{dm}^3 \text{ or } 221.68 \text{cm}^3$$

Hence volume of hydrogen gas liberated is 221.68cm^3

Applications of electrolysis

Electrolysis has various applications including:

- Electroplating of metals
- Electro – refining metals
- Extraction of metals
- Production of some non-metal elements and compounds

Electroplating of metals

Electroplating is a process whereby a thin coating of desired material is applied on a required material. This is mostly done on stainless steel to prevent rusting, or on some decorative items, so that they look attractive. On stainless steel, generally nickel-chromium plating is done. On decorative items, such as spoons, plates, jewellery items, silver, gold or other plating is done. Electroplating is cheap and cost effective. It enhances the life of the object and makes it look better in appearance.

The following method is adapted:

- First the item to be electroplated is smoothened and cleaned thoroughly. It should not have any oily or dirt marks on it.
- An electrolyte is selected whose ions are required to be deposited on the item.
- Direct current is preferred to alternating current, as alternating current may result in non-smooth deposit.
- The item to be electroplated forms the anode or cathode of the electrolytic cell. **This is the drawback of the electroplating process. The item has to be electrically conducting, or has to be made electrically conducting.**
- For a smooth coating, the electrolytic process has to be optimized for time, temperature and current in the cell.

Electro-refining of metals

Similar to the process of electro-deposition, electrolysis can be used to **purifying metals** that are obtained from the ores. The process is known as electro-refining of metals. The metals that are generally refined by this process are Zn, Ag, Ni, Cu, Pb, Al, etc.

Extraction of metals

Extraction of metals by the process of electrolysis is known as **electro-metallurgy**. This process is used in case highly reactive metals such as sodium. An ore containing sodium is used in a molten form. This forms the electrolyte. Anode and cathodes are generally carbon rods or steel. The Na atoms get attracted to the cathode of the cell and then the entire cathode with its coating is stored for further use.

Production of some non-metals and compounds

- Non-metals like hydrogen, fluorine and chlorine are produced by electrolysis.
- Compounds like NaOH, KOH, Na_2CO_3 , KClO_3 and D_2O (heavy water) are produced by electrolysis (**electro-synthesis method**).

ELECTRLYTIC CONDUCTION

Substances may be identified as strong, weak, or non-electrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with electrolytic conductivity increasing as ion concentration increases. So there are two conditions which are necessary to electrolytic conduction to take place which are:

- Presence of enough concentration of ions.
- The ions must be free to move.

Substances which satisfy the two conditions either in molten state or in aqueous solution are said to have high ability of doing electrolytic conduction and vice-versa.

Important definitions and concepts

Conductance, G

This is the reciprocal of resistance.

That is $G = \frac{1}{R}$ where R is the resistance.

Its unit is $\Omega^{-1}(\text{ohm}^{-1})$ or Siemen (S)

Also from $R = \frac{\rho l}{A}$

Where: ρ (pronounced rho) is the resistivity of the electrolyte

l is the distance between the two electrodes in half cells (electrolytes)

A is the cross section area of the electrodes.

But for the given cell, l and A are constant and hence $\frac{1}{A}$ is known as **cell constant**.

That is $\frac{1}{A} = \text{cell constant}$ and $R = \rho \times \text{cell constant}$

Whence **Conductance, G** $= \frac{1}{R} = \frac{1}{\rho \times \text{cell constant}}$

Conductivity, κ

This is the conductance of an electrolyte placed between electrodes 1metre (1m) apart and having a cross - sectional area of 1m^2

- It is denoted by Greek letter 'kappa', κ and its unit is $\Omega^{-1}\text{m}^{-1}$ or Sm^{-1}
- It is reciprocal of the resistivity. It is also known as **electrolytic conductivity, normal conductivity, or specific conductance**.

From $R = \frac{\rho l}{A}$; $\rho = \frac{AR}{l}$; From which $\kappa = \frac{1}{\rho} = \frac{1}{RA}$

But $\frac{1}{A} = \text{cell constant}$ and $\frac{1}{R} = \text{conductance}$

Hence **conductivity = conductance $\times$ cell constant**

Molar conductivity, Λ or Λ_m

Electrolytic conductivity is found to increase with dilution of electrolytic solution i.e. it increases as the concentration of the electrolyte decreases. So the electrolytic conductivity is concentration dependent. **Why electrolytic conductivity increases as the concentration of the electrolyte decreases?**

According to Ostwald dilution law of weak electrolyte; degree of dissociation of the electrolyte increases as the concentration of the electrolyte decreases (or as the dilution of the electrolyte

increases). **Increasing degree of dissociation of the electrolyte results to an increase of concentration of free ions in the solution and hence the electrolytic conductivity is found to increase.** If the electrolyte is diluted to infinity where its concentration is very close to zero, its ionisation is complete and therefore its degree of dissociation become maximum (100%) and hence the electrolytic conductivity becomes maximum too at infinite dilution.

Thus if: Λ_m (Λ is Greek capital letter 'lambda') is the electrolytic conductivity of the electrolyte at certain concentration where its degree of dissociation is α

And Λ_∞ is the electrolytic conductivity of the electrolyte at infinite dilution where its degree of dissociation is 1 (or 100%)

And as the electrolytic conductivity at certain concentration of the electrolyte varies direct proportional to the degree of dissociation of the electrolyte at that concentration,

It follows that: $\Lambda_m = k\alpha$

And $\Lambda_\infty = k \times 1$ where k is the constant for proportionality

Then $\frac{\Lambda_m}{\Lambda_\infty} = \frac{k\alpha}{k} = \alpha$

Hence $\frac{\Lambda_m}{\Lambda_\infty} = \alpha$

The conductivity at infinity dilution is known as **limiting conductivity**.

And, $\frac{\Lambda_m}{\Lambda_\infty}$ is also known as **conductance ratio**.

Definition of conductance ratio:

Is the ratio of conductivity (molar conductivity or equivalent conductivity) at given concentration to that at infinite dilution.

The formula which consider the effect of concentration in the electrolytic conductivity is **molar conductivity** (usually is denoted as Λ or Λ_m)

That is molar conductivity, $\Lambda_m = \frac{\text{Conductivity}}{\text{Molar concentration}} = \frac{\kappa}{[\]}$

But $\frac{1}{[\]} = \text{Volume of solution containing 1mole of the electrolyte, } V$

Hence $\Lambda_m = \kappa V$

Thus the **molar conductivity** can be defined as; *the conductance of that volume of solution containing one mole of an electrolyte.*

The unit of V in the formula $\Lambda_m = \kappa V$ may be m^3/mol or cm^3/mol depending on unit of conductivity, κ ;

- If the unit of κ is $\Omega^{-1}\text{m}^{-1}$ (or Sm^{-1}), then the unit V must be $\text{m}^3\text{mol}^{-1}$ and hence the unit of Λ_m will be $\Omega^{-1}\text{m}^2\text{mol}^{-1}$ (or $\text{Sm}^2\text{mol}^{-1}$)
- If the unit of κ is $\Omega^{-1}\text{cm}^{-1}$ (or Scm^{-1}), then the unit of V must be $\text{cm}^3\text{mol}^{-1}$ and hence the unit of Λ_m will be $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ (or $\text{Scm}^2\text{mol}^{-1}$)

When the solution is diluted to infinite, the molar conductivity becomes maximum. *The molar conductivity at infinity dilution* is known as **limiting molar conductivity**.

Equivalent conductivity, Λ_e or Λ_{eq}

If the conductance is divided by normality instead of concentration (molar concentration), the result is known as equivalent conductivity (Λ_{eq}).

That is; **equivalent conductivity** ($\Lambda_{eq} = \frac{\text{conductivity}}{\text{normality}}$)

But from normality = $\frac{\text{number of equivalents}}{\text{volume of solution}}$

$$\frac{1}{\text{normality}} = \frac{\text{volume of solution}}{\text{number of equivalent}} = \text{volume of solution containing one equivalent of the electrolyte.}$$

So substituting volume of solution containing one equivalent of the electrolyte to $\frac{1}{\text{normality}}$ in the formula, equivalent conductivity = $\frac{\text{conductivity}}{\text{normality}}$ gives;

$$\Lambda_{\text{eq}} = \kappa V$$

Where Λ_{eq} represents equivalent conductivity

κ represents conductivity of the solution

V represents volume of the solution containing 1 equivalent of the electrolyte.

Hence equivalent conductivity can be defined as *the conductance of that volume of solution containing one equivalent of an electrolyte*. Its unit is $\Omega^{-1}\text{m}^2\text{eq}^{-1}$ (or $\text{Sm}^2\text{eq}^{-1}$) or $\Omega^{-1}\text{cm}^2\text{eq}^{-1}$ (or $\text{Scm}^2\text{eq}^{-1}$) depending on the unit of κ .

Like in molar conductivity, when the solution is diluted to infinite, the equivalent conductivity becomes maximum. *The equivalent conductivity at infinity dilution* is known as **limiting equivalent conductivity**.

Relation between molar conductivity and equivalent conductivity

From equivalent conductivity = $\frac{\text{conductivity}}{\text{normality}}$

Normality = molar concentration $\times$ equivalent factor

Then it becomes:

$$\text{Equivalent conductivity} = \frac{\text{conductivity}}{\text{molar concentration} \times \text{equivalent factor}}$$

But $\frac{\text{conductivity}}{\text{molar concentration}} = \text{molar conductivity}$

It follows that:

$$\text{Equivalent conductivity} = \frac{\text{molar conductivity}}{\text{equivalent factor}}$$

Or Molar conductivity = Equivalent conductivity $\times$ equivalent factor of the electrolyte

Hence:

$$\Lambda_{\text{m}} = \Lambda_{\text{eq}} \times \text{equivalent factor of the electrolyte}$$

Factors affecting the conductivity of electrolyte solution

Important factors to consider here are:

- Temperature
- Nature of electrolyte
- Mobility
- Nature of solvent and its viscosity
- Concentration

Temperature

The conductance of an electrolyte solution increases with increase in temperature due to increase in the extent of ionisation.

Nature of electrolyte

The strong electrolyte undergoes complete ionisation and hence show higher conductivities since they give more number of ions whereas weak electrolyte undergoes partial ionisation and hence show comparatively low conductivities in their solution.

Mobility

The electrolyte with ions of greater mobility has higher conductance. The mobility of ions depends on whether electrolyte is in the molten state or aqueous solution.

- In the molten state, ionic mobility **decreases** with **increase** in its size and hence conductivity also decreases.
- In aqueous solution, ionic mobility **decreases** with **decrease** in its size (smaller ions are more hydrated in the solution and whence they become heavier) and hence conductivity also decreases.

As an example, in molten state, the conductivities of lithium salts are greater than those of potassium salts since the size of Li^+ ion is smaller than that of K^+ ion. However in aqueous solution, lithium salts show lower conductivities compared to those of potassium salts because Li^+ ion being smaller in size is more hydrated than K^+ ion.

Nature of solvent and its viscosity

The ionic mobility is reduced in more viscous solvent and hence conductivity decreases.

Concentration

The specific conductance increases with increase in concentration solution as the number of ions per unit volume increases whereas, both the equivalent conductivity and molar conductivity increase with decrease in concentration (i.e. upon dilution) since the extent of ionisation increases.

Kohlrausch's law

Kohlrausch's law of independent migration of ions is used to determine molar conductivity at infinite dilution for the weak electrolytes. It states that:

"The molar conductivity of an electrolyte at infinite dilution is the sum of molar conductivities of individual constituent ions present in the solution".

That is $\Lambda_{\infty}(\text{compound}) = x\Lambda_{\infty}(\text{cation}) + y\Lambda_{\infty}(\text{anion})$; where x and y are stoichiometric number of cations and anions in the chemical equation showing ionisation of the salt.

E.g. Λ_{∞} of $\text{NaCl} = \Lambda_{\infty}$ of $\text{Na}^+ + \Lambda_{\infty}$ of Cl^-

It should be noted that:

Molar conductivities of two different solutions at infinite dilution are always different although both solutions ionise by 100% at the infinite dilution, why?

This is simply because transport numbers of different ions in solution are also different. **What is transport number?**

Transport number is the fraction of the total current carried by ions.

Calculations involving electrolytic conduction

Example 5

The resistivity of 0.02M KCl solution is $361\Omega\text{cm}$ and a conductivity of a cell containing such a solution had a resistance of 550Ω .

- What is the cell constant?
- The same cell filled with 0.1M ZnSO_4 solution had a resistance of 72Ω . What is the conductivity of 0.1M ZnSO_4 solution?

Solution

- Using $R = \rho \times \text{cell constant}$

From which cell constant $= \frac{R}{\rho} = \frac{550\Omega}{361\Omega\text{cm}} = 1.5235\text{cm}^{-1}$

Hence the cell constant is 1.5235cm^{-1}

(b) Using cell constant $= \frac{R}{\rho}$; But $\frac{1}{\rho} = \text{conductivity}, \kappa$

Thus cell constant $= R \times \text{conductivity}$

$$\text{Or conductivity} = \frac{\text{cell constant}}{R} = \frac{1.5235\Omega^{-1}\text{cm}^{-1}}{72} = 0.02116\Omega^{-1}\text{cm}^{-1}$$

Hence the conductivity of 0.1MZnSO_4 is $0.02116\Omega^{-1}\text{cm}^{-1}$

Example 6

In a particular cell, 0.01M solution of KCl gave a resistance of 15Ω while 0.01M solution of HCl gave a resistance of 51.4Ω at the same temperature. If the specific conductance of 0.01MKCl is 0.1409Sm^{-1} , calculate:

- Cell constant.
- Specific conductance of HCl solution.
- Equivalent conductivity of HCl solution.

Solution

(i) Conductivity (specific conductance) $= \text{conductance} \times \text{cell constant}$

$$\text{But, conductance} = \frac{1}{\text{resistance}}.$$

$$\text{Thus specific conductance} = \frac{\text{cell constant}}{\text{resistance}}$$

Or cell constant $= \text{specific conductance} \times \text{resistance}$

Substituting given data for KCl ;

$$\text{Cell constant} = 0.14009\Omega^{-1}\text{m}^{-1} \times 15\Omega = 2.1135\text{m}^{-1}$$

Hence cell constant is 2.1135m^{-1}

(ii) Substituting given data for HCl ;

$$\text{Specific conductance} = \frac{2.1135\text{m}^{-1}}{51.4\Omega} = 0.04112\Omega^{-1}\text{m}^{-1}$$

Hence specific conductance of HCl solution is 0.04112Sm^{-1}

$$\text{(iii) Equivalent conductivity} = \frac{\text{specific conductance}}{\text{normality}}$$

Since HCl is monobasic (has basicity of 1);

$$\text{Normality of HCl} = \text{Molarity of HCl} = 0.01\text{N} = 0.01\text{eq/dm}^3 = 10\text{eq/m}^3$$

$$\text{Thus equivalent conductivity} = \frac{0.04112\text{Sm}^{-1}}{10\text{eqm}^{-3}} = 0.004112\text{Sm}^2\text{eq}^{-1}$$

Hence the equivalent conductivity for HCl is $0.004112\text{Sm}^2\text{eq}^{-1}$ or $41.12\text{Scm}^2\text{eq}^{-1}$

Example 7

A solution of 0.1MHCOOH has conductivity of $0.166\Omega^{-1}\text{m}^{-1}$ at 25°C . The molar conductivity at infinite dilution is $4.04 \times 10^{-2}\Omega^{-1}\text{m}^2\text{mol}^{-1}$, calculate:

- The degree of dissociation
- The dissociation constant of HCOOH

Solution

(i) Using $\alpha = \frac{\Lambda_m}{\Lambda_\infty}$ where $\Lambda_m = \kappa V$

$$\text{Then } \alpha = \frac{\kappa V}{\Lambda_\infty}; \text{ Where } \kappa = 0.166\Omega^{-1}\text{m}^{-1}, \Lambda_\infty = 4.04 \times 10^{-2}\Omega^{-1}\text{m}^2\text{mol}^{-1}$$

$$\text{And } V = \frac{1}{0.1\text{mol dm}^{-3}} = 10\text{dm}^3\text{mol}^{-1} = 10 \times 10^{-3}\text{m}^3\text{mol}^{-1} = 10^{-2}\text{m}^3\text{mol}^{-1}$$

$$\text{Substituting } \alpha = \frac{0.166 \times 10^{-2}}{4.04 \times 10^{-2}} = 0.041 \text{ or } 4.1\%$$

Hence degree of dissociation of 0.1M HCOOH is 0.041 or 4.1%

- (ii) Since degree of dissociation of the acid (HCOOH) is very small, Ostwald dilution law is applicable (Ostwald's dilution law cannot be applied when $\alpha > 0.1$. For Ostwald's dilution law to be applied the degree of dissociation must be negligible compared to 1)

$$\text{From Ostwald dilution law, } \alpha = \sqrt{\frac{K_a}{C}}$$

$$\text{From which } K_a = \alpha^2 C = (0.041)^2 \times 0.1 \text{ mol dm}^{-3} = 1.681 \times 10^{-4} \text{ M}$$

Hence the dissociation constant of HCOOH is $1.681 \times 10^{-4} \text{ M}$

Example 8

A solution of dichloroethanoic acid of concentration $1.25 \times 10^{-4} \text{ M}$ has conductivity at infinite dilution of $3.85 \times 10^{-2} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$. Given the conductivity of dichloroethanoic acid is $2.5 \times 10^{-3} \Omega^{-1} \text{ m}^{-1}$. Calculate the degree of dissociation and hence dissociation constant.

Solution

$$V = \frac{1}{\text{concentration}} = \frac{1}{1.25 \times 10^{-4} \text{ mol dm}^{-3}} = 8000 \text{ dm}^3 \text{ mol}^{-1} = 8 \text{ m}^3 \text{ mol}^{-1}$$

$$\text{Using: } \alpha = \frac{\Lambda_m}{\Lambda_\infty} = \frac{\kappa V}{\Lambda_\infty} = \frac{2.5 \times 10^{-3} \times 8}{3.85 \times 10^{-2}} = 0.5195 \text{ or } 51.95\%$$

Hence the degree of dissociation of the acid is 0.5195 or 51.95%

Here the degree of dissociation is large whose amount cannot be neglected compared to 1 and hence Ostwald dilution law cannot be applied i.e. the equation $\alpha = \sqrt{\frac{K_a}{C}}$ does not hold.

Dichloroethanoic acid (CHCl_2COOH) ionises according to the following equation:



At equilibrium $(1 - \alpha)C$ αC αC

$$K_a = \frac{[\text{CHCl}_2\text{COO}^-][\text{H}^+]}{[\text{CHCl}_2\text{COOH}]} = \frac{\alpha C \times \alpha C}{(1 - \alpha)C} = \frac{\alpha^2 C}{(1 - \alpha)}$$

$$\text{Substituting } K_a = \frac{(0.5195)^2 \times 1.25 \times 10^{-4}}{(1 - 0.5195)} = 7.02 \times 10^{-5} \text{ M}$$

Hence the dissociation constant for the acid is $7.02 \times 10^{-5} \text{ M}$

Example 9

The following and Λ_∞ values at 25°C in $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$;

Electrolytes	Λ_∞
CH_3COONa	91
HNO_3	421
NaNO_3	122
KNO_3	145

Calculate:

- (a) Λ_{∞} of CH_3COOK
 (b) Λ_{∞} of CH_3COOH
 (c) If the value of Λ for 0.016M CH_3COOH is $13\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at 25°C . What is the K_a value and pH of CH_3COOH ?

Solution

Given that:

$$\Lambda_1 = \Lambda_{\infty}(\text{CH}_3\text{COONa}) = \Lambda_{\infty}(\text{CH}_3\text{COO}^-) + \Lambda_{\infty}(\text{Na}^+) = 91$$

$$\Lambda_2 = \Lambda_{\infty}(\text{HNO}_3) = \Lambda_{\infty}(\text{NO}_3^-) + \Lambda_{\infty}(\text{H}^+) = 421$$

$$\Lambda_3 = \Lambda_{\infty}(\text{NaNO}_3) = \Lambda_{\infty}(\text{NO}_3^-) + \Lambda_{\infty}(\text{Na}^+) = 122$$

$$\Lambda_4 = \Lambda_{\infty}(\text{KNO}_3) = \Lambda_{\infty}(\text{NO}_3^-) + \Lambda_{\infty}(\text{K}^+) = 145$$

$$\begin{aligned} \text{(a) } \Lambda_{\infty}(\text{CH}_3\text{COOK}) &= \Lambda_{\infty}(\text{CH}_3\text{COO}^-) + \Lambda_{\infty}(\text{K}^+) \\ &= \Lambda_1 + \Lambda_4 - \Lambda_3 = 91 + 145 - 122 = 114\Omega^{-1}\text{cm}^2\text{mol}^{-1} \end{aligned}$$

Thus Λ_{∞} of CH_3COOK is $114\Omega^{-1}\text{cm}^2\text{mol}^{-1}$

$$\begin{aligned} \text{(b) } \Lambda_{\infty}(\text{CH}_3\text{COOH}) &= \Lambda_{\infty}(\text{CH}_3\text{COO}^-) + \Lambda_{\infty}(\text{H}^+) \\ &= \Lambda_1 + \Lambda_2 - \Lambda_3 = 91 + 421 - 122 = 390\Omega^{-1}\text{cm}^2\text{mol}^{-1} \end{aligned}$$

Thus Λ_{∞} of CH_3COOH is $390\Omega^{-1}\text{cm}^2\text{mol}^{-1}$

$$\text{(c) Using } \alpha = \frac{\Lambda_m}{\Lambda_{\infty}};$$

Where $\Lambda_m = 31\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ and $\Lambda_{\infty} = 390\Omega^{-1}\text{cm}^2\text{mol}^{-1}$

$$\text{Substituting } \alpha = \frac{13}{390} = \frac{1}{30}$$

Since α is small, Ostwald's dilution law is applicable

$$\text{From Ostwald dilution law } \alpha = \sqrt{\frac{K_a}{c}}$$

$$\text{It follows that, } K_a = \alpha^2 C = \left(\frac{1}{30}\right)^2 \times 0.016\text{mol dm}^{-3} = 1.78 \times 10^{-5}\text{M}$$

$$\text{Using } [\text{H}^+] = \alpha C$$

$$\text{Then pH} = -\log[\text{H}^+] = -\log\alpha C = -\log\left(\frac{1}{30} \times 0.016\right) = 3.273$$

Hence the pH of 0.016M CH_3COOH is 3.273

Example 10

At 13°C , the specific conductivity of a saturated solution of AgCl in water was $2.4 \times 10^{-6}\Omega^{-1}\text{cm}^{-1}$ and that of water was $1.16 \times 10^{-6}\Omega^{-1}\text{cm}^{-1}$

Given that:

$$\Lambda_{\infty}(\text{NaCl}) = 110.3\Omega^{-1}\text{cm}^2\text{mol}^{-1}, \Lambda_{\infty}(\text{AgNO}_3) = 116.5\Omega^{-1}\text{cm}^2\text{mol}^{-1},$$

$$\Lambda_{\infty}(\text{NaNO}_3) = 105.2\Omega^{-1}\text{cm}^2\text{mol}^{-1}.$$

Calculate the solubility, hence the solubility product of AgCl at this temperature.

Solution

From Kohlrausch's law; $\Lambda_{\infty}(\text{AgCl}) = \Lambda_{\infty}(\text{AgNO}_3) + \Lambda_{\infty}(\text{NaCl}) - \Lambda_{\infty}(\text{NaNO}_3)$

Substituting $\Lambda_{\infty}(\text{AgCl}) = 116.5 + 110.3 - 105.2 = 121.6 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$

Using $\kappa_{\text{solution}} = \kappa_{\text{AgCl}} + \kappa_{\text{H}_2\text{O}}$;

From which $\kappa_{\text{AgCl}} = \kappa_{\text{solution}} - \kappa_{\text{H}_2\text{O}}$

$$= 2.4 \times 10^{-6} \Omega^{-1} \text{cm}^{-1} - 1.16 \times 10^{-6} \Omega^{-1} \text{cm}^{-1} = 1.24 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$$

But for sparingly soluble substances like AgCl:

$$\begin{aligned} \text{Molar conductivity at infinite dilution} &= \text{Molar conductivity of saturated solution} \\ &= 121.6 \Omega^{-1} \text{cm}^2 \text{mol}^{-1} \end{aligned}$$

(This is because saturated solution of sparingly soluble substance is so dilute that it can be assumed to be the same as the solution at infinite dilution keeping in the mind that the solution contains very small amount of the solute).

Using $\Lambda_m = \kappa V$;

$$\text{Then } V = \frac{\Lambda_m}{\kappa} = \frac{121.6}{1.24 \times 10^{-6}} \text{ cm}^3 \text{mol}^{-1} = \frac{121.6}{1000 \times 1.24 \times 10^{-6}} \text{ dm}^3 \text{mol}^{-1} = 98064.516 \text{ dm}^3 \text{mol}^{-1}$$

Using $\left[\right] = \frac{1}{V}$; where V is dilution

$$\text{Then molar solubility of AgCl} = \frac{1}{98064.51} \text{ mol dm}^{-3} = 1.0197 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{And its solubility (mass solubility)} = 1.0197 \times 10^{-5} \times 143.5 \text{ g dm}^{-3} = 1.4633 \times 10^{-3} \text{ g dm}^{-3}$$

$$\begin{aligned} \text{And } K_{\text{sp}} [\text{Ag}^+][\text{Cl}^-] &= (1.0197 \times 10^{-5})^2 \text{ mol}^2 \text{dm}^{-6} \\ &= 1.0398 \times 10^{-10} \text{ mol}^2 \text{dm}^{-6} \end{aligned}$$

Be aware of this: Example 9 and 10 summarises **applications of Kohlrausch's law** which are:

- Determination of molar electrolytic conductivity of weak electrolytes at infinite dilution.
- Determination of degree of dissociation (ionisation) of weak electrolytes.
- Determination of dissociation (ionisation) constant of weak electrolytes.
- Determination of solubility and hence solubility product of sparingly soluble salts.

DIGGING DEEPER EXERCISE 22

Use $1F = 96485.309 \text{ C}$

EXERCISE 22A: BINDER QUESTIONS

Question 1

Calculate the quantity of electricity (Coulombs) necessary to deposit 100g of copper from a CuSO_4 solution.

Question 2

How many minutes will take to plate out 40.00 g of Ni from a solution of NiSO_4 using a current of 3.4500A?

Question 3

What is the equivalent weight of a metal if a current of 0.2500A causes 0.5240 g of metal to plate out a solution undergoing electrolysis in 1 hour?

Question 4

How many hours will it take to plate out copper in 200.0mL of a 0.15M Cu^{2+} solution using a current of 0.200A?

Question 5

A constant electric current deposits 0.3650 g of silver metal in 12960 seconds from a solution of silver nitrate. What is the current?

Question 6

The specific conductance of a 0.02M solution of KCl at 25°C is $0.002765\Omega^{-1}\text{cm}^{-1}$. If the resistance of cell containing this solution is 400Ω , what is the cell constant?

Question 7

The resistance of a 0.01M solution of an electrolyte is 210Ω at 25°C . Calculate the molar conductance of the solution at the same temperature. The cell constant is 0.88cm^{-1} .

Question 8

The resistance of 0.5M solution of an electrolyte in a cell was found to be 45Ω . Calculate the molar conductance of the solution if the electrodes of the cell are 2.2cm apart and have an area of 3.8cm^2 .

Question 9

0.5N solution of a salt placed between two platinum electrodes, 20cm apart and of area 4cm^2 has a resistance of 25Ω . Calculate equivalent conductance of the solution.

Question 10

The resistance of decinormal solution of a salt occupying a volume between two platinum electrodes 1.80cm apart and 5.4cm^2 in area was found to be 32Ω . Calculate equivalent conductance of the solution.

Question 11

The resistance of 0.1N solution is 2500Ω . Calculate equivalent conductance of the solution. Cell constant = 1.15cm^{-1} .

EXERCISE 22B: REAL QUESTIONS**Question 12**

Why solid table salt does not conduct electricity although it is known as strong electrolyte?

Question 13

Explain at least three challenges of applying Faraday's second law in real life.

Question 14

When two different solutions, one containing 0.1M CH_3COOH and another containing 0.1M HCl are diluted to 0.01M of each, the acetic acid solution shows greater increase in its molar conductivity than the hydrochloric acid. Explain.

Question 15

Your friend **Kipute** argued to you, *"I know you know that molar conductivity depends on the extent of ionisation. And I know you know that strong electrolytes ionises completely in the solution and for that reason, dilution does not affect their extent of ionisation."* She then concluded, *"Dilution does not affect molar conductivity of strong electrolytes."*

Do you agree to **Kipute's** conclusion? Explain.

Question 16

In a conductivity test, 5 different solutions were set up with light bulbs. The following observations were recorded:

Solution A glowed brightly.

Solution B glowed dimly.

Solution C glowed dimly.

Solution D did not glow.

Solution E glowed brightly.

- (a) Which solution(s) could contain strong bases?
- (b) Which solution(s) could contain weak acids?
- (c) Which solution(s) could contain ions?
- (d) Which solution(s) could contain pure water?
- (e) Based solely on these observations, would it be possible to distinguish between acidic and basic solutions? Explain.

EXERCISE 22C: HOT QUESTIONS**Question 17**

How many Faradays are required to oxidize the following?

- (a) One mole of sodium thiosulphate solution
- (b) Two moles of hydrogen peroxide solution
- (c) 500cm^3 of 1M oxalic acid

Question 18

In an electrolytic cell, Cu(s) is produced by the electrolysis of $\text{CuSO}_4(\text{aq})$. Calculate the maximum mass of Cu(s) that can be deposited by a direct current of 100amperes passed through 5.00L of 2.00M $\text{CuSO}_4(\text{aq})$ for a period of 1.00hour.

Question 19

In an electrolytic cell, a current of 0.250ampere is passed through a solution of a chloride of iron, producing Fe(s) and $\text{Cl}_2(\text{g})$.

- (a) Write the equation for the reaction that occurs at the anode.
- (b) When the cell operates for 2.00hours, 0.521gram of iron is deposited at one electrode. Determine the formula of the chloride of iron in the original solution.

- (c) Write the balanced equation for the overall reaction that occurs in the cell.
- (d) How many litres of $\text{Cl}_2(\text{g})$, measured at 25°C and 750mmHg , are produced when the cell operates as described in part (b)?
- (e) Calculate the current that would produce chlorine gas at a rate of 3.00 grams per hour.

Question 20

A conductivity cell is filled with 0.05M KCl . Its specific conductance and observed resistance is $0.00667\Omega^{-1}\text{cm}^{-1}$ and 243Ω , respectively. When the cell is filled with 0.01M NaOH , observed resistance is 681Ω . Calculate specific and molar conductance of 0.01M NaOH .

Question 21

The specific conductance of water is 0.076Sm^{-1} and the specific conductance of 0.1M aqueous solution of KCl is 1.1639Sm^{-1} . A cell has a resistance of 33.20Ω when filled with 0.1M KCl solution and 300Ω when filled with 0.1M CH_3COOH solution. Calculate the molar conductance of acetic acid.

Question 22

The conductivity of 0.001M CH_3COOH is $4.95 \times 10^{-5}\text{Scm}^{-1}$. Calculate its dissociation constant, given that $\Lambda_\infty(\text{CH}_3\text{COOH}) = 390.5\text{Scm}^2\text{mol}^{-1}$

Question 23

Molar conductivity at infinite dilution for NH_4Cl , NaOH and NaCl at 298K are respectively 129.8 , 218.4 and $108.9\text{Scm}^2\text{mol}^{-1}$ and molar conductivity of 0.01M NH_4OH is $9.33\text{Scm}^2\text{mol}^{-1}$. Calculate the degree of dissociation of NH_4OH at 298K .

EXAMINATION QUESTIONS FOR PART SIX

Question 1

- (a) Complete and balance the following redox reaction: $\text{MnO}_4^- + \text{H}_2\text{S} + \text{H}^+ \rightarrow$
- (b) A standardization of potassium manganate (VII) solution yielded the following data: 0.16g of the potassium salt, $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ needed 24.5cm^3 of the manganate (VII) solution. What is the molarity of the manganate (VII) solution?

Question 2

9.85g of pure ammonium iron (II) sulphate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) were made up to 250cm^3 of solution in cold, boiled – out, dilute sulphuric acid. 25cm^3 of the solution reacted completely with 24.75cm^3 of a potassium manganate (VII) solution.

Calculate:

- (a) The molarity of the manganate (VII) solution
- (b) The concentration of the manganate in gdm^{-3}
- (c) The dilution needed to convert the remaining 1800cm^3 of it (KMnO_4) to exactly 0.02M concentration
- (d) Why the simple iron (II) sulphate (FeSO_4) should not be used in this titration experiment?

Question 3

- (a) Explain how mobility of ions in the solution are affected by concentration of electrolyte?
- (b) Calculate the percentage by mass of iron (III) in a salt from the following data: 25g of the salt were dissolved in water and reduced to an iron (II) solution by zinc and dilute sulphuric acid. The mixture was filtered and the filtrate and washings made up to 1dm^3 . 20cm^3 of this solution required 20.7cm^3 of 0.01M KMnO_4 for oxidation.

Question 4

- (a) Although potassium dichromate (VI) is strongly coloured, it is not used as self-indicator in the redox titrations; why?
- (b) 1.5g of a mixture of anhydrous sodium ethanedioate and ethanedioic acid crystals was made up to 100cm^3 of aqueous solution. 20cm^3 of this solution required 19.8cm^3 of 0.1M NaOH for neutralisation, phenolphthalein as indicator. How many cm^3 of 0.01M KMnO_4 will be necessary to oxidize 25cm^3 of the original solution in the presence of excess dilute sulphuric acid?

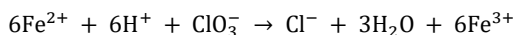
Question 5

100cm^3 of solution of hydrogen peroxide were diluted to 1dm^3 with water. 25cm^3 of this solution, when acidified with dilute sulphuric acid, reacted with 47.8cm^3 of 0.02M KMnO_4

- (a) What is the concentration of the original hydrogen peroxide solution in gdm^{-3} ?
- (b) What is the 'volume' rating of this solution (referred to s.t.p)?

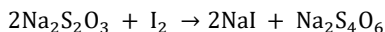
Question 6

- (a) Why an end point of redox titration involving potassium permanganate as self-indicator is pink in colour?
- (b) Calculate the concentration in gdm^{-3} of a solution of potassium chlorite (V) from the following data: 50cm^3 of a solution of ammonium iron (II) sulphate ($\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) (acidified) were boiled for ten minutes with 25cm^3 of potassium chlorate solution. After cooling the excess iron (II) salt was oxidised by 24.6cm^3 of 0.02M KMnO_4 solution. 25cm^3 of the same acidified ammonium iron (II) sulphate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) solution required 24.2cm^3 of 0.02M KMnO_4 .



Question 7

Sodium thiosulphate reacts with iodine according to the equation:



- Explain whether the iodine molecules are being oxidised or reduced.
- What is the mass of iodine would be required to react with 30cm^3 of 0.1M thiosulphate($\text{Na}_2\text{S}_2\text{O}_3$).
- Is the titration iodimetry or iodometry? Why?

Question 8

In a standardization of sodium thiosulphate solution, 25cm^3 of 0.0204M potassium manganate (VII) solution were added to excess of acidified potassium iodide solution. The iodine liberated required 24.4cm^3 of sodium thiosulphate solution for reduction.

- Write down the balanced ionic equation:
 - Taking place between potassium manganate (VII) and potassium iodide
 - Taking place between sodium thiosulphate and iodine
- What is the overall reaction equation for above experiment?
- Calculate the molarity of the sodium thiosulphate solution
- If 1750cm^3 of sodium thiosulphate remain, how may it made exactly decimolar?
- Is the titration iodo or iodimetry? Give a reason for your choice.

Question 9

- Which medium favours oxidation and which one favours reduction?
- 2.5g of a sample of bleaching powder were ground with successive amounts of water, transferred to a measuring flask and made up to 250cm^3 of mixture. 25cm^3 of it, added to excess of potassium iodide solution and acidified, liberated iodine requiring 24.2cm^3 of decimolar sodium thiosulphate solution. Calculate the percentage of available chlorine in the bleaching power.

Question 10

A weight 3.9g of an ore is composed of haematite and siderite. Haematite is Fe_2O_3 and siderite is FeCO_3 . The ore is dissolved in acid and titrated against 0.1M cerium sulphate. The volume of cerium (IV) sulphate used was 100cm^3 . The reduction of Ce^{4+} is given by the equation: $\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$

- Calculate the % of each compound in the ore.
- Suppose a similar weight of the ore is first reduced to +2 oxidation state by suitable reagents then titrated with 0.1M cerium (IV) sulphate solution. What volume of cerium (IV) sulphate would be required?
- If instead of using cerium (IV) sulphate, 0.05M KMnO_4 solution was used in (ii), what volume of KMnO_4 would be used?

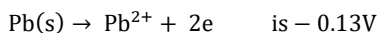
Question 11

- The e.m.f of a cell corresponding to the reaction:
 $\text{Zn(s)} + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(0.1\text{M}) + \text{H}_2(\text{g}, 1\text{ atm})$ is 0.58V , at 25°C . Calculate the pH of the solution at hydrogen electrode $E_{\text{Zn}^{2+}/\text{Zn}}^\theta = 0.76\text{V}$
- Calculate the equilibrium constant for the reaction: $\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$

$$\left(\text{Given: } E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\theta = +1.44, E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\theta = +0.68\text{V} \right)$$

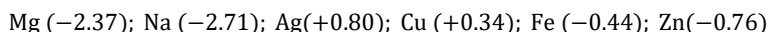
Question 12

- What does the positive value for E_{cell}^θ in case of galvanic cell like $\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}$ indicate?
- The standard electrode potential for the half reaction:



What is the standard electrode potential for the half reaction: $2\text{Pb(s)} \rightarrow 2\text{Pb}^{2+}(\text{aq}) + 4\text{e}^-$

- Arrange the following metals in the increasing order of the reactivity. The value in brackets are that of reduction electrode potentials



- (ii) Which one is the stronger reducing agent?
- (iii) Which one is the weakest reducing agent?
- (iv) Construct a cell with greatest e.m.f (write a cell diagram of the cell).

Question 13

- (a) What is meant by the following statements:
 - (i) "The reduction electrode potential of zinc is $-0.76V$ "
 - (ii) "The reduction electrode potential of copper is $+0.34V$ "
- (b) When does a cell formulation represent a non – spontaneous activity of galvanic cell?

Question 14

- (a) What are spontaneous reactions? Are spontaneous reactions exothermic or endothermic?
- (b) Calculate the electrode potential of the half-cell, $Fe^{3+}(aq)/Fe^{2+}(aq)$ when Fe^{3+} concentration is 1M and Fe^{2+} concentration is 0.6M (Given: $E_{Fe^{3+}/Fe^{2+}}^{\theta} = 0.771V$)

Question 15

- (a) What does each of the following terms represent?
 - (i) Standard electrode potential
 - (ii) Redox reaction
- (b) Calculate e.m.f of a Daniel cell at $35^{\circ}C$ using a 2.0M zinc sulphate solution and 0.5M copper (II) sulphate solution. Electrode reduction potentials are given as:

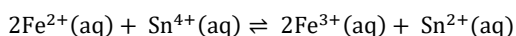
$Ag^{+}(aq)/Ag(s)$	$E^{\theta}/V = +0.8V$
$Cu^{2+}(aq)/Cu(s)$	$E^{\theta}/V = +0.34V$
$Mg^{2+}(aq)/Mg(s)$	$E^{\theta}/V = -2.37V$
$Zn^{2+}(aq)/Zn(s)$	$E^{\theta}/V = -0.76V$

Question 16

- (a) Explain the function of moisture in the rusting process.
- (b) Zinc rod is dipped in 0.1M $ZnSO_4$. The salt is 95% dissociated at this dilution at 298K. Calculate the electrode potential. Given that: $E_{Zn^{2+}/Zn}^{\theta} = -0.76V$.

Question 17

- (a) What is the meaning of each of the following terms?
 - (i) Corrosion
 - (ii) Disproportionation reaction
- (b) Calculate equilibrium constant of the following redox reaction



Given that:

$$E_{Fe^{3+}/Fe^{2+}}^{\theta} = 0.771V$$

$$E_{Sn^{4+}/Sn^{2+}} = 0.150V$$

Question 18

- (a) Why is it necessary to use a salt bridge in a galvanic cell?
- (b) Electrode potential value of the copper electrode, were determined by varying concentration of copper ions in solution at 298K. The following data were obtained:

Concentration of Cu^{2+} in $mol\,dm^{-3}$	0.1	0.2	0.3	0.4	0.5
Electrode potential in volts	0.310	0.320	0.324	0.328	0.331

Use these data to construct a graph which you will then use to determine the standard electrode potential of copper electrode

Question 19

- (a) A salt bridge is used to connect the two half-cells.
- State what chemical is contained in the salt bridge.
 - Give a possible reason why the salt bridge cannot be replaced by an unreactive metal wire.
- (b) If the cost of electricity to produce magnesium is xTsh per one kilogram of the metal, what is the cost of electricity for producing ykg of aluminium at the same rates?

Question 20

- (a) Briefly explain how voltaic cell differ from electrolytic cells.
- (b) A steady current of 0.65A is passed for 5.5hours through solutions of sulphuric acid and copper (II) sulphate in series at 13°C and 100000Nm⁻² (750mmHg) pressure. Calculate:
- The volume of hydrogen liberated from the acid.
 - The volume oxygen liberated from the acid.
 - The mass of copper precipitated.

Question 21

- (a) Briefly explain any two methods for rusting prevention.
- (b) After making allowance for conductivity of water, the conductivity of saturated solution of silver chloride at 25°C is $1.5 \times 10^{-4} \Omega^{-1}\text{m}^{-1}$. If molar conductivity at infinite dilution of Ag⁺ is $6.2 \times 10^{-3} \Omega^{-1}\text{m}^2\text{mol}^{-1}$. and that of Cl⁻ is $7.6 \times 10^{-3} \Omega^{-1}\text{m}^2\text{mol}^{-1}$. Calculate molar solubility of silver chloride.

Question 22

Given the following reduction potentials:

Half reaction	E ⁰ (V)
$\text{Cl}_2(\text{g}) + 2\text{e} \rightarrow 2\text{Cl}^-$	+1.36
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33
$\text{Cr}^{3+} + \text{e} \rightarrow \text{Cr}^{2+}$	-0.50
$\text{Cr}^{3+} + 3\text{e} \rightarrow \text{Cr}$	-0.73
$\text{S}_4\text{O}_6^{2-} + 2\text{e} \rightarrow 2\text{S}_2\text{O}_3^{2-}$	+0.17

- (i) Determine the standard e.m.f of the following cell with the following cell reaction:
 $\text{Cr}^{3+}(1\text{M}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(1\text{M}) + \text{Cl}^-(1\text{M})$
- (ii) Sketch the galvanic cell based on the reaction in (i) above and show the direction of the electron flow
- (iii) Calculate the equilibrium constant for the following reaction:
 $\text{S}_4\text{O}_6^{2-}(\text{aq}) + \text{Cr}^{2+}(\text{aq}) \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + \text{S}_2\text{O}_3^{2-}(\text{aq})$
- (iv) What conclusion can be made from the equilibrium constant obtained in (iii) above?

Question 23

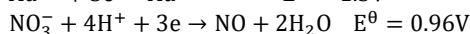
- (a) Differentiate between an electronic conductors and electrolytic conductors.
- (b) A conductivity cell with electrodes 2 cm³ in area and 1 cm apart has a resistance of 7.25Ω when filled with 5% potassium chloride solution;
- Calculate the cell constant.
 - Determine the conductivity of potassium chloride solution.
 - If the cell was filled with 0.02M KCl, with resistivity of 361Ωcm, what would the cell resistance be?

Question 24

- (a) What do the following mean?
- (i) Cathode
 - (ii) Anode
 - (iii) Standard electrode potential
 - (iv) Concentration cell
- (b) The standard electrode potential for Zn^{2+}/Zn is -0.76V and for Cu^{2+}/Cu is $+0.34\text{V}$
- (i) Draw a cell diagram of a cell that can be formed from Cu and Zn electrodes.
 - (ii) Write the cell reaction and calculate its e.m.f under standard conditions.
 - (iii) Calculate the equilibrium constant for the reaction.

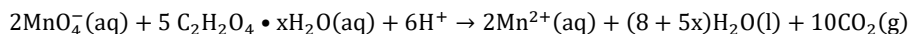
Question 25

- (a) Using the following half reactions:



Predict whether 1M HNO_3 will dissolve gold metal to form 1M Au^{3+} solution or not.

- (b) Isolation of an acid from aqueous solution gave crystals **C** of molecular formula $\text{C}_2\text{H}_2\text{O}_4 \cdot x\text{H}_2\text{O}$. The acid can be oxidised quantitatively to carbon dioxide and water by acidified aqueous manganate (VII) above 60°C . This reaction can be represented by the equation:



Given that 0.126g of **C** required 20.00 cm^3 of aqueous manganate (VII) of concentration 0.02M for complete reaction, calculate the value of x in $\text{C}_2\text{H}_2\text{O}_4 \cdot x\text{H}_2\text{O}$

PART SEVEN

THERMOCHEMISTRY

Chapter 24

INTRODUCTION TO THERMOCHEMISTRY

Thermochemistry is the branch of physical chemistry which deals with the study of measurement of heat change in various chemical reactions. In the chemical reactions heat may be either evolved to the surroundings or absorbed from the surroundings. When heat is evolved to the surroundings the chemical reaction is said to be **exothermic** and when heat is absorbed from the surrounding the reaction is said to be **endothermic**.

IMPORTANT CONCEPTS AND DEFINITIONS

Before defining various terms concerning to thermochemistry, the reader should note the following points which are important for ensuring proper understanding of definitions:

- The terms relating to thermochemistry may **start with** the word 'standard' or **without** the word 'standard' e.g. '**standard** heat of reaction' or just, 'heat of reaction'
- **With** the word standard, the definition must end with '*under standard conditions (25°C and 1atm).*'
- **Without** the word standard, the definition must end with '*under given conditions of temperature and pressure.*'
- The '*standard conditions of temperature and pressure*' is different to '*standard temperature and pressure*' which is normally abbreviated as **STP**.
- Standard conditions are temperature of 25°C (room temperature) and pressure of 1 atmosphere (760 mmHg) which are useful in measurement of standard values of heat changes of various chemical reactions.
- Standard temperature and pressure (STP) is temperature of 0°C (273K) and pressure of 1 atmosphere (760 mmHg) which are useful in measurement of standard volume and pressure of gases.
- **Heat change, heat absorbed and heat evolved;** the three should be used at the beginning of various definitions with a little care as explained below:
 - **Heat change** is used for reactions which may be either endothermic or exothermic under different circumstances e.g. any chemical reaction may be either exothermic or endothermic so in defining '*heat of the reaction*' the definition must start with; '*is the heat change*' as the change may be either positive (endothermic) or negative (exothermic).
 - **Heat absorbed (or required)** is used for the reaction which is always endothermic e.g. '*ionisation energy*' must start with; '*is the heat absorbed*' It is **wrong** to start with; '*is the heat change.....*' Because the word 'change' implies that the energy change may be either positive (heat absorbed) or negative (heat evolved) while the reality is that: energy change in the ionisation process **must** be positive.
 - **Heat evolved** is used for the reaction which is always exothermic e.g. in combustion, heat must be evolved to the surroundings as the process is exothermic. So in defining '*combustion energy*' the definition must start with '*is the heat evolved.....*'
 - Definitions which must start with; '*is the heat change.....*' Implying that their values may be either positive or negative include:
 - ✓ Heat (or enthalpy) of reaction
 - ✓ Heat (or enthalpy) of solution
 - ✓ Heat (or enthalpy) of dilution
 - ✓ Electron affinity
 - ✓ Heat (or enthalpy) of transition
 - ✓ Heat (or enthalpy) of formation

However, the reader should note that for stable compounds heat of formation is negative (heat is evolved). So as most of compounds which exist are stable, in most cases heat of formation is negative.

- Definitions which must start with; '*is the heat absorbed (or required)*' implying that their values are always positive include:
 - ✓ Heat (enthalpy) of atomisation or atomisation energy
 - ✓ Dissociation energy
 - ✓ Ionisation energy
 - ✓ Second electron affinity
- Definitions which must start with '*is the heat evolved (or liberated)*' implying that their values are always negative include:
 - ✓ Heat (enthalpy) of combustion
 - ✓ Heat (enthalpy) of neutralisation
 - ✓ Heat (enthalpy) of hydration
 - ✓ Lattice energy
 - ✓ Heat (or enthalpy) of hydrogenation
 - ✓ First electron affinity.
- Heat and enthalpy are commonly used interchangeably as the term '**enthalpy**' stand for *heat measured at given (constant) temperature and pressure*.
- If the given temperature and pressure are 25°C and 1atm respectively which are **standard conditions**, then the term *standard heat* or *standard enthalpy* are used.

Standard enthalpy of reaction

This is the heat change when the molar quantities, represented by the equation react under standard conditions (at temperature of 25°C and pressure of 760mmHg), the substance being in their normal physical state for these conditions.

Key words to remember are:

- ✓ Heat change.
- ✓ Molar quantities.
- ✓ Standard conditions (25°C and 1atm)
- ✓ Normal physical states.

Heat change for the reaction is denoted by ΔH and the standard heat change for the reaction is denoted as $\Delta H^\ominus$ whereby superscript ' $\ominus$ ' always stand for standard value.

Very important to understand that: Reactions with more negative heat of reactions (more exothermic chemical reactions) or with less positive heat of reactions (less endothermic reactions) are more thermally favoured and hence are more likely to occur. So heat of reaction is very important in determining the easiest for the reaction to occur.

- Also products of exothermic reactions are thermally more stable because have less energy than reactants.

Heat of reaction for reversible reactions

For reversible reaction it is possible to calculate heat of reaction from activation energy of forward and reverse (backward) reactions and it is given by the following equation:

$$\Delta H = E_{af} - E_{ab}$$

Where:

E_{af} represents activation energy of forward reaction,

E_{ab} represents activation energy of backward reaction and

ΔH represents heat of reaction for forward reaction.

Whereby heat of reaction for backward reaction is equal in magnitude but opposite in sign to that of forward reaction,

That is;

Heat of reaction for backward reaction = –Heat of reaction for forward reaction

The two relationships can be easily deduced from energy profile diagram as follows:

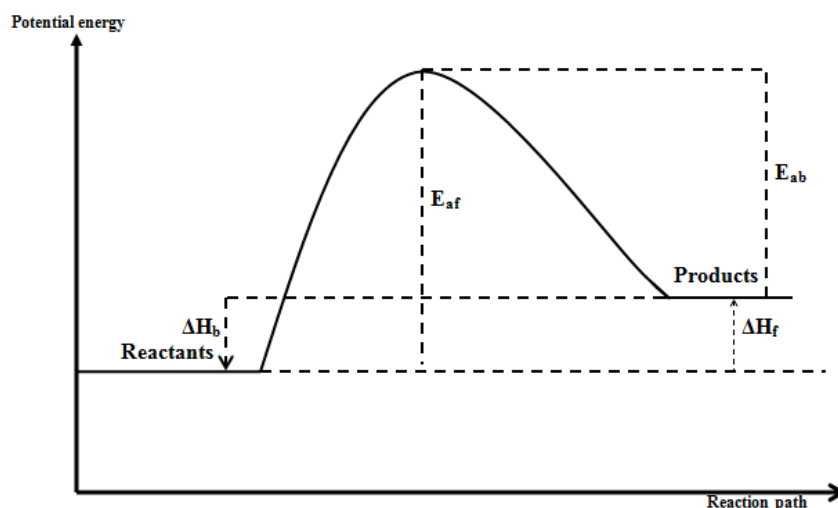


Figure 25.1 Energy profile diagram for reversible reaction

From the **figure 25.1**; it is clearly understood that:

$$\Delta H_f = E_{af} - E_{ab} \text{----- (i)}$$

$$\Delta H_b = E_{ab} - E_{af} \text{----- (i)}$$

$$\text{From which; } \Delta H_b = E_{ab} - E_{af} = -(E_{af} - E_{ab}) = -\Delta H_f$$

Where:

E_{af} and E_{ab} are activation energies for forward and backward reaction respectively

ΔH_f and ΔH_b are heat of reactions for forward and backward reactions respectively

Standard heat of formation (ΔH_f°)

This is the heat change which occurs when one mole of a compound is formed from its elements in their normal physical states under the standard conditions of temperature and pressure (25°C and 1atm).

Whereas the **heat of formation** is the heat change which occurs when one mole of a compound is formed from its elements in their normal physical states measured at given conditions of temperature and pressure.

Key words to remember are:

- ✓ Heat change
- ✓ One mole of a compound.
- ✓ Elements in their normal physical states,
- ✓ Standard conditions (for **standard** heat of formation)
- ✓ Given conditions of temperature and pressure (For heat of formation **without** the prefix 'standard')

The reader should understand that: normal physical states of elements are physical states of elements at standard conditions of temperature and pressure.

Heat of formation is important in determining stability of compounds. **Compounds with more negative heat of formation (highly exothermic compounds) are more stable**; while **compounds with large positive heat of formation (highly endothermic compounds) are unstable**.

Heat of formation is also important in determining heat of reactions. For a given heat chemical reactions, heat of reaction is given by the following equation:

$$\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

Where: ΔH_r is the heat of reaction,

ΔH_f is the heat of formation and

$\sum$ is the summation of

With given standard values, the equation becomes:

$$\Delta H_r^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

Where:

ΔH_r° is the standard heat of reaction.

ΔH_f° is the standard heat of formation.

It should be noted that: **the enthalpy of formation of an element in its natural state is zero**. For example; heat of formation of oxygen gas is zero or heat of formation solid aluminium is zero also etc.

Standard enthalpy of combustion (ΔH_c°)

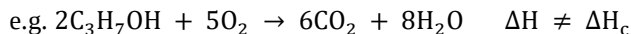
This is the heat evolved when one mole of an element or compound is completely burned in oxygen under standard conditions of temperature and pressure (25°C and 1atm).

Key words to remember are:

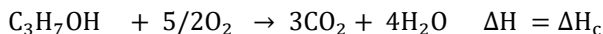
- ✓ Heat evolved
- ✓ One mole
- ✓ Completely burned in oxygen
- ✓ Standard conditions

The term 'molar enthalpy of combustion' is commonly used in place of 'enthalpy of combustion'.

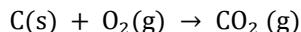
In writing a thermochemical equation to show heat of combustion, the stoichiometric coefficient of the substance (element or compound) which is burned must be one.



The above equation is well balanced and the reaction is combustion, but since there are 2 molecules of $\text{C}_3\text{H}_7\text{OH}$ in the equation, the heat change represented by the equation is twice the heat of combustion; i.e. $\Delta H = 2\Delta H_c$. The correct equation to show heat of combustion of $\text{C}_3\text{H}_7\text{OH}$ is found by dividing throughout the equation by 2 giving to the following equation:



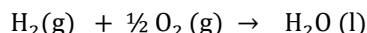
The thermo chemical equation to show heat of combustion of carbon is shown below;



Since in burning one mole of carbon, one of mole CO_2 (compound) is formed; therefore according to the definition of the heat of formation; **heat of combustion of carbon is equal to heat of formation of CO_2** .

$$\text{i.e. } \Delta H_f(\text{CO}_2) = \Delta H_c(\text{carbon})$$

The thermochemical equation to show heat of combustion of hydrogen is shown below;



By similar explanation to the case of combustion of carbon above;

$$\Delta H_f(\text{H}_2\text{O}) = \Delta H_c(\text{hydrogen gas})$$

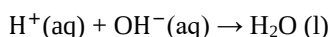
Enthalpy of neutralisation (ΔH_n)

This is the heat evolved when a dilute solution containing sufficient mass of acid to provide one mole of H^+ ions reacts with a dilute solution containing sufficient alkali to provide one mole of OH^- ions so as to give one mole of water, under given conditions of temperature and pressure.

Key words to remember are:

- ✓ Heat evolved
- ✓ Dilute solution
- ✓ One mole of H^+ and mole of OH^- (This automatically gives one mole water so it is not necessary to write one mole of water)
- ✓ Given conditions of temperature and pressure (if the given conditions are 25°C and 1 atm which are standard conditions then the enthalpy change become standard enthalpy of neutralisation)

In any neutralisation reaction the important and common change is:



So the heat of neutralisation reaction expresses the easiest of acid and base to react together so as to give water. If the heat of neutralisation is more negative, then the process of neutralisation in acid-base reaction is more thermally favoured (it is more likely to occur).

Among neutralisation reactions, the reaction between strong acids and strong bases have most negative heat of neutralisation because it is easiest for neutralisation to take place between strong solutions while reactions between weak acids and weak bases being relatively most difficult, have least negative heat of neutralisation.

Thus if:

(i) Strong + Strong base $\rightarrow$ salt + water	$\Delta H_n^\theta = -X_1 \text{ kJ/mol}$
(ii) Weak acid + strong base $\rightarrow$ salt + water	$\Delta H_n^\theta = -X_2 \text{ kJ/mol}$
(iii) Weak acid + weak base $\rightarrow$ salt + water	$\Delta H_n^\theta = -X_3 \text{ kJ/mol}$

Then $X_1 > X_2 > X_3$
 $\xrightarrow{\text{Decrease in heat of neutralisation}}$

Standard enthalpy of hydrogenation

This is the heat evolved when one mole of an unsaturated compound is converted to the corresponding saturated compounds by the reaction with hydrogen under standard conditions of temperature and pressure.

Key words to remember are:

- ✓ Heat evolved
- ✓ One mole of unsaturated compound
- ✓ Saturated compound
- ✓ Reaction with hydrogen
- ✓ Standard conditions

Standard enthalpy of atomisation (ΔH_a^θ)

This is the heat required to convert an element in its normal state into one mole of its corresponding gaseous atoms under standard conditions of temperature and pressure.

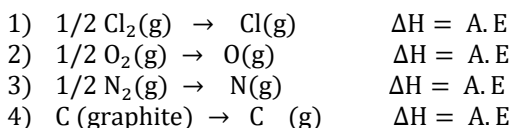
Here 'normal state' means the molecular state and physical state of the element at room temperature and pressure e.g. normal state of oxygen is *diatomic molecule (molecular state)* and *gas (physical state)*

Key words to remember are:

- ✓ Heat required (or absorbed)
- ✓ An element in its normal state
- ✓ One mole of gaseous atoms
- ✓ Standard conditions.

Enthalpy (heat) of atomisation is also known as **atomisation energy (A.E)**.

Examples of thermochemical equations representing atomisation energy are:



The reader should note that: In atomisation of the element which is in solid state, the element **sublimes** from the solid to gas phase and hence the term 'atomisation energy' can be replaced by the term: **sublimation energy**.

Thus: **Atomisation energy = Sublimation energy for solid elements**

Hence sublimation energy can be defined as follows:

Sublimation energy is the energy required to convert a solid element in its normal molecular state into one mole of its corresponding gaseous atoms at given conditions of temperature and pressure.

e.g. $\text{Al}(\text{s}) \rightarrow \text{Al}(\text{g}) \quad \Delta H = \text{Atomisation energy} = \text{Sublimation energy}$

The enthalpy of atomisation is also known as the **enthalpy of vapourisation** if it involves conversion of liquid element into corresponding gaseous atoms.

Thus enthalpy of vapourisation can be defined as follows:

Enthalpy of vapourisation is the heat required to convert a liquid element in its normal molecular state into one mole of its corresponding gaseous atoms at given conditions of temperature and pressure.

e.g. $\text{Br}_2(\text{l}) \rightarrow 2\text{Br}(\text{g}) \quad \Delta H = \text{Atomisation energy} = \text{Vapourisation energy}$

Dissociation energy (D.E)

This is the energy required to break one mole of molecules to their corresponding gaseous atoms under given conditions of temperature and pressure.

e.g. $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g}) \quad \Delta H = \text{D.E}$

Key words to remember are:

- ✓ Energy required
- ✓ One mole of diatomic molecule
- ✓ Gaseous atoms
- ✓ Given conditions of temperature and pressure

Since in the dissociation of one **diatomic molecule** two gaseous atoms are formed while in the atomisation one gaseous atom only is formed then for diatomic molecule:

$$\text{Dissociation energy (D.E)} = 2 \times \text{Atomisation energy (A.E)}$$

Heat (enthalpy) of solution (ΔH_{soln})

This is the heat change when one mole of a substance (solute) dissolves in a specified amount of solvent (water) to give a solution under given conditions of temperature and pressure.

- Usually the solvent used is water but others like alcohol or liquid ammonia may be used.

Key words to remember are:

- ✓ Heat change
- ✓ One mole of solute (substance)
- ✓ Specified amount of solvent
- ✓ Given conditions of temperature and pressure.

Heat of dilution

This is the heat change when one mole of substance is added to so much water that further addition of water produces no further heat change under given conditions of temperature and pressure.

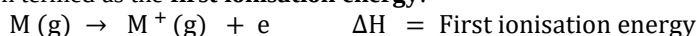
When addition of more water to the solution does not produce more change in energy the solution is said to be at **infinite dilution**.

Thus: **Heat of dilution = Heat of solution at infinite dilution.**

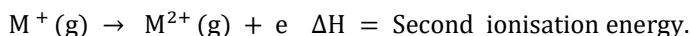
Ionisation energy (I.E)

This is the energy required to remove completely the most loosely bound electron each from one mole of gaseous atom or ion at given conditions of temperature and pressure.

If an electron is removed from a gaseous neutral atom to form monopositive charged ion, the energy is then termed as the **first ionisation energy**.



If an electron is removed from a monopositive gaseous ion to form dipositive charged ion, the energy is then termed as the **second ionisation energy**.



Electron affinity (E.A)

This is the energy change when electrons are added to one mole of gaseous atom or ion at given conditions of temperature pressure.

If electrons are added to neutral gaseous atom, the energy is then termed as the **first electron affinity** and the energy is always negative.

First electron affinity is the energy evolved when electrons are added to one mole of neutral gaseous atom to give mononegative anion at given conditions of temperature and pressure.



If electrons are added to one mole of mononegative charge ion, the energy is then termed as the **second electron affinity** which is always positive.

Second electron affinity is the energy absorbed when electrons are added to one mole of mononegative charged ion to give dinegative charged ions under given conditions of temperature and pressure, e.g. $O^-(g) + e \rightarrow O^{2-}(g) \quad \Delta H = \text{Second electron affinity}$

Second electron affinity is always positive (endothermic process) because extra energy is required to overcome repulsion of first added electron before adding the second electron.

Lattice energy (L.E)

Lattice energy is the energy evolved when one mole of the solid ionic crystal is formed from its corresponding gaseous ions under given conditions of temperature and pressure.



The same amount of energy evolved in forming ionic bonds of ionic crystal will be required to break the bonds.

i.e. **Lattice energy = Energy absorbed in breaking ionic bonds of solid ionic crystal**

So lattice energy is very important in determining stability of ionic compounds. Ionic compounds with more negative lattice energy have higher stability ionic and the bond between the ions (cation and anion) is stronger. Compounds with positive lattice energy are unstable and normally do not exist.

Hydration energy (H.E)

Generally, the hydration energy (or **enthalpy of hydration**) is the *heat evolved when **one mole of gaseous ions** is dissolved in water to give one mole of **aqueous ions** at given condition of temperature and pressure.*

In the case of hydration (crystallisation) of anhydrous salt, hydration energy may be defined as *the heat evolved when **one mole of anhydrous salt** reacts with a **fixed number of moles of water** to give a crystal lattice of hydrated salt under given conditions of temperature and pressure.*

Hydration energy is related to lattice energy by the following equation;

$H.E = \Delta H_{\text{soln}} - |L.E|$; where $|L.E|$ stands for positive L.E (magnitude of lattice energy).

The student should understand that:

The energy released (evolved) in forming crystal lattice by hydration is equal to the energy required to break the crystal lattice.

Hence **hydration energy is equal to the energy absorbed in breaking one mole of the crystal lattice of the hydrated salt.**

Heat of transition

This is the heat change when one mole of one allotropic form of an element changes to another at given conditions of temperature and pressure.

e.g. $S(\text{monoclinic}) \rightarrow S(\text{rhombic})$ $\Delta H = \text{Heat of transition}$

$C(\text{graphite}) \rightarrow C(\text{diamond})$ $\Delta H = \text{Heat of transition}$

CALORIMETRY

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as **calorimetry**. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object called calorimeter. The temperature change measured by the calorimeter is used to derive the amount of heat transferred by the process under study. The process under study involves substance or substances undergoing chemical or physical change. We can call this process a **system** and under this context, **surroundings** will represent all other matter, including components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system.

A **calorimeter** is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure 25.1). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

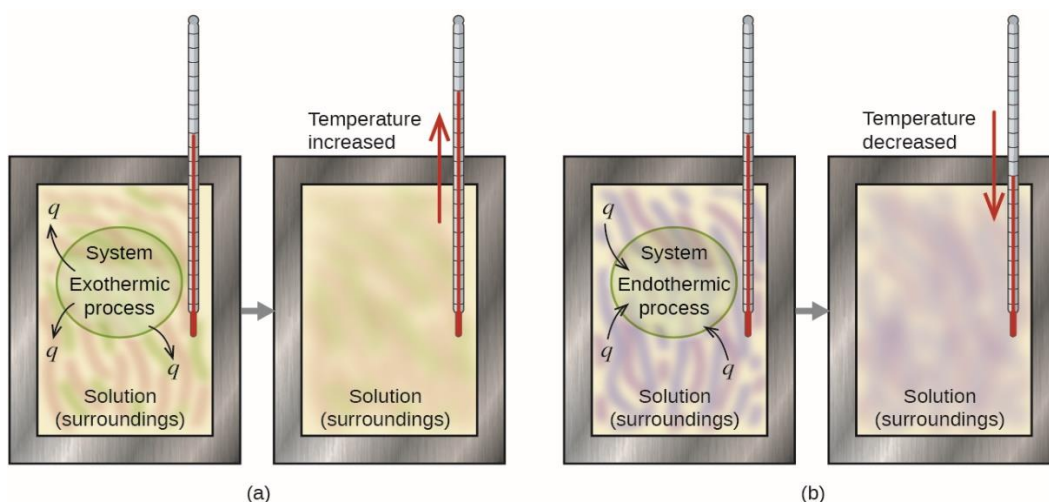


Figure 23.1 Calorimetry for exothermic and endothermic reactions.

With this calorimetric model, calorimeters should be well-insulated so that they prevent heat exchange (in most cases, heat loss) to non-system components including the calorimeter itself. This enables the accurate determination of the heat involved in chemical processes.

In normal laboratories, we often use simple calorimetric model constructed from polystyrene cups (Figure 24.2). These ‘coffee cup’ calorimeters are easy to use but they allow more heat exchange with the outside environment, and therefore produce less accurate energy values.

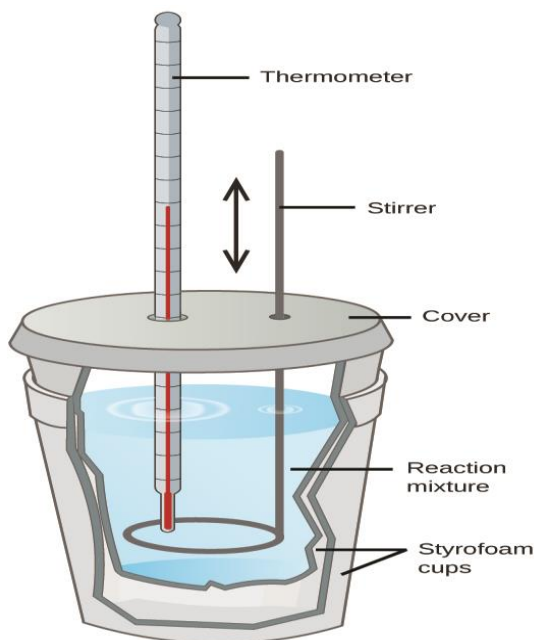


Figure 23.2 A simple calorimeter.

To have better understanding of calorimetry, we are going to use calorimetric determination of enthalpy of neutralisation as an example.

Determination of enthalpy of neutralisation

Neutralisation reactions are exothermic. So when acid and base are mixed in the calorimeter (Figure 24.2) the temperature of the vessel and its contents increases.

Then:

$$\text{Heat rise in the vessel } (\Delta H \text{ or } q) = m_v C_v \Delta T$$

Where: m_v is the mass of the vessel,

C_v is the specific heat capacity of the vessel and

ΔT is the rise in temperature.

$$\text{Heat rise in the contents} = m_c C_c \Delta T$$

Where: m_c is the mass of contents,

C_c is the specific heat capacity of contents and

ΔT is the rise in temperature.

$$\text{Total heat released} = m_v C_v \Delta T + m_c C_c \Delta T = \Delta T (m_v C_v + m_c C_c)$$

But from the definition; **heat of neutralisation**

= Total heat released when one mole of water is formed from acid- base reaction

$$\text{Hence Heat of neutralisation} = \frac{\text{Total heat evolved}}{\text{Number of moles of water}} = \frac{\Delta T (m_v C_v + m_c C_c)}{n_{H_2O}}$$

You may include negative sign in the formula before $\Delta T (m_v C_v + m_c C_c)$ to insist that the reaction is exothermic and the formula for calculating the heat of neutralisation become:

$$\text{Heat of neutralisation} = \frac{-\Delta T (m_v C_v + m_c C_c)}{n_{H_2O}}$$

However, in actual sense, the negative sign has already contained by the word 'evolved' of the 'heat evolved' from the definition of the heat of neutralisation.

It is better to understand that: when heat capacity is given instead of specific heat capacity;

Heat rise in the contents (or vessel) = Heat capacity $\times$ temperature rise

Example 1

125 cm³ of 0.5M potassium hydroxide were mixed in a suitable lagged calorimeter of mass 53.5g with 125 cm³ of 0.5M hydrochloric acid, both being at 14°C. The temperature (after suitable correction) reached a maximum of 17.3°C. Assuming the dilute solutions to have the same specific heat capacity as water (4.18 Jg⁻¹°C⁻¹) and the calorimeter to have specific heat capacity of 0.390 Jg⁻¹°C⁻¹. Calculate the enthalpy of neutralisation.

Solution

$$\text{Total enthalpy change} = \Delta T (m_v C_v + m_c C_c)$$

Where:

$$\Delta T \text{ is the temperature change} = (17.3 - 14)^\circ\text{C} = 3.3^\circ\text{C}$$

$$m_v \text{ is the mass of the vessel (calorimeter)} = 53.5\text{g}$$

$$C_c \text{ is the specific heat capacity of contents (solution)} = 4.18\text{Jg}^{-1}\text{°C}^{-1}$$

$$C_v \text{ is the specific heat capacity of the calorimeter} = 0.390\text{Jg}^{-1}\text{°C}^{-1}$$

$$m_c \text{ is the mass contents (solution) = Density of solution } \times \text{ volume}$$

$$= 1 \text{ g/cm}^3 \times (125 + 125) \text{ cm}^3 = 250 \text{ g}$$

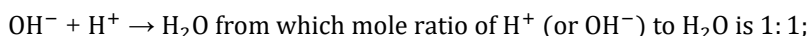
(If density of solution is not given, it is recommended to assume that the density of dilute solution is equal to that of water which is 1 g/cm^3)

$$\text{Total enthalpy change} = -(53.5 \times 0.39 + 250 \times 4.18) \times 3.3 \text{ J} = -3518 \text{ J}$$

$$125 \text{ cm}^3 \text{ of } 0.5 \text{ M KOH contains } \frac{125}{1000} \times 0.5 \text{ mol of OH}^- = 6.25 \times 10^{-2} \text{ mol}$$

$$125 \text{ cm}^3 \text{ of } 0.5 \text{ M HCl contains } \frac{125}{1000} \times 0.5 \text{ mol of H}^+ = 6.25 \times 10^{-2} \text{ mol}$$

Because: OH^- and H^+ combine to give water according to the following equation:



Then number of moles of water formed is also $6.25 \times 10^{-2} \text{ mol}$

$$\text{Using; enthalpy of neutralisation} = \frac{\text{Total enthalpy rise in neutralisation}}{\text{Number of moles of water formed}}$$

$$= \frac{-3518 \text{ J}}{6.25 \times 10^{-2} \text{ moles}} = -56288 \text{ J/mol or } -56.288 \text{ kJ/mol}$$

(The negative sign indicate that heat energy is released to the surroundings as the reaction is exothermic)

Hence enthalpy of neutralisation is -56.288 kJ/mol

Example 2

500 cm^3 of 0.1 M sodium hydroxide solution at 15.5°C was quickly added to 500 cm^3 of 0.1 M nitric acid in a calorimeter which was also at a temperature of 15.5°C . The calorimeter had a mass of 540 g and a specific heat capacity of $0.39 \text{ Jg}^{-1}\text{C}^{-1}$. If the maximum temperature recorded was 16.15°C , calculate the enthalpy of neutralisation. Assume the specific heat capacity of the solution to be the same as that of water i.e. $4.2 \text{ Jg}^{-1}\text{C}^{-1}$.

Solution

$$\text{Total enthalpy change} = \Delta T(m_v C_v + m_c C_c)$$

Where: $\Delta T = (16.15 - 15.5)^\circ\text{C} = 0.65^\circ\text{C}$, $m_v = 540 \text{ g}$,

$$C_v = 0.39 \text{ Jg}^{-1}\text{C}^{-1}, C_c = 4.2 \text{ Jg}^{-1}\text{C}^{-1} \text{ and } m_c = \rho_c V_c$$

$$\text{But } \rho_c = 1 \text{ g/cm}^3 \text{ and } V_c = (500 + 500) \text{ cm}^3 = 1000 \text{ cm}^3$$

$$\text{Then } m_c = 1 \text{ g/cm}^3 \times 1000 \text{ cm}^3 = 1000 \text{ g}$$

$$\text{So that enthalpy change} = -(0.39 \times 540 + 4.2 \times 1000) \times 0.65 \text{ J} = -2866.89 \text{ J}$$

The equation for the reaction is: $\text{NaOH (aq)} + \text{HNO}_3(\text{aq}) \rightarrow \text{NaOH(aq)} + \text{H}_2\text{O (l)}$

From which mole ratio of NaOH (or HNO_3) to H_2O is 1:1

Thus number of moles of NaOH = number of moles of water formed

$$\frac{500}{1000} \times 0.1 \text{ mol} = 5 \times 10^{-2} \text{ mol}$$

$$\text{Using enthalpy of neutralisation} = \frac{\text{Total enthalpy change}}{\text{Number of moles of water produced}}$$

$$= \frac{-2866.89 \text{ J}}{5 \times 10^{-2} \text{ moles}} = 57337.8 \text{ J/mol or } 57.3378 \text{ kJ/mol}$$

Hence enthalpy of neutralisation is 57.3378 kJ/mol

Example 3

Calculate the enthalpy of neutralisation of potassium hydroxide by hydrochloric acid from the following data:

250cm³ of 0.5MKOH at 12°C were mixed in a plastic beaker of negligible heat capacity with an equal volume of 0.5MHCl at the same temperature. The final temperature was 15.4°C. Assume the specific heat capacity of the solution to be 4.2 Jg⁻¹°C⁻¹.

Solution

$$\text{Total enthalpy change} = \Delta T(m_v C_v + m_c C_c)$$

But $C_v = 0$ (**Plastic** beaker has negligible heat capacity)

$$\text{Then: total enthalpy change} = m_c C_c \Delta T$$

$$\text{Where: } C_c = 4.2 \text{ Jg}^{-1} \text{°C}^{-1}$$

$$m_c = \rho_c V_c = 1 \text{ g/cm}^3 \times (250 + 250) \text{ cm}^3 = 500 \text{ g}$$

$$\Delta T = (15.4 - 12) \text{°C} = 3.4 \text{°C}$$

$$\text{It follows that enthalpy change} = -500 \times 4.2 \times 3.4 \text{ J} = -7140 \text{ J}$$

$$\text{Using enthalpy of neutralisation} = \frac{\text{Total enthalpy change}}{\text{Number of moles of water produced}}$$

But from the equation of the reaction: $\text{KOH (aq)} + \text{HCl (aq)} \rightarrow \text{KCl (aq)} + \text{H}_2\text{O (l)}$;

mole ratio of KOH (or HCl) to H₂O is 1:1

Thus number of moles of water produced = Number of moles of KOH

$$= \frac{250}{1000} \times 0.5 \text{ mol} = 0.125 \text{ mol}$$

$$\text{So enthalpy of neutralisation} = \frac{-7140 \text{ J}}{0.125 \text{ moles}} = -57120 \text{ J/mol or } -57.12 \text{ kJ/mol}$$

Hence enthalpy of neutralisation is -57.12 kJ/mol.

Further worked examples in calorimetry**Example 4**

40cm³ of hydrochloric acid and with a concentration of 2mol dm⁻³ were poured into a polystyrene breaker. The same volume of sodium hydroxide with the same concentration was added to the acid, the temperature rise was found to be 13.7K. Calculate the approximate enthalpy of neutralisation for the reaction.

Given that the specific heat capacity of water is 4.184 × 10⁻³ kJg⁻¹K⁻¹

Solution

$$\text{Total enthalpy change} = \Delta T(m_v C_v + m_c C_c)$$

But **polystyrene beaker** has zero heat capacity, thus $C_v = 0$

$$\text{So total enthalpy change} = m_c C_c \Delta T$$

$$\text{But } m_c = \rho_c V_c$$

Where ρ_c is the density of the contents (solution) = 1g/cm³

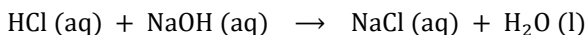
$$V_c \text{ is the volume of contents} = (40 + 40) \text{ cm}^3 = 80 \text{ cm}^3$$

$$\text{Then } m_c = 1 \text{ g/cm}^3 \times 80 \text{ cm}^3 = 80 \text{ g}$$

Therefore;

Total enthalpy change = $-80 \times 4.184 \times 10^{-3} \times 13.7 \text{ kJ} = -4.586 \text{ kJ}$

Equation for the reaction is:



From which mole ratio of HCl (or NaOH) to H_2O is 1:1

Thus number of moles of H_2O produced = number of moles HCl = $\frac{40}{1000} \times 2 \text{ mol} = 8 \times 10^{-2} \text{ mol}$

Using enthalpy of neutralisation = $\frac{\text{Total enthalpy change}}{\text{Number of moles of water produced}} = \frac{-4.586 \text{ kJ}}{8 \times 10^{-2} \text{ moles}} = -57.325 \text{ kJ/mol}$

Hence enthalpy of neutralisation is -57.325 kJ/mol .

Example 5

75 cm^3 of 0.2M Lithium hydroxide solution was added to 75 cm^3 of 0.2M hydrochloric acid in a vacuum flask of water equivalent 10g. The original temperature of reactants before the reaction was 14.7°C and it rose to 16°C . Calculate the enthalpy of neutralisation under the conditions.

Given that: Specific heat capacity of solution is the same as that of water which is $4.2 \text{ Jg}^{-1}\text{C}^{-1}$

Solution

Total enthalpy change = specific heat capacity $\times$ total mass $\times$ temperature change

But mass of volume flask = 10g of water (the flask is of water equivalent 10g)

And mass of water = $1 \text{ g/cm}^3 \times (75 + 75) \text{ cm}^3 = 150 \text{ g}$

Hence total mass is $(150 + 10) \text{ g} = 160 \text{ g}$ of water

And temperature change = $(16 - 14.7)^\circ\text{C} = 1.3^\circ\text{C}$

Then: Total enthalpy change = $-4.2 \times 160 \times 1.3 \text{ J} = -873.6 \text{ J}$

Using enthalpy of neutralisation = $\frac{\text{Total enthalpy change}}{\text{Number of moles of water produced}}$

From the equation of the reaction: $\text{LiOH(aq)} + \text{HCl (aq)} \rightarrow \text{LiCl (aq)} + \text{H}_2\text{O (l)}$

Mole ratio of LiOH (or HCl) to H_2O is 1:1

Thus number of moles of water produced = Number of moles of LiOH

$$= \frac{75}{1000} \times 0.2 \text{ mol} = 0.015 \text{ mol}$$

Then enthalpy of neutralisation = $\frac{-873.6 \text{ J}}{0.015 \text{ mol}} = 58240 \text{ J/mol}$ or 58.24 kJ/mol

Example 6

When 1g of graphite is burnt in excess oxygen, the energy of 32kJ is liberated. Calculate heat of combustion of the graphite.

Solution

Graphite is allotropic form of carbon whose molar mass is 12 g/mol

From the definition of the heat combustion;

Heat of combustion = $\frac{\text{Heat energy liberated}}{\text{Number of moles of graphite (carbon)}}$

Using; number of moles = $\frac{\text{Given mass}}{\text{Molar mass}}$

Then; number of moles of graphite = $\frac{1}{12}$ moles

Thus; heat of combustion of graphite = $\frac{-32\text{kJ}}{\frac{1}{12}\text{mol}} = -32 \times 12\text{kJ/mol} = -384\text{ kJ/mol}$

Hence heat of combustion of graphite is -384kJ/mol .

Example 7

The combustion of 1.6g sample of methanol in a flame calorimeter result into a temperature rise of 7.8K. When a 12V supply of electricity with a current of 2A was passed through the contents of the calorimeter for 20minutes the temperature rose by 6.2K. Calculate the molar enthalpy of combustion under the conditions of this experiment.

Solution

Enthalpy change due to combustion of methanol is given by;

Enthalpy change = heat capacity $\times$ temperature change

But temperature rise after combustion is 7.8K

So enthalpy change in combustion = $7.8 \times$ heat capacity of the calorimeter

But also:

Heat change due to passage of electricity = heat capacity $\times$ temperature rise
 $= 6.2 \times$ heat capacity of the calorimeter

But electric energy = heat change due to passage of the electricity

Then $VIt = 6.2 \times$ heat capacity of the calorimeter

Where V is the potential difference = 12V

I is the current = 2A

t is the time = 20×60 seconds = 1200 seconds.

And $VIt =$ Electric energy

So heat capacity of the calorimeter = $\frac{VIt}{6.2} = \frac{12 \times 2 \times 1200\text{JK}^{-1}}{6.2} = 4645.1613\text{JK}^{-1}$

Thus heat capacity of the calorimeter = 4645.1613JK^{-1}

Then enthalpy change due to combustion = $-7.8 \times 4645.1613\text{ J} = -36232.258\text{J}$

Number of moles of methanol $\text{CH}_3\text{OH} = \frac{\text{mass of CH}_3\text{OH}}{\text{molar mass of CH}_3\text{OH}} = \frac{1.6\text{g}}{32\text{g mol}^{-1}} = 0.05\text{mol}$

Using Enthalpy of combustion = $\frac{\text{Enthalpy change}}{\text{Number of moles of the substance (CH}_3\text{OH)}}$

$= \frac{-36232.258\text{J}}{0.05\text{mol}} = -724645.16\text{ J/mol}$ or $= -724.645\text{ kJ/mol}$

Hence the molar enthalpy of combustion of methanol is -724.645kJ/mol .

Example 8

1.5 g of ammonium nitrate (NH_4NO_3) was added to 35 g of water in a plastic beaker and stirred until the salt is dissolved. The temperature of the solution dropped from 22.7°C to 19.4°C . Basing on the given information respond to the following:

- Is the process endothermic or exothermic? Explain.
- Calculate the heat of solution of NH_4NO_3 in kJ/mol ; given that specific heat capacity of water is $4.184\text{J/g}^\circ\text{C}$.

Solution

(i) Endothermic

Explanation

The temperature decreased from 22.7°C to 19.4°C suggesting that heat was absorbed from the surroundings (solution) and hence the process is endothermic.

(ii) Total heat absorbed = Heat absorbed by contents + Heat absorbed by vessel

But because plastic beaker does not allow the passage heat;

Heat absorbed by vessel = 0 (specific heat capacity of plastic beaker is negligible).

Total heat absorbed, ΔH = Heat absorbed by contents

But Heat absorbed by contents = $m_c C_c \Delta T$

Where $m_c = (1.5 + 36)g = 36.5g$

$C_c = 4.184 Jg^{-1}C^{-1}$ (Specific heat capacity of solution is equal to that of water)

$\Delta T = (22.7 - 19.4)^\circ C = 3.3^\circ C$

Substituting $\Delta H = 36.5 \times 4.184 \times 3.3J = 503.9628J$

But Heat of solution,

$$\Delta H_{\text{soln}} = \frac{\text{Heat change}}{\text{Number of moles of solute (NH}_4\text{NO}_3\text{)}}$$

Then using $n = \frac{m}{M_r}$; Where $M_r(\text{NH}_4\text{NO}_3) = 80 g/mol$

Number of moles of $\text{NH}_4\text{NO}_3 = \frac{1.5g}{80 g/mol} = 0.01875 mol$

It follows that:

$$\Delta H_{\text{soln}} = \frac{503.9628J}{0.01875mol} = 26878J/mol$$

= 26.878 kJ/mol

Hence the heat of solution is +26.878 kJ/mol

Example 9

Two liquids; trichloromethane (CHCl_3) and ethoxyethane ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$) form intermolecular hydrogen bonds when mixed. In a certain experiment, 0.05moles of trichloromethane and 0.3moles of ethoxyethane were weighed into the same calorimeter. When the temperature of both liquids had equalized, the liquids were mixed. The temperature increase of 5.4°C were recorded upon mixing. Assume that the heat capacity of calorimeter is negligible, while heat capacities of trichloromethane and ethoxyethane are $0.98Jg^{-1}C^{-1}$ and $2.28Jg^{-1}C^{-1}$ respectively. Calculate:

(i) Heat change in this experiment.

(ii) Enthalpy change of mixing one mole of trichloromethane with excess ethoxyethane.

Solution

Using $m = nM_r$;

Mass of trichloromethane, $m_t = 0.05mol \times 119g/mol = 5.975g$

Mass of ethoxyethane, $m_e = 0.3mol \times 74g/mol = 22.2g$

Since the temperature increased, the heat change is negative (The process is exothermic)

Thus $\Delta H = -(m_t C_t \Delta T + m_e C_e \Delta T)$

Substituting; $\Delta H = -((5.975 \times 0.98 \times 5.4) + (22.2 \times 2.28 \times 5.4))J = -304.95J$

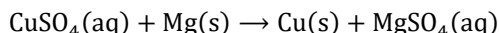
The heat change in the experiment is the experiment is -304.95J

$$\text{The molar enthalpy change} = \frac{\text{Heat change}}{\text{Number of moles of CHCl}_3} = \frac{-304.95\text{J}}{0.05\text{mol}} = -6099\text{Jmol}^{-1} = -6.099\text{kJmol}^{-1}$$

The enthalpy change of mixing one mole of trichloromethane with excess ethoxyethane is -6.099kJ .

Example 10

Magnesium will displace copper from copper (II) sulphate according to the following equation:



When an excess of magnesium was added to 100cm^3 of 1mol dm^{-3} copper (II) sulphate, the temperature increased by 46.3°C . It is known that density and specific heat capacity of the solution are 1gcm^{-3} and $4.18\text{Jg}^{-1}\text{C}^{-1}$ respectively. Calculate:

- The molar enthalpy change for the reaction.
- The minimum quantity of magnesium required.
- The change in temperature if only 0.8g of magnesium was added.

Solution

- Since the reaction accompanied with the temperature rise, it is exothermic.

Then; heat change, $\Delta H = -mc\Delta T$

$$\text{But } m = \rho_{\text{soln}} V_{\text{soln}}$$

$$\text{Thus; } \Delta H = -\rho_{\text{soln}} V_{\text{soln}} c\Delta T$$

$$\begin{aligned}\text{Substituting } \Delta H &= -1\text{gcm}^{-3} \times 100\text{cm}^3 \times 4.18\text{Jg}^{-1}\text{C}^{-1} \times 46.3^\circ\text{C} \\ &= -19353.4\text{J} = -19.3534\text{kJ}\end{aligned}$$

$$\text{Number of moles of CuSO}_4 = \frac{100}{100} \text{dm}^3 \times 1\text{mol dm}^{-3} = 0.1\text{mol}$$

Then using;

$$\text{Molar enthalpy change} = \frac{\text{Heat change}}{\text{Number of moles of CuSO}_4}$$

$$\text{Molar enthalpy change} = \frac{-19.3534\text{kJ}}{0.1\text{mol}} = -193.534\text{kJ/mol}$$

The molar enthalpy change for the reaction is -193.534kJ/mol

- From the given equation; mole ratio of CuSO_4 to Mg is 1:1

Thus the minimum number of moles of Mg required is 0.1mol

Using $m = nM_r$;

$$\text{Mass of Mg} = 0.1\text{mol} \times 24\text{gmol}^{-1} = 2.4\text{g}$$

The minimum quantity of magnesium required is 2.4g

$$\text{(iii) Number of moles of magnesium } n = \frac{0.8\text{g}}{24\text{gmol}^{-1}} = \frac{1}{30} \text{mol}$$

$$\text{Thus; Number of moles of CuSO}_4 = \text{Number of moles of Mg} = \frac{1}{30} \text{mol}$$

$$\begin{aligned}\text{And; Heat change} &= \text{molar enthalpy change} \times \text{Number of molar of CuSO}_4 \\ &= -193.534\text{kJmol}^{-1} \times \frac{1}{30} \text{mol} = -6.45\text{kJ} = 6450\text{J}\end{aligned}$$

$$\text{From } \Delta H = -\rho_{\text{soln}} V_{\text{soln}} c\Delta T$$

$$-6450\text{J} = -1\text{gcm}^{-3} \times 100\text{cm}^3 \times 4.18\text{Jg}^{-1}\text{C}^{-1} \times \Delta T$$

From which; $\Delta T = 15.43^\circ\text{C}$

DIGGING DEEPER EXERCISE 23

EXERCISE 23A: BINDER QUESTIONS

Question 1

Classify each of the following processes as endothermic or exothermic. In each case, indicate which has greater heat content (enthalpy), reactants or products.

- (a) Combustion of natural gas
- (b) Dehydrogenation of ethene
- (c) Splitting of carbon dioxide into carbon and oxygen
- (d) Solidification of melted wax
- (e) Formation of sodium chloride (NaCl) from its elements
- (f) Neutralisation of NaOH by HCl

Question 2

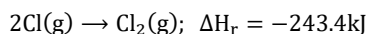
Predict the value $\Delta H_f^\ominus$ for the following scenarios:

- (a) $\text{Br}_2(\text{g})$ (b) $\text{Br}_2(\text{l})$ (c) $\text{I}_2(\text{g})$ (d) $\text{I}_2(\text{s})$

In each case, give a reason for your prediction.

Question 3

Consider the following reaction, which occurs at standard state:



Which has the higher, more positive, enthalpy under these conditions, $\text{Cl}(\text{g})$ or $\text{Cl}_2(\text{g})$? Give reason(s) for your choice.

Question 4

When 100.0mL of 1.00M NaOH is added to 100.0mL of 1.00M HCl in an insulated container the temperature rises from 21.0°C to 27.8°C. Calculate the enthalpy change for the neutralisation reaction. Specific heat capacity of water is $4.18\text{J K}^{-1}\text{g}^{-1}$.

Question 5

A vessel and its contents of total heat capacity 120J/K were heated using a methane burner. Calculate the maximum theoretical temperature rise when 0.10g of methane was completely burned. The standard enthalpy of combustion of methane is -890 kJ/mol .

Question 6

To change the temperature of a particular calorimeter and the water it contains by one degree Celsius requires 6485Joules. The complete combustion of 1.40g of ethylene gas, C_2H_4 , in the calorimeter causes a temperature rise of 10.7 degrees. Find the heat of combustion of ethylene gas.

EXERCISE 23B: REAL QUESTIONS**Question 7**

The following scenarios are real life processes which involve heat change. State whether each process is endothermic or exothermic.

- Water is added to sodium hydroxide pellets, and the flask becomes hot.
- The body metabolises glucose, producing carbon dioxide and water.
- Ammonium nitrate crystals are dissolved in water, causing the solution to become cool.

Question 8

On diluting an acid, it is advised to add acid to water and not water to acid. Explain why it is so advised?

Question 9

When a human is exposed to hot water or solution with a temperature of 60°C , leads to a serious burn within a second. So care must be taken in preparing solutions of solutes that liberate heat on dissolving. Our laboratory technician, **Mr. Akilikubwa**, was preparing 500mL of 7M NaOH and he forgot to take necessary precautions during the preparation. Immediately after mixing NaOH and water at 21°C , he contacted the resulting solution to his face. Did **Mr. Akilikubwa** get burn injury?

Given that:

The heat of solution of NaOH = -42 kJ/mol .

The specific heat of the solution formed = $4.18 \text{ Jg}^{-1}\text{K}^{-1}$

(Assume the density of solution is equal to the density of water).

Question 10

Kipute, your lovely classmate was asked to determine the enthalpy of neutralisation by taking 100cm^3 of 0.3MNaOH and mixing it with 115cm^3 of 0.3MHNO_3 in a polystyrene beaker. If both solutions were initially at 35°C and the temperature of the resulting solution was recorded as 39°C and he was told to assume that there was no heat lost to the calorimeter or surroundings; but by mistake she took 100cm^3 of 0.3MNaOH and mixed 20cm^3 of distilled water in a beaker unknowingly. This led Kipute to have an error to her experimental results. Assists **Kipute** to calculate the percentage error enthalpy between the real expected and the one she calculated.

Question 11

On another day, **Kipute** performed an experiment to determine the standard molar enthalpy of neutralisation of a strong acid by a strong base. She added 50cm^3 of hydrochloric acid to 50cm^3 of sodium hydroxide solution in a polystyrene cup. The temperature rose by 6.5°C . The initial concentration of each solution was 1mol dm^{-3}

- (a) What result did **Kipute** get?

(Assume that the final solution has a specific heat capacity of $4.18\text{JK}^{-1}\text{g}^{-1}$ and a density of 1gcm^{-3}).

- (b) When all other students in **Kipute's** class performed this experiment, the average of the results was -55kJ/mol . The accepted value for the standard molar enthalpy of neutralization of a strong acid by a strong base is -57.7kJ/mol . Explain two likely sources of experimental error that could account for the result obtained by the class.

Question 12

Mr. Akilikubwa performed an experiment that involved neutralisation reaction. He took 50cm^3 of a 0.500M solution of potassium hydroxide then mixed rapidly in a glass beaker with 50cm^3 of a 0.500M solution of hydrochloric acid. He recorded temperature as follows:

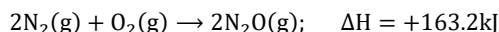
Initial temperature of each solution = 19.6°C

Final temperature of the mixture = 23.1°C

- State with a reason whether the reaction was exothermic or endothermic.
- Explain why the solutions were mixed rapidly.
- Calculate the enthalpy change in kJ/mol . Assume that the specific heat capacity of the solution is the same as that of water ($4.18\text{JK}^{-1}\text{g}^{-1}$).
- If **Mr. Akilikubwa** repeated experiment with an HCl concentration of 1M ; state and explain what the temperature change would be.

EXERCISE 23C: HOT QUESTIONS**Question 13**

Calculate amount of energy transferred when 10.00g of $\text{N}_2\text{O}(\text{g})$ is produced by the following reaction:

**Question 14**

Given the following reaction: $2\text{P}(\text{s}) + 3\text{Cl}_2(\text{g}) \rightarrow 2\text{PCl}_3(\text{g}); \quad \Delta H = -574\text{kJ}$

- (a) How many moles of phosphorus are needed to produce 488 kJ?
- (b) How much heat is released when 122g of PCl_3 are produced?
- (c) How many grams of Cl_2 are needed to produce 27.0kJ?

Question 15

When 50cm^3 of 1M HCl is mixed rapidly with 50cm^3 of 1M NaOH, the temperature of the resulting solution increases by 6°C . Determine the temperature change when:

- (a) 100cm^3 (instead of 50cm^3) of each of these solutions is mixed.
- (b) 2M (instead of 1M) of each solution is mixed.

Question 16

In an experiment, an excess of solid magnesium oxide was added to 50cm^3 of 3M hydrochloric acid. The initial temperature of the solution was 21°C . After reaction, the temperature had risen to 53°C . (The specific heat capacity of water is $4.2\text{ JK}^{-1}\text{g}^{-1}$)

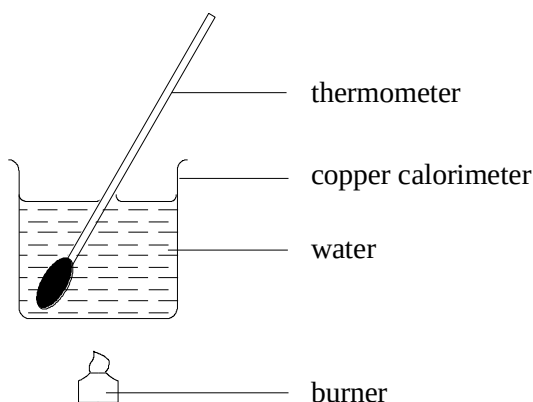
Use this information to calculate the enthalpy change for the reaction of one mole of magnesium oxide with hydrochloric acid. For your calculation you should assume that all the heat from the reaction is used to raise the temperature of 50g of water.

Question 17

An experiment was conducted to determine the enthalpy of combustion of liquid methanol. The energy obtained from burning 2.12g of methanol was used to heat 150g of water. The temperature of the water rose from 298K to 362 K. (The specific heat capacity of water is $4.18\text{ JK}^{-1}\text{g}^{-1}$). Calculate a value for the enthalpy of combustion of liquid methanol.

Question 18

A value for the enthalpy of combustion of the alcohol $\text{C}_3\text{H}_7\text{OH}$ was determined in the laboratory using the apparatus shown below. The following results were obtained.



Mass of water in the calorimeter = 200g

Initial temperature of water = 15°C

Final temperature = 30°C

Mass of alcohol burned = 0.90g

- (a) Calculate the heat energy required to raise the temperature of the water from 15°C to 30°C. The specific heat capacity of water is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$.
- (b) Calculate the number of moles of the alcohol, $\text{C}_3\text{H}_7\text{OH}$, burned.
- (c) Hence, calculate a value for the enthalpy of combustion of the alcohol.
- (d) Give at least **two** possible reasons why your answer in (c) is not a hundred percent correct.

Chapter 25

HESS'S LAW OF CONSTANT HEAT SUMMATION

INTRODUCTION

One of the most important generalisations of thermochemistry is Hess's law. This generalisation is primarily based on the fact that enthalpy is a path independent thermodynamic function. In other words, the enthalpy change in a chemical reaction is same whether it occurs in one step or in more than one step. This may be stated in the form of Hess's law (named in honour of its discoverer, the Russian chemist, German Henry **Hess**) as follows:

"The total energy change resulting from a chemical reaction is dependent only on the initial and final state of the reactants and is independent of the route."

Thus according to the Hess's law, the standard enthalpy of reaction is the sum of algebraic sum of the standard enthalpies of reactions into which the overall reaction may be divided.

Hess's law is an application of **first law of thermodynamic** which is actually the **law of conservation of energy** which can be stated as:

Energy cannot be destroyed or created but merely changed in form or distributed in different ways.

Hess's law is also known as the **law of constant heat summation** or **second law of thermochemistry**.

To have better understanding of the concept, consider the enthalpy change from reactants **A** to products **B** via various routes as shown in **figure 25.1** below:

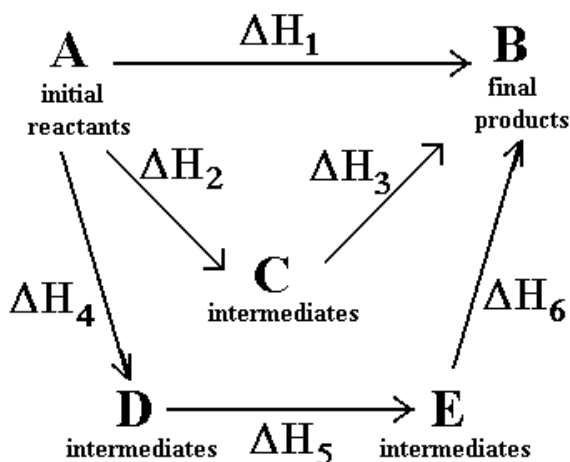


Figure 24.1 Illustration of Hess's law

From above figure:

$\Delta H_1 = \Delta H(\text{A to B})$: Route 1 the most direct route with no intermediate stages.

The from Hess's law:

$\Delta H_1 = \Delta H_2 + \Delta H_3$: Route 2 involves two steps and one set of intermediates **C**.

or $\Delta H_1 = \Delta H_4 + \Delta H_5 + \Delta H_6$: Route 3 involving three steps with two sets of intermediates **D** and **E**.

So there is no limit to the complexity of the Hess's law cycle as long as A and B are constant.

METHODS OF APPLYING HESS'S LAW

In applying Hess's law, the following methods may be used:

- Hess's law cycle
- Combining thermochemical equations
- Thermochemical calculations by using enthalpy of formations
- Born-Haber cycle
- Thermochemical calculations by using bond energies

In this chapter, we are going to discuss above methods; one after another.

Hess's law cycle

Consider a process involving the conversion of reactant **A** into **B** in one step (**route 1**). The enthalpy change of the process is represented by ΔH . Then suppose the process is carried out in two steps involving a change from **A** to **C** and **C** to **B** according to **route 2** (**Figure 28.2**). If ΔH_1 and ΔH_2 are enthalpy changes from **A** to **C** and **C** to **B** respectively. Then according to Hess's law;

Enthalpy change in **route 1** = total enthalpy change in **route 2**

And hence $\Delta H = \Delta H_1 + \Delta H_2$

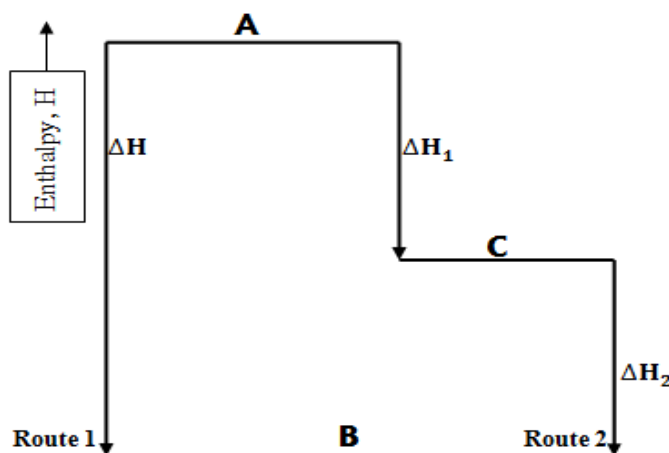


Figure 24.2 Hess's law cycle

Example 1

If the enthalpy of formation of SO_2 and enthalpy of combustion of SO_2 have been found to be -297.4 kJ/mol and -97.9 kJ/mol respectively; by using Hess's law cycle, determine enthalpy of formation of SO_3 .

Solution

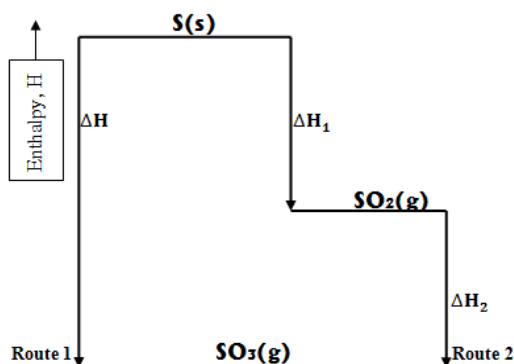
Possible routes for forming SO_3 :

Route 1: Direct formation from its constituent elements, sulphur and oxygen by one step only as per equation: $\text{S(s)} + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$

Route 2: Conversion of sulphur to SO_2 followed by further reaction with O_2 to form SO_3 as per equations: $\text{S(s)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$

Then $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$

Then the Hess's law cycle can be drawn as follows:

Figure 24.3 Hess's law cycle for formation of SO_3

Where: $\Delta H_1 = -297.4 \text{ kJ/mol}$, $\Delta H_2 = -97.9 \text{ kJ/mol}$

Then by Hess law; $\Delta H = \Delta H_1 + \Delta H_2$,

Substituting $\Delta H = -297.4 + -97.9 = -395.3 \text{ kJ/mol}$

Hence enthalpy of formation of SO_3 is -395.3 kJ/mol

Example 2

By using Hess's law, calculate enthalpy of transition of rhombic sulphur to monoclinic sulphur. Given that:

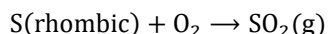
Enthalpy of combustion of monoclinic sulphur is -296.4 kJ/mol

Enthalpy of combustion of rhombic sulphur is -295.1 kJ/mol

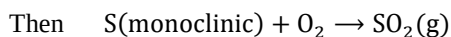
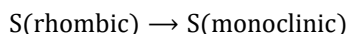
Solution

Possible routes in formation of SO_2 :

Route 1: Direct conversion of rhombic sulphur to SO_2 by one step only as per equation;



Route 2: Converting rhombic sulphur to monoclinic sulphur, thereafter the monoclinic sulphur is converted to SO_2 as per equations:



So if **S(M)** stands for monoclinic sulphur and **S(R)** stands for rhombic sulphur, the Hess's law cycle for combustion of rhombic sulphur can be drawn as follows:

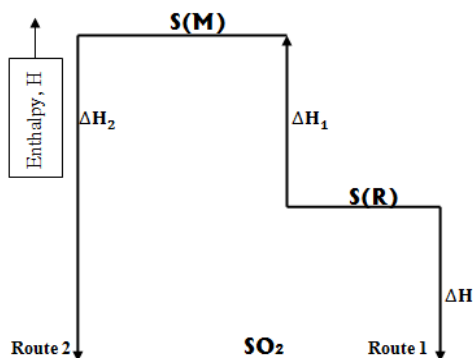


Figure 24.4 Hess's law cycle for combustion of rhombic sulphur

Where:

ΔH_1 = Unknown enthalpy of transition of rhombic sulphur to monoclinic sulphur

ΔH_2 = Enthalpy of combustion of monoclinic sulphur = -296.4kJ/mol

ΔH = Enthalpy of combustion of rhombic sulphur is -295.1kJ/mol

Then by Hess's law; $\Delta H = \Delta H_1 + \Delta H_2$,

From which; $\Delta H_1 = \Delta H - \Delta H_2 = -295.1 - (-296.4) = +1.3\text{kJ/mol}$

Hence heat of transition of rhombic sulphur to monoclinic sulphur is $+1.3\text{kJ/mol}$

Example 3

Hydrated copper (II) sulphate can be formed by reaction between anhydrous CuSO_4 and water according to the following equation: $\text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$

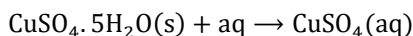
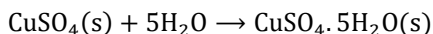
Calculate hydration enthalpy of copper (II) sulphate if enthalpies of dissolution of hydrated copper sulphate and that of anhydrous copper sulphate have been experimentally found to be $+11.70\text{kJ/mol}$ and -66.5kJ/mol respectively.

Solution

Possible routes for making solution of CuSO_4 :

Route 1: Direct dissolving of anhydrous CuSO_4 in excess water by one step only as per equation: $\text{CuSO}_4(\text{s}) + \text{excess H}_2\text{O} \rightarrow \text{CuSO}_4(\text{aq})$

Route 2: Converting anhydrous CuSO_4 into crystalline $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ followed by dissolving the crystalline to give solution of CuSO_4 as per equations:



Thus Hess's law cycle for making solution of CuSO_4 can be drawn as follows:

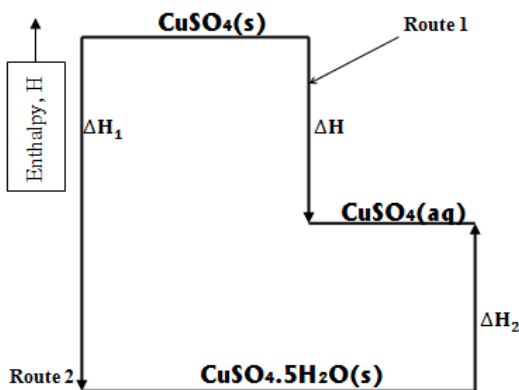


Figure 24.5 Hess's law cycle for dissolving CuSO_4

Where: $\Delta H_2 = 11.7\text{kJ/mol}$, $\Delta H = -66.5\text{kJ/mol}$ and $\Delta H_1 = ?$

Then by Hess law; $\Delta H = \Delta H_1 + \Delta H_2$,

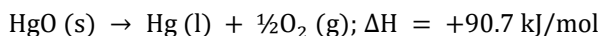
From which; $\Delta H_1 = \Delta H - \Delta H_2 = -66.5 - 11.7 = -78.2\text{kJ/mol}$

Hence heat of hydration of copper (II) sulphate is -78.2kJ/mol

Combining thermochemical equations

Thermochemical equation is a balanced stoichiometric chemical equation that includes the enthalpy change, ΔH .

For example; $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}); \Delta H = -285.8 \text{ kJ/mol}$

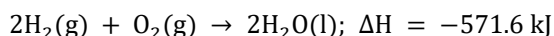
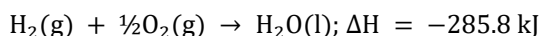


In relation to thermochemical calculations, certain rules apply when using thermochemical equations:

Rule 1

ΔH is directly proportional to the quantity of a substance that reacts or is produced by a reaction.

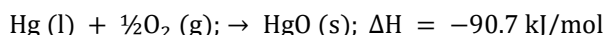
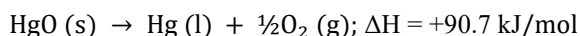
Enthalpy is directly proportional to mass. Therefore, if you double the coefficients in an equation, then the value of ΔH is multiplied by two. For example:



Rule 2

ΔH for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction.

For example:



This law is commonly applied to phase changes, although it is true when you reverse any thermochemical reaction.

It is also known as **first law of thermochemistry** (or **first thermochemical law**). Another name is **Laplace law**.

Rule 3

ΔH is independent of the number of steps involved.

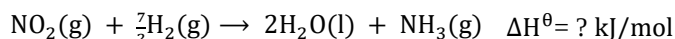
This rule is called **Hess's Law**. According to the law, ΔH for a reaction is the same whether it occurs in one step or in a series of steps provided that first reactants and final products remain the same.

So if: $\text{Reaction}(1) + \text{Reaction}(2) = \text{Reaction}(3)$; then $\Delta H_3 = \Delta H_1 + \Delta H_2$

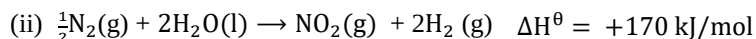
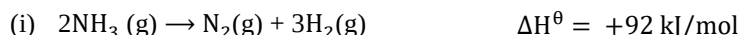
Good understanding of above three rules is the basis of indirect determination of enthalpy of reaction by combining thermochemical equations. And it is good to hear that all problems which are solved by Hess's law cycle can be solved by this method too.

Example 4

Use the following data to determine the enthalpy (ΔH^θ) of following reaction:

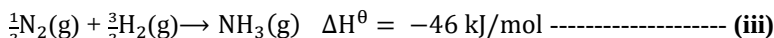


Given that:



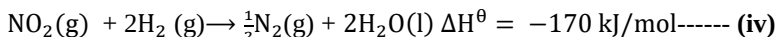
Solution

1) To get only one NH_3 on the right-hand side like in the required equation, equation (i) is reversed and divided by two as follows:



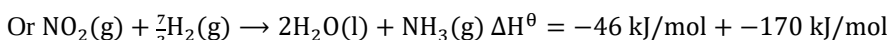
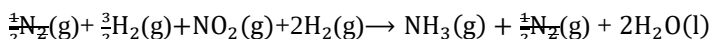
Notice that the sign changed on the ΔH and its numerical value was halved.

2) To get only one NO_2 on the left-hand side like in the required equation, equation (ii) is reversed as follows:



Notice that the sign changed on the ΔH .

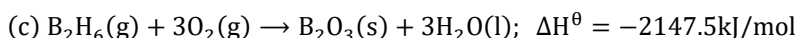
3) The required equation is found by taking (iii) + (iv) and cancelling terms which appear as both reactant and product as shown below:



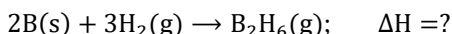
Hence enthalpy of given reaction is -216 kJ/mol

Example 5

The standard molar enthalpy of formation, ΔH_f^θ , of diborane cannot be determined directly because the compound cannot be prepared by reaction of boron and hydrogen. However, the value can be calculated. Calculate the standard enthalpy of formation of gaseous diborane (B_2H_6) using the following thermochemical information:

**Solution**

Thermochemical equation for formation of diborane

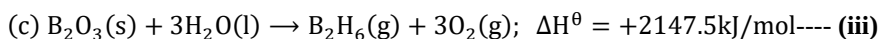
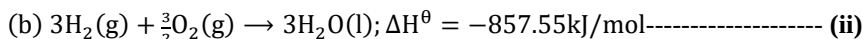
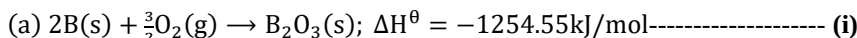


Remember that in writing thermochemical equation for heat of formation, **one** mole of target substance (in this case diborane) must be formed.

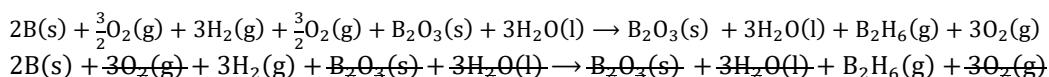
In order to get to our formation reaction, the following should be done to equations (a), (b) and (c):

- Equation (a) is divided through by 2 so as to get 2B like in the required equation
- Equation (b) is multiplied through by $3/2$ to give 3H_2 like in the required equation
- Equation (c) is reversed to put B_2H_6 on the right-hand side like in the required equation

After above adjustments, the three equations become:



The required equation is obtained by taking (i) + (ii) + (iii) as follows:



Whence $2\text{B(s)} + 3\text{H}_2(\text{g}) \rightarrow \text{B}_2\text{H}_6(\text{g})$;

And $\Delta H = (-1254.55 + -857.55 + 2147.5)\text{kJ} = +35.4\text{kJ/mol}$

Hence enthalpy of formation of diborane is $+35.4\text{kJ/mol}$

Example 6

Consider the following reaction:



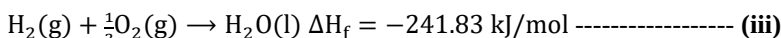
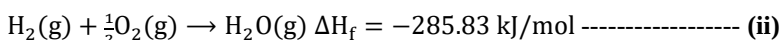
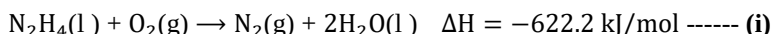
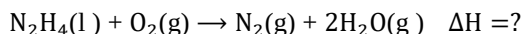
Given the following data, calculate the heat of reaction for the same reaction where water is a gaseous product instead of a liquid:

$$\Delta H_f \text{ for } \text{H}_2\text{O}(\text{g}) = -285.83 \text{ kJ/mol}$$

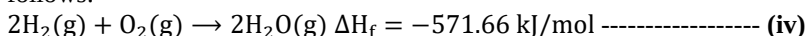
$$\Delta H_f \text{ for } \text{H}_2\text{O}(\text{l}) = -241.83 \text{ kJ/mol}$$

Solution:

Required equation:



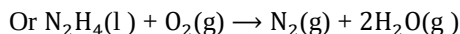
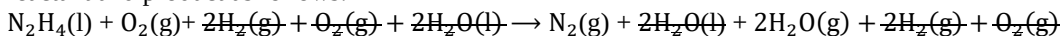
To get two $\text{H}_2\text{O}(\text{g})$ on right-hand side like in the required equation, equation (ii) is multiplied by 2 as follows:



To eliminate two $\text{H}_2\text{O}(\text{l})$ from right-hand side of equation (i), equation (iii) is reversed and multiplied by 2 as follows:



The required equation is found by taking (i) + (iv) + (v) and cancelling terms which appear as both reactant and product as follows:



And $\Delta H = (-622.2 + -571.66 + 483.66)\text{kJ/mol} = -710.2\text{kJ/mol}$

Hence if water is gaseous product, the heat of reaction would be -710.2kJ/mol

Thermochemical calculations by using enthalpy of formations

Hess's law can also be used for the determination of standard heat of the reaction from the knowledge of standard heats of formation of various reactants and the products. The Hess's law cycle for elements in their standard states, reactants and products can be drawn as shown in **Figure 25.6**.

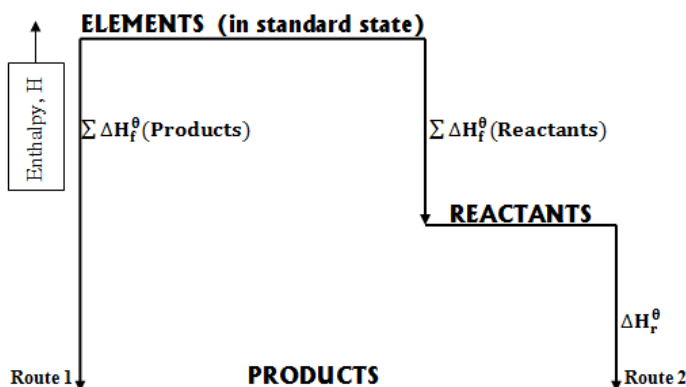


Figure 24.6 Hess's law cycle for enthalpy of reaction

Then by Hess's law:

Enthalpy change in **route 1** = enthalpy change in **route 2**

Substituting $\sum \Delta H_f^\theta(\text{Products}) = \sum \Delta H_f^\theta(\text{Reactants}) + \Delta H_r^\theta$

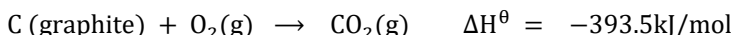
From which $\Delta H_r^\theta = \sum \Delta H_f^\theta(\text{Products}) - \sum \Delta H_f^\theta(\text{Reactants})$

The final equation is very useful in determination of enthalpy of reaction. Most of (if not all) problems which are solved by first and second method can be solved by this method (equation) and in most cases, it is the shorter method. However, the student must be able to use all three methods because in some cases examiners give restriction on method to be applied in obtaining enthalpy of reaction.

Example 7

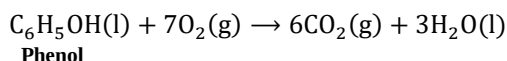
The standard enthalpy of formation of phenol is -209.3 kJ/mol .

Calculate its standard enthalpy of combustion, given:



Solution

The equation for the combustion of phenol is:



And we are given with:

$$\Delta H_f^\theta(\text{CO}_2) = -393.5\text{ kJ/mol}, \Delta H_f^\theta(\text{H}_2\text{O}) = -285.9\text{ kJ/mol}$$

$$\Delta H_f^\theta(\text{C}_6\text{H}_5\text{OH}) = -209.3\text{ kJ/mol}$$

$$\text{Using } \Delta H_r^\theta = \sum \Delta H_f^\theta(\text{Products}) - \sum \Delta H_f^\theta(\text{Reactants})$$

Then from the equation of combustion of phenol:

$$\Delta H_c^\ominus(\text{C}_6\text{H}_5\text{OH}) = 6\Delta H_f^\ominus(\text{CO}_2) + 3\Delta H_f^\ominus(\text{H}_2\text{O}) - \Delta H_f^\ominus(\text{C}_6\text{H}_5\text{OH}) - 7\Delta H_f^\ominus(\text{O}_2)$$

But $\Delta H_f^\ominus(\text{O}_2) = 0$ (Heat of formation of an element in its natural state must be zero)

Then substituting given values:

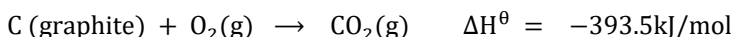
$$\Delta H_c^\ominus(\text{C}_6\text{H}_5\text{OH}) = (6 \times -393.5) + (3 \times -285.9) - (-209.3)$$

$$\Delta H_c^\ominus(\text{C}_6\text{H}_5\text{OH}) = -3009.4 \text{ kJ/mol}$$

Hence standard enthalpy of combustion of phenol is -3009.4 kJ/mol .

Example 8

Calculate the standard enthalpy of formation of propane, C_3H_8 , from the data:

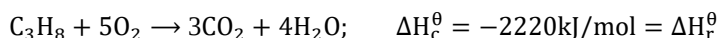


The standard enthalpy of combustion of propane is -2220 kJ/mol

Solution

Given that:

$$\Delta H_f^\ominus(\text{CO}_2) = -393.5 \text{ kJ/mol}, \quad \Delta H_f^\ominus(\text{H}_2\text{O}) = -285.9 \text{ kJ/mol}$$



$$\text{Using } \Delta H_r^\ominus = \sum \Delta H_f^\ominus(\text{Products}) - \sum \Delta H_f^\ominus(\text{Reactants})$$

$$\text{Then } \Delta H_c^\ominus(\text{C}_3\text{H}_8) = 3\Delta H_f^\ominus(\text{CO}_2) + 4\Delta H_f^\ominus(\text{H}_2\text{O}) - \Delta H_f^\ominus(\text{C}_3\text{H}_8) - 5\Delta H_f^\ominus(\text{O}_2)$$

But $\Delta H_f^\ominus(\text{O}_2) = 0$ (Heat of formation of an element in its natural state must be zero)

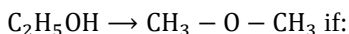
$$\text{So } -2220 = (3 \times -393.5) + (4 \times -285.9) - \Delta H_f^\ominus(\text{C}_3\text{H}_8)$$

$$\text{From which } \Delta H_f^\ominus(\text{C}_3\text{H}_8) = -104.1 \text{ kJ/mol}$$

Hence the standard enthalpy of formation of propane is -104.1 kJ/mol .

Example 9

Calculate the heat of isomerisation reaction:



(i) Heat of formation of $\text{C}_2\text{H}_5\text{OH}$ is -850 kJ/mol

(ii) Heat of combustion of $\text{CH}_3 - \text{O} - \text{CH}_3$ is -1452 kJ/mol

(iii) Heat of formation of CO_2 is -395 kJ/mol

(iv) Heat of formation of H_2O is -284 kJ/mol

Solution

$$\text{Using } \Delta H_r = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$$

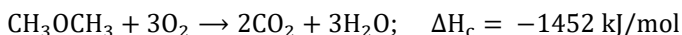
Notice the omission of superscript ' $\ominus$ ' because the enthalpies given are not standard.

Thus:

Heat of isomerisation reaction =

$$\Delta H_f(\text{CH}_3\text{OCH}_3) - \Delta H_f(\text{C}_2\text{H}_5\text{OH}) = \Delta H_f(\text{CH}_3\text{OCH}_3) - (-850) \dots (i)$$

Equation for combustion of CH_3OCH_3 is:



$$\text{Then } \Delta H_c(\text{CH}_3\text{OCH}_3) = 2\Delta H_f(\text{CO}_2) + 3\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{CH}_3\text{OCH}_3) - 3\Delta H_f(\text{O}_2)$$

$$\text{But } \Delta H_f(\text{O}_2) = 0$$

Substituting given values:

$$-1452 = (2 \times -395) + (3 \times -284) - \Delta H_f(\text{CH}_3\text{OCH}_3)$$

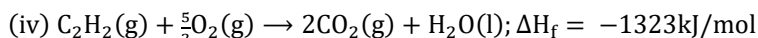
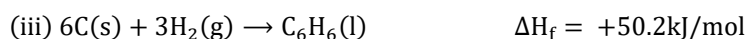
$$\text{From which: } \Delta H_f(\text{CH}_3\text{OCH}_3) = -190 \text{ kJ/mol} \dots \dots \dots \text{(ii)}$$

Substituting (ii) in (i) gives;

$$\text{Heat of the isomerisation reaction} = -190 - (-850) = 660 \text{ kJ/mol.}$$

Example 10

If:



Calculate:

- The heat of formation of ethyne
- The heat of polymerization of ethyne to benzene.

Solution

$$\text{Using } \Delta H_r = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$$

So from equation (iv);

$$\Delta H_c = 2\Delta H_f(\text{CO}_2) + \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_2\text{H}_2) - \frac{5}{2}\Delta H_f(\text{O}_2)$$

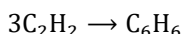
$$\text{But } \Delta H_f(\text{O}_2) = 0$$

$$\text{Then substituting given values gives: } -1323 = (2 \times -393) + -286 - \Delta H_f(\text{C}_2\text{H}_2)$$

$$\text{From which } \Delta H_f(\text{C}_2\text{H}_2) = 251 \text{ kJ/mol}$$

Hence heat of formation of ethyne is 251 kJ/mol

Equation of polymerization of ethyne to benzene is;



Ethyne

Benzene

From which:

$$\text{Heat of polymerization reaction} = \Delta H_f(\text{benzene}) - 3\Delta H_f(\text{ethyne})$$

$$= 50.2 - (3 \times 251) = -702.8 \text{ kJ/mol}$$

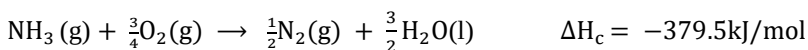
Hence heat of polymerization of ethyne to benzene is -702.8 kJ/mol

Example 11

What is the heat of formation of NH_3 if its heat of combustion is -379.5 kJ/mol and heat of formation of H_2O is -286 kJ/mol .

Solution

Equation for combustion of NH_3 is,



Using $\Delta H_r = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$

$$\text{Then } \Delta H_c(\text{NH}_3) = \frac{3}{2}\Delta H_f(\text{H}_2\text{O}) + \frac{1}{2}\Delta H_f(\text{N}_2) - \frac{3}{4}\Delta H_f(\text{O}_2) - \Delta H_f(\text{NH}_3)$$

But $\Delta H_f(\text{N}_2) = 0$ and $\Delta H_f(\text{O}_2) = 0$

Substituting given values to above equation gives,

$$-379.5 = \frac{3}{2} \times -286 - \Delta H_f(\text{NH}_3); \quad \Delta H_f(\text{NH}_3) = -49.5\text{kJ/mol}$$

Thus heat of formation of NH_3 is -49.5 kJ/mol

Example 12

Calculate the heat of formation of anhydrous aluminium chloride (Al_2Cl_6) from the following data:

- (i) $2\text{Al}(\text{s}) + 6\text{HCl}(\text{aq}) \rightarrow 2\text{AlCl}_3(\text{aq}) + 3\text{H}_2(\text{g}) \quad \Delta H = -1003\text{ kJ/mol}$
- (ii) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g}) \quad \Delta H = -184.1\text{kJ/mol}$
- (iii) $\text{HCl}(\text{g}) + \text{aq} \rightarrow \text{HCl}(\text{aq}) \quad \Delta H = -73.2\text{kJ/mol}$
- (iv) $\text{Al}_2\text{Cl}_6(\text{s}) + \text{aq} \rightarrow 2\text{AlCl}_3(\text{aq}) \quad \Delta H = -643.1\text{kJ/mol}$

Hint: $2(\text{aq}) = 3(\text{aq}) = n(\text{aq}) = \text{aq}$

Solution

Using $\Delta H_r = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$

From equation (iv);

$$-643.1 = 2\Delta H_f(\text{AlCl}_3(\text{aq})) - \Delta H_f(\text{Al}_2\text{Cl}_6(\text{s})) \dots \dots \dots (1)$$

$$\text{From equation (iii)} \quad -73.2 = \Delta H_f(\text{HCl}(\text{aq})) - \Delta H_f(\text{HCl}(\text{g})) \dots \dots \dots (2)$$

$$\text{But from equation (ii)} \quad 2\Delta H_f(\text{HCl}(\text{g})) = -184.1\text{kJ/mol}$$

$$\text{From which } \Delta H_f(\text{HCl}(\text{g})) = \frac{-184.1}{2}\text{kJ/mol} = -92.05\text{kJ/mol}$$

Substituting $\Delta H_f(\text{HCl}(\text{g})) = -92.05\text{kJ/mol}$ to (2);

$$-73.2 = \Delta H_f(\text{HCl}(\text{aq})) - (-92.05)$$

$$\Delta H_f(\text{HCl}(\text{aq})) = -165.25\text{kJ/mol}$$

From equation (i);

$$-1003 = 2\Delta H_f(\text{AlCl}_3(\text{aq})) - 6\Delta H_f(\text{HCl}(\text{aq}))$$

$$(\Delta H_f(\text{Al}) = 0 \text{ and } \Delta H_f(\text{H}_2) = 0)$$

$$\text{But } \Delta H_f(\text{HCl}(\text{aq})) = -165.25\text{kJ/mol.}$$

$$\text{Therefore } -1003 = 2\Delta H_f(\text{AlCl}_3(\text{aq})) - (6 \times -165.25)$$

$$\text{From which } \Delta H_f(\text{AlCl}_3(\text{aq})) = -997.25\text{kJ/mol} \dots \dots \dots (3)$$

$$\text{Substituting (3) into (1); } -643.1 = 2 \times -997.25 - \Delta H_f(\text{Al}_2\text{Cl}_6(\text{s}))$$

$$\text{From which } \Delta H_f(\text{Al}_2\text{Cl}_6(\text{s})) = -1351.4\text{kJ/mol.}$$

Therefore, the heat of formation of Al_2Cl_6 is -1351.4kJ/mol

Born-Haber cycle

The **Born – Haber cycle** (Named after and developed by the two German scientists Max **Born** and Fritz **Haber**) is the enthalpy diagram used in calculation of **lattice energy**. It is a system that allows for the calculation of the amount of energy released during the formation of an ionic bond.

- The cycle shows all necessary steps in the formation if ionic compounds.
- The formation of an ionic bond is actually a step wise process. After forming gaseous metallic and non-metallic atoms the following steps are involved in the process:
 1. An electron is removed from the metal atom to make a positive ion in the ionisation of the metal. This value is usually positive.
 2. The electron is transferred to the non-metal atom. This energy value is usually negative.
 3. The ions then attract one another, forming an ionic bond.

However, it is impossible to determine the amount of energy required to make an ionic compound from its ions (**lattice energy**) in just one step.

Instead the Born-Haber cycle is used. It is a step wise process, which is based on Hess's Law.

- Below are some examples for deeper understanding of the concept.

Example 13

Calculate the lattice energy of sodium chloride from the following data: The standard enthalpy of formation of sodium chloride is -411kJ/mol , enthalpies of atomisation of sodium and chlorine are respectively $+108$ and $+121\text{ kJ/mol}$ of gaseous atoms, the ionisation energy of sodium is $+493\text{ kJ/mol}$ and the electron affinity of chlorine is -364kJ/mol .

Solution

The following Born Haber cycle for NaCl can be drawn (not drawn to scale).

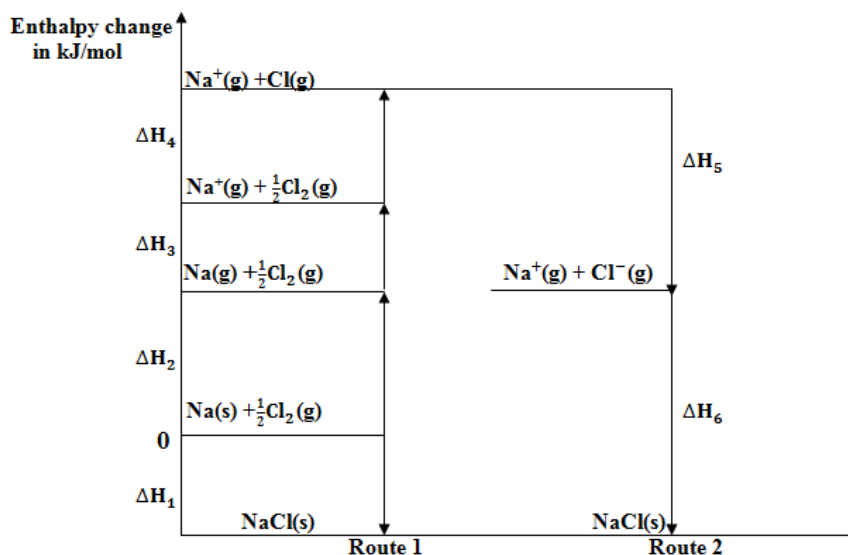


Figure 24.7 Born-Haber cycle for NaCl

Where:

ΔH_1 is the standard enthalpy of formation of sodium chloride = -411kJ/mol

ΔH_2 is the standard enthalpy of atomisation of sodium = $+108\text{kJ/mol}$

ΔH_3 is the ionisation energy of sodium = $+493\text{kJ/mol}$

ΔH_4 is the standard enthalpy of atomisation of chlorine = $+121\text{kJ/mol}$

ΔH_5 is the electron affinity of chlorine = -364kJ/mol

ΔH_6 is the lattice energy of sodium chloride

Then by Hess's law of constant heat summation:

Enthalpy change in **Route 1** = Enthalpy change in **Route 2**

Therefore; $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$

Substituting $-411 = 108 + 493 + 121 - 364 + \Delta H_6$

$\Delta H_6 = -769\text{kJ/mol}$

The lattice energy of sodium chloride is -769kJ/mol

Example 14

Calculate the lattice energy of potassium chloride from the following data:

The standard enthalpy of formation of potassium chloride = -436kJ/mol

The standard enthalpy of atomisation of potassium = $+90\text{kJ/mol}$

The standard enthalpy of atomisation of chlorine = $+121\text{kJ/mol}$

The standard electron affinity of chlorine = -364kJ/mol

The standard ionisation energy of potassium = $+420\text{kJ/mol}$

Solution

Consider the Born- Haber cycle of formation of KCl as shown below:

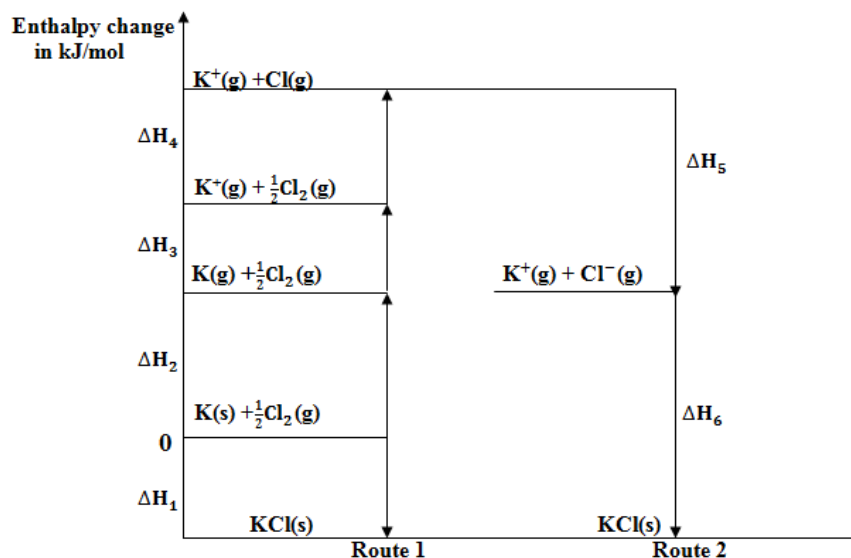


Figure 24.8 Born-Haber cycle for KCl

Where:

ΔH_1 is the standard enthalpy of formation of potassium chloride = -436kJ/mol

ΔH_2 is the standard enthalpy of atomisation of potassium = $+90\text{kJ/mol}$

ΔH_3 is the ionisation energy of potassium = $+420\text{kJ/mol}$

ΔH_4 is the standard enthalpy of atomisation of chlorine = +121kJ/mol

ΔH_5 is the electron affinity of chlorine = -364kJ/mol

ΔH_6 is the lattice energy of potassium chloride

Then by Hess's law of constant heat summation:

Enthalpy change in **Route 1** = Enthalpy change in **Route 2**

Therefore; $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$

Substituting $-436 = 90 + 420 + 121 - 364 + \Delta H_6$

$\Delta H_6 = -703\text{kJ/mol}$

The lattice energy of potassium chloride is -703kJ/mol

Example 15

For calcium, the heat of sublimation (atomisation) is 11kJ/mol and the first and second ionisation potentials are 33kJ/mol and 65.2kJ/mol respectively. For Cl_2 the heat of dissociation is 13.9kJ/mol and electron affinity of chlorine gaseous atom is -20.8kJ/mol. The standard heat of formation of CaCl_2 is -45.4kJ/mol

(i) Draw Born- Haber cycle for CaCl_2

(ii) Calculate the lattice energy for the process: $\text{Ca}^{2+}(\text{g}) + 2\text{Cl}^-(\text{g}) \rightarrow \text{CaCl}_2(\text{s})$

(iii) If Ca^{2+} and Cl^- ions formed a hypothetical crystal CaCl , the lattice energy would be +43kJ/mol. Use this value to calculate the heat of formation of the hypothetical CaCl .

(iv) Which one has more stable crystal lattice, CaCl_2 or CaCl ? Give reasons.

Solution

(i) Born- Haber cycle for CaCl_2

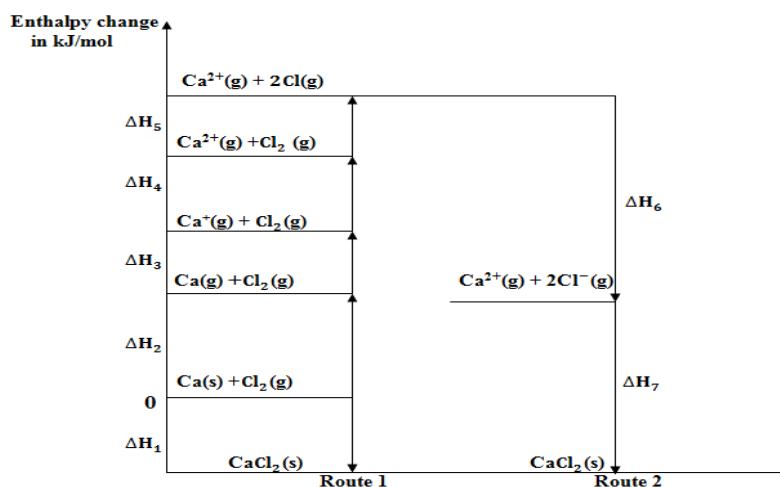


Figure 24.9 Born-Haber cycle for CaCl_2

Where:

ΔH_1 = The standard heat of formation of $\text{CaCl}_2 = -45.4\text{kJ/mol}$

ΔH_2 = Heat of sublimation of $\text{Ca} = 11\text{kJ/mol}$

ΔH_3 = First of ionisation energy of $\text{Ca} = 33\text{kJ/mol}$

ΔH_4 = Second ionisation energy of $\text{Ca} = 65.2\text{kJ/mol}$

ΔH_5 = Dissociation energy of $\text{Cl}_2 = 13.9\text{kJ/mol}$

ΔH_6 = Twice the electron affinity of chlorine = $2 \times -20.8 = -41.6\text{kJ/mol}$.

ΔH_7 = Lattice energy of CaCl_2

By Hess's law; Enthalpy change in **Route 1** = Enthalpy change in **Route 2**

Thus; $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7$

Substituting $-45.4 = 11 + 33 + 65.2 + 13.9 - 41.6 + \Delta H_7$

$\Delta H_7 = -126.9 \text{ kJ/mol}$

(ii) So lattice energy for the process; $\text{Ca}^{2+}(\text{g}) + 2\text{Cl}^{-}(\text{g}) \rightarrow \text{CaCl}_2(\text{s})$ is -126.9 kJ/mol

(iii) When Ca^+ and Cl^- forms a hypothetical crystal CaCl :

- There is not second ionisation energy of Ca, so ΔH_4 is ignored
- Dissociation energy of Cl_2 is replaced by its atomisation energy as only one atom is required, such that $A.E = \frac{1}{2}D.E$
- Twice the electron affinity of chlorine is replaced by simply electron affinity (for one atom only) because unlike CaCl_2 which need two atoms of chlorine during its formation, CaCl needs one atom only.

So electron affinity of chlorine is -20.8 kJ/mol

Thus using: $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_5 + \Delta H_6 + \Delta H_7$ (with above modifications)

Where:

ΔH_1 = Heat of formation of CaCl

ΔH_2 = Heat of sublimation of Ca = 11 kJ/mol

ΔH_3 = First of ionisation energy of Ca = 33 kJ/mol

ΔH_5 = Atomisation energy of chlorine = $\frac{1}{2} D.E = \frac{1}{2} \times 13.9 = 6.95 \text{ kJ/mol}$

ΔH_6 = Electron affinity of chlorine = -20.8 kJ/mol

ΔH_7 = Lattice energy of CaCl = $+43 \text{ kJ/mol}$

Then $\Delta H_1 = 11 + 33 + 6.95 - 20.8 + 43 = 73.15 \text{ kJ/mol}$

The heat of formation of hypothetical CaCl is 73.15 kJ/mol

(iv) CaCl_2 has more stable crystal lattice than CaCl .

Reasons:

- 1) CaCl_2 has more negative heat of formation (CaCl_2 has negative value while CaCl has positive heat of formation)
- 2) CaCl_2 has more negative lattice energy (CaCl_2 has negative value while CaCl has positive lattice energy)

Example 16

Carefully study the information given below:

Atomisation energy of Ca = $+177 \text{ kJ/mol}$

First ionisation energy of Ca = $+590 \text{ kJ/mol}$

Second ionisation energy of Ca = $+1110 \text{ kJ/mol}$

Heat of atomisation of oxygen = $+249 \text{ kJ/mol}$

First electron affinity of oxygen = -149 kJ/mol

Second electron affinity of oxygen = $+790 \text{ kJ/mol}$

Heat of formation of CaO = -636 kJ/mol

From this information draw a fully labelled Born Haber diagram for CaO and calculate the lattice energy of CaO .

Born – Heber cycle for CaO

Before drawing Born – Heber cycle, it is important to determine the amount of total electron affinity (First electron affinity + second electron affinity)

- This enables us to understand whether the electron affinity is positive or negative; thus knowing the direction of the cycle with respect electron affinity whether is upward (for positive total) or downward (for negative total)

Total electron affinity of oxygen = First electron affinity + Second electron affinity

$$= (-149 + 790) \text{ kJ/mol} = +641 \text{ kJ/mol}$$

(On your own draw the Born Heber cycle of CaO without determining this, i.e. by indicating separately first and second electron affinity of the oxygen).

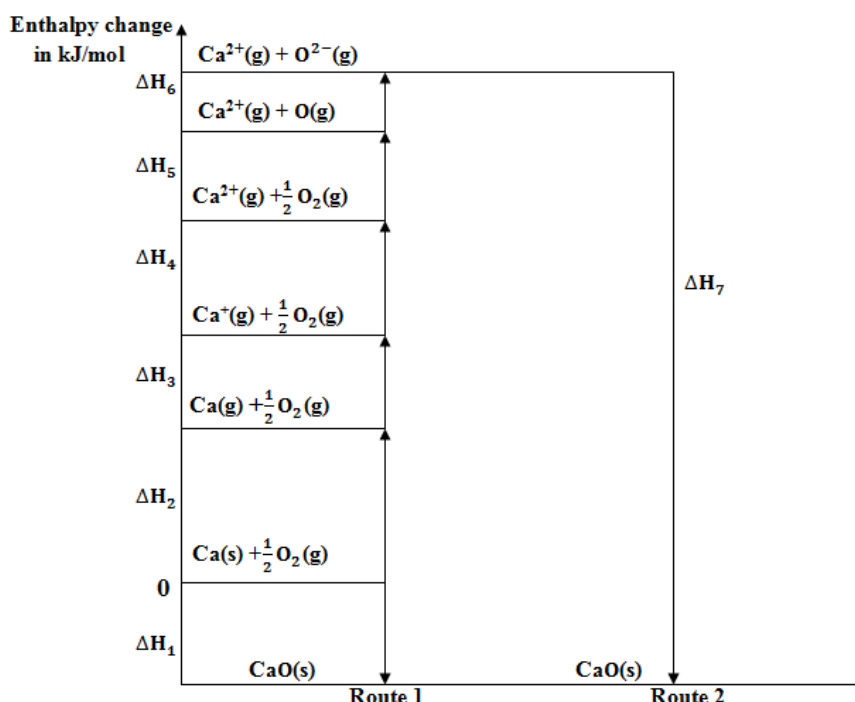


Figure 24.10 Born-Haber cycle for CaO

Where:

ΔH_1 = Heat of formation of CaO = -636 kJ/mol

ΔH_2 = Atomisation energy of Ca = $+177 \text{ kJ/mol}$

ΔH_3 = First ionisation energy of Ca = $+590 \text{ kJ/mol}$

ΔH_4 = Second ionisation energy of Ca = $+1110 \text{ kJ/mol}$

ΔH_5 = Heat of atomisation of oxygen = $+249 \text{ kJ/mol}$

ΔH_6 = Total electron affinity oxygen = $+641 \text{ kJ/mol}$

ΔH_7 = Lattice energy of CaO.

By the Hess's law:

Enthalpy change in **Route 1** = Enthalpy change in **Route 2**.

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7$$

Substituting $-636 = 177 + 590 + 1110 + 249 + 641 + \Delta H_7$

$$\Delta H_7 = -3403 \text{ kJ/mol}$$

So lattice energy for CaO is -3403 kJ/mol

Thermochemical calculations by using bond energies

For better understanding of this method, we must firstly understand the term, bond energy. The term, bond energy is closely related to another term, bond dissociation energy. Good understanding of the two terms (bond dissociation energy and bond energy) is crucial in understanding thermochemical calculations by using bond energies.

Bond dissociation energy versus bond energy

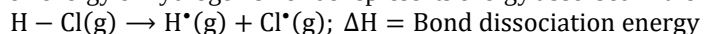
When a bond breaks, energy is absorbed. So the process of bond breaking is endothermic process.

The energy required to break the bond is termed as **bond dissociation energy** (or **bond dissociation enthalpy**).

As an example to bond dissociation enthalpy (BDE); to break up 1 mole of gaseous hydrogen chloride molecules into separate gaseous hydrogen and chlorine atoms takes 432 kJ. The $+432 \text{ kJ mol}^{-1}$ is then known as the bond dissociation energy for the H–Cl bond.

By definition; **Bond dissociation energy (enthalpy)** is the energy (enthalpy) required (absorbed) per mole of a gaseous compound to break homolytically a particular covalent bond to produce gaseous fragments.

Being homolytic (in breaking the bond each atom takes one electron from the two bonded electrons), the bond dissociation energy of hydrogen chloride represents energy absorbed in the following process:



And **not** in the following process:



We have seen the example of bond dissociation in the simple molecule with two atoms only (diatomic molecule) where there is only one bond; **what if there is more complex molecule where there are more than two covalent bonds?**

To understand this, consider two cases of water molecule (H_2O) and methane molecule (CH_4).

For H_2O :

Here water has two O – H covalent bonds and the two bonds break in steps.

An HO – H bond of a water molecule (H – O – H) has 498 kJ/mol of bond dissociation energy, and 430 kJ/mol is needed to break the remaining O – H bond as per following equations:

First step: $\text{HO} - \text{H} \rightarrow \text{HO}^\bullet + \text{H}^\bullet$; $\Delta H = 498 \text{ kJ/mol}$

Water

Second step: $\text{H} - \text{O}^\bullet \rightarrow \text{O}^\bullet + \text{H}^\bullet$; $\Delta H = 430 \text{ kJ/mol}$

A little bit confusion!

The same kinds of O – H bonds in the same molecule of water have different bond dissociation energy! **If we want to mention the value of bond dissociation energy for O-H bond what is its real value?**

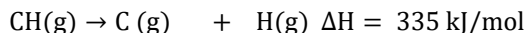
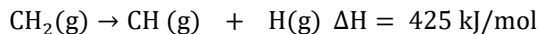
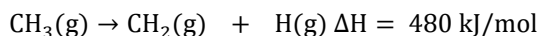
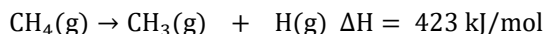
To answer above question, the **bond energy term** was introduced. It is an average of all bond dissociation energies of the same kind present in the molecule.

$$\text{Thus for O} - \text{H bond; } \text{Bond energy} = \frac{498 + 430}{2} = 464 \text{ kJ/mol}$$

Bond energy is also termed as **mean bond energy** or **average bond energy** (Although in most cases the prefix 'mean' or 'average' is dropped to remain with simply 'bond energy')

For CH₄:

In the same way for removing successive hydrogen atoms from methane the bond dissociation energies are 423 kJ/mol for breaking CH₃ – H bond, 480 kJ/mol for breaking CH₂ – H bond, 425 kJ/mol for breaking CH – H bond and finally 335 kJ/mol for breaking C – H bond.



Thus for C – H bond;

$$\text{Bond energy} = \frac{423+480+425+335}{4} = 416 \text{ kJ/mol (By approximation)}$$

Notice that none of the C – H bond dissociation energy is 416 kJ/mol.

So the following conclusion can be made on the use of two terms; bond dissociation energy and dissociation energy:

In a **diatomic molecule** (a molecule with two atoms only. The two atoms may be the same like in Cl₂ or different like in HCl) only one bond breaks per molecule and such that there is only one figure of the bond dissociation energy and hence for diatomic molecule;

Bond dissociation energy = Bond energy

For a molecule with more than one bond, an average must be found as the bond dissociation energies are always different and hence for a **polyatomic molecule** (a molecule with more than two atoms);

Bond dissociation energy = Bond energy

By definition; **bond energy (enthalpy)** is the average energy (enthalpy) required to dissociate bonds of the same type in 1 mole of a given gaseous compound.

Very important to note!

The reader should note the importance of use of word '**gaseous**' in both definition of bond dissociation energy and bond energy. You can only use bond energies directly if everything you are working with is in the gas state.

You cannot use bond energies to do calculations directly from substances starting in the liquid or solid state.

If you have liquid or solid present, you need an extra energy term to work out the enthalpy change when you convert them to gas. That term is the atomisation energy (enthalpy of atomisation) or more specific; **sublimation energy** for converting solid to gas or **vapourisation energy** for converting liquid to gas.

Significance of bond energy

When bond breaks heat energy is absorbed from the surroundings (endothermic process) while when a new bond is formed heat energy is evolved to the surroundings (exothermic process). So there are two main information which can be deduced from the bond energy which are:

1. It gives amount of energy required to break the bond thus determining stability of the bond

A bond with greater amount of energy is more stable and therefore the compound containing those bonds is more stable too.

2. It gives amount of energy released during the formation of the bond

Amount of energy released when a new bond is formed is numerically equal (but opposite in sign) to the amount of bond energy of the bond.

For Example, If C – H bond energy is 416 kJ/mol it means that:

- The process of breaking C – H bond requires the energy of 416 kJ/mol by average.
- During formation of C – H bond, the average energy of 416 kJ/mol is released to surroundings.

Being aware of that two information, enthalpy of reaction can be determined from bond energies as discussed in the next section.

In summary:

- Bond energy explain the stability of covalent bond and compound.
- Bond energy enables indirect determination (calculation) of heat of reaction.

It should be understood that:

Bond energy which applies for covalent bond is equivalent to lattice energy which applies for ionic bond. Bond energy gives the strength of covalent bond while lattice energy gives the strength the ionic bond.

Example 17

It takes 1656kJ/mol to break all bonds in methane (CH₄) and 4006 kJmol⁻¹ to break all bonds in propane, C₃H₈. Based on these data calculate the average bond energy of the C – C bond?

Solution

Methane has **four** C – H bonds

$$\text{So bond energy of C – H} = \frac{\text{Total energy for dissociating all four bonds}}{4} = \frac{1656}{4} = 414\text{kJ/mol}$$

Propane (C₃H₈) has **eight** C – H bonds and **two** C – C (On your own write the structure of propane to deduce this fact).

$$\text{So total bond energies in propane} = 8(\text{C – H}) + 2(\text{C – C}) = 4006$$

$$\text{Substituting } (8 \times 414) + 2(\text{C – C}) = 4006; \text{C – C} = \frac{694}{2} = 347\text{kJ/mol}$$

Hence the average bond energy for C – C bond is 347kJ/mol.

Relationship between bond energies and heat of reaction

In chemical reactions, bonds are broken in the reactants and are formed in the products. The difference between the total energy absorbed in breaking the bonds and the total energy released in formation of bonds of products results to heat of the reaction.

Thus if: $\sum \text{B. E}(\text{reactants})$ represents summation of bond energies in reactants side,

$\sum \text{B. E}(\text{products})$ represents summation of bond energies in products side,

$$\text{Then } \Delta H_r = \sum \text{B. E}(\text{reactants}) - \sum \text{B. E}(\text{products})$$

Example 18

Calculate the standard enthalpy of the reaction: CH₂ = CH₂ + H₂(g) → CH₃CH₃(g)

Mean standard bond enthalpies are (in kJ/mol)

$$\text{C – H} = 416, \text{C} = \text{C} = 612, \text{C – C} = 348, \text{H – H} = 436$$

Solution

In reactants side there are:

One C = C, four C – H, one H – H

In products side there are:

One C – C, six C – H

$$\begin{aligned} \text{Using } \Delta H_r &= \sum \text{B. E}(\text{reactants}) - \sum \text{B. E}(\text{products}) \\ &= (\text{C} = \text{C}) + 4(\text{C – H}) + (\text{H – H}) - (\text{C – C}) - 6(\text{C – H}) \end{aligned}$$

$$= (\text{C} = \text{C}) + (\text{H} - \text{H}) - 2(\text{C} - \text{H}) - (\text{C} - \text{C}) \quad (\text{By combining like terms})$$

$$= 612 + 436 - (2 \times 416) - 348 = -132 \text{ kJ/mol}$$

So the standard enthalpy of the reaction is -132 kJ/mol .

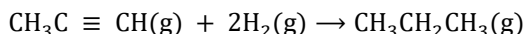
Example 19

Calculate the enthalpy of hydrogenation of propyne from the following bond energies;

Bond	Bond energy in kJ/mol
$\text{C} \equiv \text{C}$	837
$\text{C} = \text{C}$	611
$\text{C} - \text{C}$	347
$\text{C} - \text{H}$	414
$\text{H} - \text{H}$	437

Solution

The balanced equation for hydrogenation of propyne is:



In reaction side, there are: Four $\text{C} - \text{H}$, two $\text{H} - \text{H}$, One $\text{C} - \text{C}$, One $\text{C} \equiv \text{C}$

In products side, there are; Two $\text{C} - \text{C}$, eight $\text{C} - \text{H}$

Using: $\Delta H_r = \sum \text{B.E}(\text{reactants}) - \sum \text{B.E}(\text{products})$

$$= 4(\text{C} - \text{H}) + 2(\text{H} - \text{H}) + (\text{C} - \text{C}) + (\text{C} \equiv \text{C}) - 2(\text{C} - \text{C}) - 8(\text{C} - \text{H})$$

$$= 2(\text{H} - \text{H}) + (\text{C} \equiv \text{C}) - (\text{C} - \text{C}) - 4(\text{C} - \text{H}) \quad (\text{By combining like terms})$$

$$= (2 \times 437) + 837 - 347 - (4 \times 414) = -292 \text{ kJ/mol}$$

So the enthalpy of hydrogenation of propyne is -292 kJ/mol .

Example 20

Given that, average bond energies; $(\text{C} - \text{H}) = 413 \text{ kJ/mol}$, $(\text{C} - \text{C}) = 348 \text{ kJ/mol}$, $(\text{O} - \text{H}) = 463 \text{ kJ/mol}$. Atomisation energy of hydrogen and oxygen are 217 kJ/mol and 247 kJ/mol respectively. The enthalpy of formation of gaseous $\text{C}_2\text{H}_5\text{OH}$ is -235.4 kJ/mol and atomisation energy of carbon is 716.7 kJ/mol . Calculate the $\text{C} - \text{O}$ bond energy.

Solution

An equation to show formation of $\text{C}_5\text{H}_5\text{OH}$ is: $2\text{C}(\text{s}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g})$

In reactants side:

- $2 \times 716.7 = 1433.4 \text{ kJ/mol}$ are absorbed in atomizing 2 moles of carbon atoms so as to form 2 moles of gaseous carbon atoms.
- $6 \times 217 = 1302 \text{ kJ/mol}$ are absorbed in atomizing 6 moles of hydrogen atoms so as to form 6 moles of gaseous hydrogen atoms.
- 247 kJ/mol is absorbed in atomizing 1 mole of oxygen atom so as to form one mole of gaseous oxygen atom.

Thus the total energy absorbed in reactants side is: $(1433.4 + 1302 + 247) \text{ kJ} = 2982.4 \text{ kJ}$

In products side:

- $5 \times 413 = 2065\text{kJ}$ are released in forming 5 moles of C – H bonds.
- 348 kJ are released in forming 1 mole of C – C bond.
- 463kJ are released in forming 1 mole of O – H bond.
- Unknown energy is released in forming 1 mole C – O bond

Total energy released in products side = $2065 + 348 \times 463 + (\text{C} - \text{O}) = 2876 + (\text{C} - \text{O})$

Thus the total energy released in products side is $2876 + (\text{C} - \text{O})$

Using: $\Delta H_r = \sum \text{B. E}(\text{reactants}) - \sum \text{B. E}(\text{products})$

But in this question: Heat reaction = Heat of formation of $\text{C}_2\text{H}_5\text{OH}$

Then: $-235.4 = 2982.4 - 2876 - (\text{C} - \text{O}); \text{C} - \text{O} = 341.8\text{kJ/mol}$

The bond energy of C – O bond is 341.8kJ/mol .

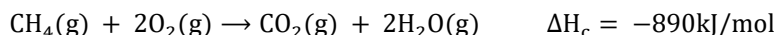
Example 21

The heats of combustion of methane, carbon and hydrogen are 890kJ/mol , 393kJ/mol and 285.8kJ/mol respectively. The heat of sublimation of carbon is 720kJ/mol and heat of dissociation of hydrogen molecule is 431kJ/mol . Calculate the C – H bond energy in methane.

Solution

Very important to note that: Heat of combustion **must be negative** because combustion is exothermic. So in calculation we **must** use values which include negative signs (In some cases signs of thermochemical values are deliberately ignored because are yet contained in their definitions e.g. heat of combustion is the heat evolved So someone may consider the negative sign has been contained in the word '**evolved**' thus making unnecessary to include the sign in the value of heat of combustion. However, it is not allowed to ignore the sign in calculations).

Equation for combustion of methane is:



But $\Delta H_c(\text{Carbon}) = \Delta H_f(\text{CO}_2) = -393\text{kJ/mol}$

$\Delta H_c(\text{Hydrogen gas}) = \Delta H_f(\text{H}_2\text{O}) = -285.8\text{kJ/mol}$

And $\Delta H_f(\text{O}_2) = 0$

Using $\Delta H_r = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$

Then: $\Delta H_c(\text{CH}_4) = \Delta H_f(\text{CO}_2) + 2\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{CH}_4)$

$-890 = -393 + (2 \times -285.8) - \Delta H_f(\text{CH}_4)$

$\Delta H_f(\text{CH}_4) = -74.6\text{kJ/mol}$

Thermochemical equation to show formation of methane: $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$

In the reactants side:

- 720kJ/mol is absorbed in sublimating (atomizing) carbon atoms so as to form one mole of gaseous carbon atoms.
- $2 \times 431 = 862\text{kJ/mol}$ is absorbed in dissociating 2 moles of hydrogen molecules so as form 4 moles of gaseous atoms.

In the products side:

- Unknown energy is released in forming four (C – H) bonds.

Using $\Delta H_r = \sum \text{B. E}(\text{reactants}) - \sum \text{B. E}(\text{products})$

But in this problem; Heat of reaction = Heat of formation of CH_4 .

Then $-74.6 = 720 + 862 - 4(\text{C} - \text{H}); 4(\text{C} - \text{H}) = 1656.6\text{kJ/mol}$

From which $(C - H) = \frac{1656.6}{4} = 414.15 \text{ kJ/mol}$

Hence bond energy of C – H bond is 414.15 kJ/mol.

APPLICATIONS OF HESS'S LAW

The main significance of Hess's law is to allow the enthalpy change (ΔH) for a reaction to be calculated even when it cannot be measured directly. This is accomplished by performing basic algebraic operations based on the chemical equation of reactions using previously determined values for the enthalpies of formation.

Hess's law of constant heat summation is useful in the determination of enthalpies of the following:

1. Enthalpy of formation

There are a large number of compounds such as methane, benzene, ethane, ethyne which cannot be directly synthesized from their elements. Hence, their enthalpy of formation cannot be determined by the calorimetric method.

Other compounds like carbon monoxide, CO, and nitrogen monoxide, NO, are very unstable intermediates (as they are easily oxidised by oxygen into CO₂ and NO₂ respectively) such that even though they can be synthesized from their constituent elements (C and O for CO₂ or N and O₂ for NO), it is very difficult to control the amount of oxygen so as to prevent their further oxidation.

In case of such substances the enthalpy of formation can be determined by an indirect method based upon Hess's law as done in the **example 8, 10(a)** etc.

2. Enthalpy of transition

Transition implies *the conversion of one allotropic form of a substance to another*.

For example, change of graphite to diamond, red phosphorus to yellow phosphorus and rhombic sulphur to monoclinic sulphur.

Such reactions have so small enthalpy change accompanying them that cannot be measured directly. However, Hess's law is quite helpful in determining the enthalpy of transition as done in the **example**

3. Enthalpy of reaction

Some reactions are too slow to measure their enthalpy of reaction directly. Hess's law enables indirect measurement of enthalpy of these reactions from the knowledge of standard enthalpy of formation of various reactants and the products as done in the **example 9, 10(b)** etc.

4. Enthalpy of hydration of anhydrous salt

Hydration means the conversion of an anhydrous salt into its hydrate by combining with specific number of moles of water.

Direct measurement of enthalpy of hydration is not possible. However, the use of Hess's law makes it possible as done in the **example 3**.

5. Lattice enthalpy

Lattice energies of ionic substances are always indirectly determined by Hess's law through construction of Born-Haber cycles if the electron affinity to form the anion is known (Born-Haber cycle will be discussed in the next chapter).

6. Electron affinity

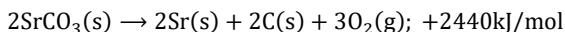
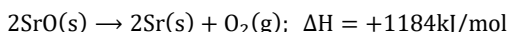
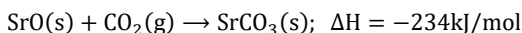
Electron affinities can also be indirectly determined by using Born-Haber cycle with theoretical lattice energy.

DIGGING DEEPER EXERCISE 24

EXERCISE 24A: BINDER QUESTIONS

Question 1

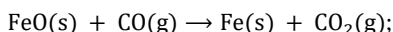
Given the following data:



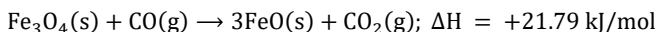
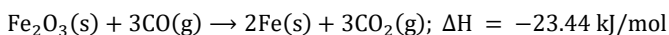
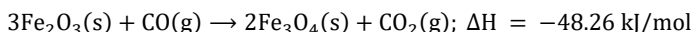
Find the ΔH of the following reaction: $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$

Question 2

What is the standard enthalpy of reaction for the reduction of iron (II) oxide by carbon monoxide?

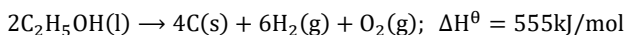
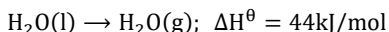
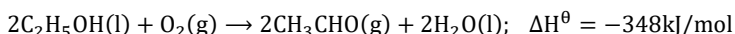
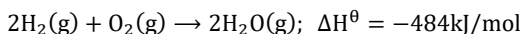
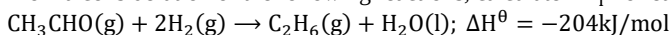


Given the following information:



Question 3

From a consideration of the following reactions, calculate ΔH_f^θ for ethane, $\text{C}_2\text{H}_6\text{(g)}$.



Question 4

If the heat of combustion data for diamond and graphite is -395.4 kJ/mol and -393.5 kJ/mol respectively; calculate the heat of transition of diamond to graphite.

Question 5

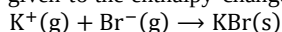
Some standard enthalpy change of combustion values are listed below:

Substance	$\Delta H^\theta / \text{kJmol}^{-1}$
C (graphite)	-393.5
$\text{H}_2\text{(g)}$	-285.8
ethane $\text{C}_2\text{H}_6\text{(g)}$	-1560.0

- Write thermochemical equation for the standard enthalpy change of combustion of ethane
- Use the data to calculate the standard enthalpy change of formation of ethane. Draw Hess's law cycle as part of your answer.

Question 6

(a) What name is given to the enthalpy change of the following reaction?



(b) Use the following data to construct a fully-labelled energy diagram and use it to calculate the enthalpy change in (a).

	$\Delta H^\theta / \text{kJ mol}^{-1}$
$\text{Br}_2(\text{l}) \rightarrow 2\text{Br}(\text{g})$	+224
$\text{Br}(\text{g}) + \text{e} \rightarrow \text{Br}^-(\text{g})$	-348
$\text{K}(\text{s}) + \frac{1}{2}\text{Br}_2(\text{l}) \rightarrow \text{KBr}(\text{s})$	-392
$\text{K}(\text{s}) \rightarrow \text{K}(\text{g})$	+90
$\text{K}(\text{g}) \rightarrow \text{K}^+(\text{g}) + \text{e}$	+424

Question 7

The following data relate to lithium chloride.

Standard molar enthalpy change of solution is -37 kJ/mol .

Lattice enthalpy is -846 kJ/mol .

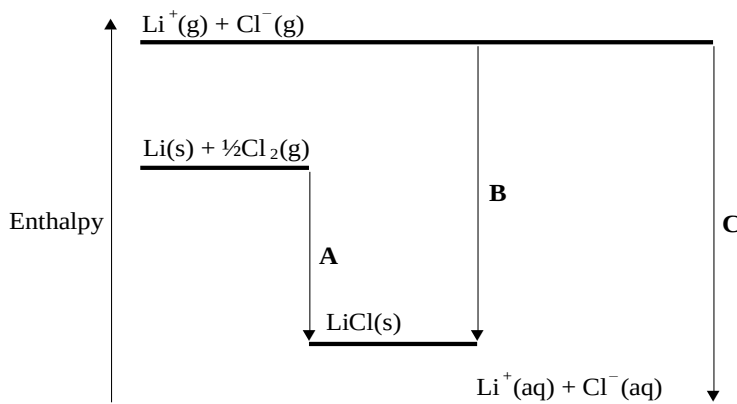


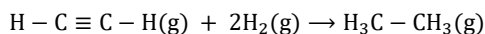
Figure 24.11 Enthalpy diagram for question 7

(a) Give the name of each of the changes **A** and **B**.

(b) Calculate the value of the enthalpy change represented by **C** and suggest the name(s) of the enthalpy change(s).

Question 8

Hydrogenation of double and triple bonds is an important industrial process. Calculate (in kJ/mol) the standard enthalpy change ΔH for the hydrogenation of ethyne (acetylene) to ethane:



Bond enthalpies (in kJ/mol): $\text{C}-\text{C}$ (347); $\text{C}\equiv\text{C}$ (839); $\text{C}-\text{H}$ (413); $\text{H}-\text{H}$ (432)

Question 9

Under suitable conditions decane ($\text{C}_{10}\text{H}_{22}$) can undergo cracking to give butane (C_4H_{10}) and cyclopropane (C_3H_6) as per equation: $\text{C}_{10}\text{H}_{22} \rightarrow \text{C}_4\text{H}_{10} + 2\text{C}_3\text{H}_6$

Assuming bonds broken and formed only, what is the enthalpy change for the above reaction?

Question 10

Calculate the bond energy of the $\text{Cl}-\text{F}$ bond using the following data:



Bond enthalpies (in kJ/mol): $\text{Cl}-\text{Cl}$ (239); $\text{F}-\text{F}$ (159)

EXERCISE 24B: REAL QUESTIONS**Question 11**

Born-Haber cycle is an important tool that helps us to indirectly determine lattice energy of compounds. This is because direct determination of lattice energy through experiment is impossible. However, lattice energy determined by the Born-Haber cycle are not realised in practice for most compounds.

- (i) Why direct determination of lattice energy by calorimetry is impossible?
- (ii) Explain why lattice energy of most ionic compounds cannot be precisely determined by Born-Haber cycle?
- (iii) Which compounds can Born-Haber cycle used to determine their lattice energy more accurate?

Question 12

Calculations of heat of reaction from bond energy is very simple method of applying Hess's law. However, when we come to real life, chemists prefer heat of formation to the bond energy. Give two reasons to support chemists' decision.

Question 13

Practically it is possible to convert one allotropic form of an element to another allotropic form; as an example, diamond can be converted to graphite under suitable conditions. However, we cannot measure heat change in these kind of reactions, why?

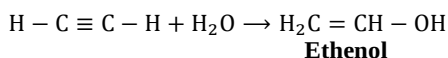
Question 14

Blue crystals of hydrated copper (II) sulphate can be formed by reaction between anhydrous CuSO_4 and water according to the following equation: $\text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$. However, we cannot apply calorimetry to determine the enthalpy change for this reaction.

- (i) Why the calorimetric method is not applicable?
- (ii) Give any two methods which can be applied to determine the enthalpy of the above reaction.

Question 15

Alkynes such as ethyne, $\text{H} - \text{C} \equiv \text{C} - \text{H}$, are unsaturated compounds and undergo addition reactions in a similar fashion to alkenes. Under suitable conditions, ethyne will react with water, and the reaction might be expected to be;



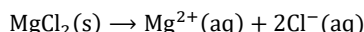
Using the bond enthalpies given below, suggest why in real life, the product of this reaction is not ethenol, but its structural isomer ethanal, CH_3CHO .

$$\Delta\text{H}/\text{kJ mol}^{-1}: \quad \text{C} - \text{H} \ 412, \text{C} = \text{C} \ 612, \text{C} - \text{O} \ 360, \text{C} = \text{O} \ 743, \text{O} - \text{H} \ 463$$
$$\text{C} - \text{C} \ 348, \text{C} \equiv \text{C} \ 837$$

EXERCISE 24C: HOT QUESTIONS**Question 16**

The magnesium ions in seawater are mainly associated with chloride ions.

- (a) Use the following ΔH_f^θ values to calculate a value for the ΔH^θ of the following reaction:

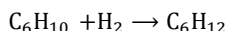


Species	ΔH_f^θ in kJ/mol
$\text{MgCl}_2(\text{s})$	-641
$\text{Mg}^{2+}(\text{aq})$	-467
$\text{Cl}^-(\text{aq})$	-167

- (b) Use your answer to explain why MgCl_2 is very soluble in water.

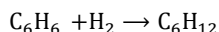
Question 17

- (a) Cyclohexene, C_6H_{10} , contains one $\text{C}=\text{C}$ double bond in its molecule, of the type found in ethene. It reacts with hydrogen to form cyclohexane, C_6H_{12} , as follows:



Calculate ΔH for this reaction, given that the enthalpies of formation of cyclohexene and cyclohexane are -36kJ/mol and -156kJ/mol respectively.

- (b) Benzene undergoes a similar reaction with hydrogen to form cyclohexane:



Predict the value of ΔH for this reaction, assuming that benzene contains three $\text{C}=\text{C}$ double bonds of the type found in ethene.

- (c) The actual value of ΔH for the reaction in (c) is -207kJ/mol . What can you deduce from this about the stability of the benzene ring? Use an enthalpy diagram to illustrate your answer.

Question 18

- (a) Using the data provided, construct a Born-Haber cycle for magnesium chloride, MgCl_2 , and from it determine the electron affinity of chlorine.

$\Delta H/\text{kJ mol}^{-1}$

Enthalpy of atomisation of chlorine	+122
Enthalpy of atomisation of magnesium	+148
First ionisation energy of magnesium	+738
Second ionisation energy of magnesium	+1451
Lattice enthalpy of magnesium chloride	-2526
Enthalpy of formation of magnesium chloride	-641

- (b) The theoretically calculated value for the lattice enthalpy of magnesium chloride is -2326kJ/mol . Explain the difference between the theoretically calculated value and the experimental value given in the data in (a), in terms of the bonding of magnesium chloride.

Question 19

A Born-Haber cycle for the formation of calcium oxide is shown below.

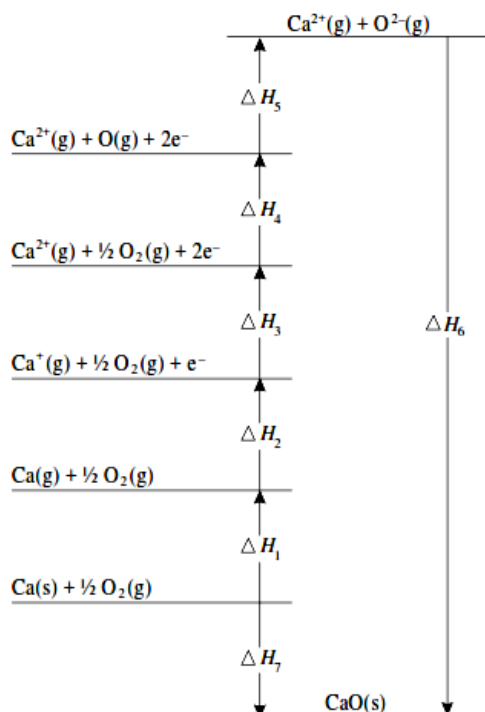


Figure 24.12 Born Haber cycle for question 19

Data $\Delta H/\text{kJ mol}^{-1}$:

$$\Delta H_1 = +193; \Delta H_2 = 590; \Delta H_3 = +1150; \Delta H_4 = +248; \Delta H_6 = -3513; \Delta H_7 = -635.$$

- Identify the change which represents the lattice enthalpy of CaO.
- What enthalpy change does the value of ΔH_2 represent?
- Use the data above to calculate ΔH_5
- Use this value of ΔH_5 to calculate the first electron affinity of oxygen, given that the second electron affinity of oxygen is +844 kJ/mol.

Question 20

A Born–Haber cycle for the formation of calcium sulphide is shown below. The cycle includes enthalpy changes for all Steps except Step F. (The cycle is not drawn to scale.)

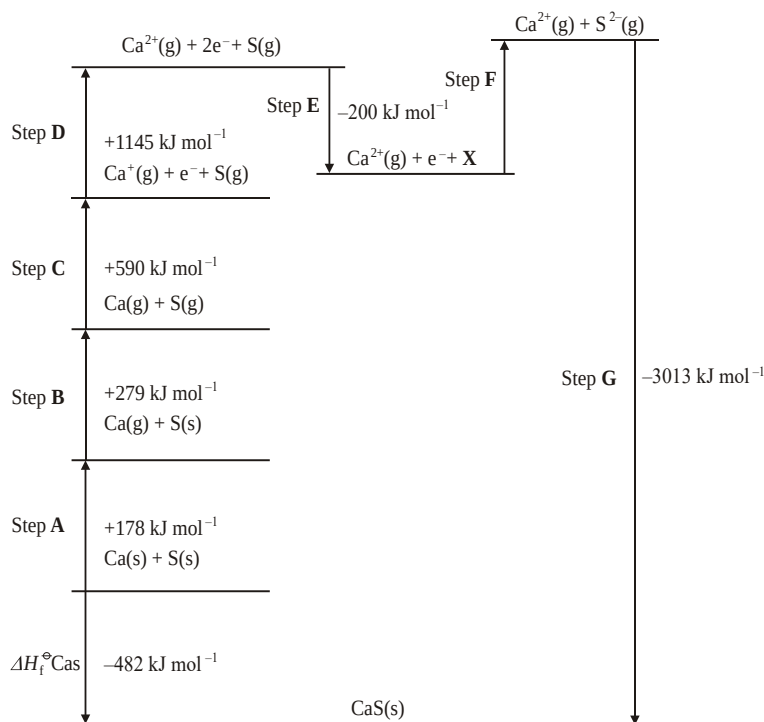


Figure 24.13 Born Haber cycle for question 20

- Identify the species **X** formed in Step E.
- Suggest why Step **F** is an endothermic process.
- Name the enthalpy change for each of the following steps.
 - Step **B**
 - Step **D**
 - Step **F**
- Explain why the enthalpy change for Step **D** is larger than that for Step **C**.
- Use the data shown in the cycle to calculate a value for the enthalpy change for Step **F**.

Question 21

- Construct a Born-Haber cycle for the formation of calcium chloride, CaCl_2 , from its elements. Name each step in the cycle and mark on the cycle each species involved together with its state symbol.
 - When calcium reacts with chlorine under normal laboratory conditions, CaCl_2 is formed not CaCl . Identify the stages in the Born-Haber cycle for the formation of CaCl which differ from those in the cycle for the formation of CaCl_2 .
- Use the data given below to calculate the standard enthalpy of solution of CaCl_2 . Draw appropriate cycle as part of your solution.

$$\text{Lattice dissociation enthalpy of } \text{CaCl}_2 = +2255 \text{ kJ mol}^{-1}$$

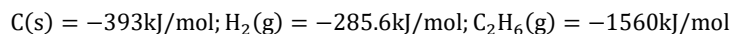
$$\text{Hydration enthalpy of calcium ions} = -1650 \text{ kJ mol}^{-1}$$

$$\text{Hydration enthalpy of chloride ions} = -384 \text{ kJ mol}^{-1}$$

- Using your answer to part (b)(i), deduce how the solubility of CaCl_2 changes as temperature is increased. Explain your answer.

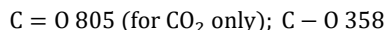
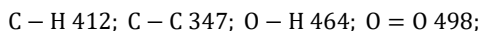
Question 22

- (a) Given the following standard enthalpies of combustion, ΔH_f^θ ,



Calculate standard enthalpy of formation of ethane

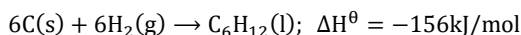
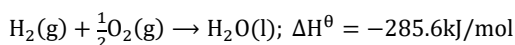
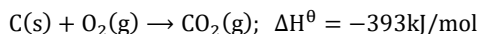
- (b) Given the following bond enthalpies (bond energies) in kJ/mol :



- (i) Calculate the enthalpy of combustion of ethane assuming all species are gaseous.
(ii) Why in (i) do you not get the value of -1560kJ/mol ?

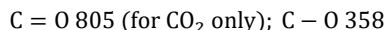
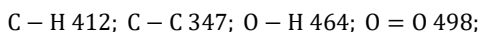
Question 23

- (a) Given that:



Calculate the standard enthalpy of combustion of cyclohexane.

- (b) Given the following bond enthalpies in kJ/mol;



Calculate theoretical enthalpy of combustion of cyclohexane, assuming all reactants and products are gases.

- (c) If the enthalpy of vapourisation of water is $+40.7\text{kJ/mol}$ and the enthalpy of vapourisation of cyclohexane is $+30.0\text{kJ/mol}$, from your answer to (b), **recalculate** the enthalpy of combustion of cyclohexane.
(d) Compare and comment on your answers to (a), (b) and (c).

EXAMINATION QUESTIONS FOR PART SEVEN

Question 1

- (a) State whether the following quantities are exothermic or endothermic.
- Ionisation energy for lithium
 - Electron affinity for iodine
 - Electron affinity for oxygen leading to O^- and O^{2-}
- (b) When a 6.5g sample of solid NaOH dissolves in 100cm^3 of water in a coffee-cup calorimeter, the temperature rises from 21.6°C to 37.8°C . Calculate the enthalpy of solution of NaOH. (Assume the specific heat of the solution formed is $4.18\text{Jg}^{-1}\text{K}^{-1}$).

Question 2

- (a) With one exception, the standard heats of formation of Mg(s) , $\text{I}_2(\text{s})$, $\text{N}_2(\text{g})$, $\text{NO}_2(\text{g})$, $\text{Br}_2(\text{l})$, $\text{Cl}_2(\text{g})$, Cu(s) and $\text{O}_2(\text{g})$ are identical. What is the exception? Explain.
- (b) For the reaction $\text{CO(g)} + \text{NO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{NO(g)}$ the amounts of activation energy for the forward and reverse reaction are known to be 32 kJmol^{-1} and 82.1 kJmol^{-1} respectively;
- Calculate the heat of reaction.
 - Draw the energy profile (i.e. potential energy) diagram for this system indicating the heat of reaction and the activation energy for forward and backward reaction.

Question 3

- (a) The Standard enthalpy changes of formation of MgCl , MgCl_2 , MgCl_3 are -110 kJ/mol , -650 kJ/mol and $+4000\text{ kJ/mol}$ respectively. How do you compare the energetic stabilities of MgCl(s) , $\text{MgCl}_2(\text{s})$ and $\text{MgCl}_3(\text{s})$ with respect to their constituent elements?
- (b) When 15.3g of sodium nitrate was dissolved in water in a calorimeter, the temperature fell from 25°C to 21.56°C . If the heat capacity of the solution and the calorimeter is $1071\text{ J/}^\circ\text{C}$, what is the enthalpy of solution of sodium nitrate?

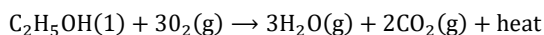
Question 4

- (a) Given the hypothetical compounds have the lattice energies as tabulated below:

Hypothetical compound	XN	XO_2	X_2C	XS_3
Lattice energy (kJ/mol)	-700	-195.3	-630	-912

Arrange the compounds in order of increasing of their stabilities.

- (b) Ethanol, which is used as a fuel, burns in air according to the equation shown below;



In an experiment to determine the heat value of ethanol, the heat produced by an ethanol burner was used to heat 200cm^3 of water. The following result were obtained:

Initial mass of lamp + ethanol = 56.69g

Final mass of lamp + ethanol = 56.46g

Initial temperature of water = 25.00°C

Final temperature of water = 31.24°C

- Assuming there were no heat loss, calculate the heat value of ethanol.
- If the experiment was carried out at standard temperature and pressure (STP), what volume of carbon dioxide gas was produced?

(C = 12, H = 1, O = 16; specific heat capacity of water, $c = 4.18\text{ kJ/kg K}$; molar volume of gas at STP = $22.41\text{ dm}^3/\text{mol}$)

Question 5

- (a) Why is it important to give the physical state of a substance in thermochemical reaction?
 (b) The standard molar enthalpy changes of neutralisation for some aqueous neutralisation reactions are given below.

	Acid	Base	$\Delta H/\text{kJmol}^{-1}$
1.	HCl	NaOH	-57.1
2.	HCl	KOH	-57.2
3.	HNO ₃	NaOH	-57.3
4.	HF	NaOH	-68.6
5.	HCl	NH ₃	-52.2
6.	CH ₃ COOH	NaOH	-55.2
7.	HCN	NH ₃	-5.4

Account qualitative for:

- The similarities of values in 1, 2 and 3.
- The differences between the values 5, 6 and those in 1, 2 and 3.
- Very high negative values in 4 and the low negative in 7.

Question 6

- (a) Identify each heat change by name and classify each change as exothermic or endothermic for the following:
 (i) $\text{C}_2\text{H}_5\text{OH}(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g})$
 (ii) $\text{NaNO}_3(\text{s}) + 20\text{kJ/mol} \rightarrow \text{NaNO}_3(\text{aq})$
 (iii) $\text{NaCl}(\text{s}) \rightarrow \text{NaCl}(\text{l})$
 (iv) $1\text{mol HF}(\text{g}) \rightarrow 1\text{mol HF}(\text{l})$
 (v) $1\text{mol H}_2\text{O}(\text{l}) \rightarrow 1\text{mol H}_2\text{O}(\text{s})$
 (b) When 1g of anhydrous copper (II) sulphate (CuSO_4) was dissolved in large amount of water, 0.418kJ of heat was liberated. When 5g of copper (II) sulphate pentahydrate crystalline salt ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were dissolved in a large amount of water, 0.230kJ of heat were absorbed. From this data, calculate the heat change in the following reaction:

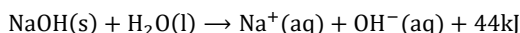


Question 7

- (a) Consider the following statement, "The more negative the value of heat of formation, the more stable the compound." Is this statement true or false? Explain.
 (b) 100cm^3 of 1.00mol dm^{-3} sodium hydroxide solution and 100cm^3 of 1.00mol dm^{-3} ethanoic acid are mixed in a calorimeter. All the three were at the same temperature. The heat capacity of the calorimeter was 90J/K and the rise in temperature was 5.3K . Calculate the standard enthalpy of neutralisation (specific heat capacity of solution is $4.2\text{J g}^{-1}\text{K}^{-1}$).

Question 8

- (a) Sodium hydroxide dissolves in water according to the following equation:



Would this process increase or decrease the temperature of the water? Explain.

- (b) 100cm^3 of 1M KOH and 100cm^3 of 1M HCl were mixed in a calorimeter. The temperature rise was 6.25K . The heat capacity of calorimeter was 95J/K and specific heat capacity of the solution mixture was 4.2J/K/g . Calculate the standard enthalpy of neutralisation.

Question 9

- (a) Why the enthalpy of neutralization involving strong acid and strong base is higher compared to those involving strong acid and weak base or weak acid and strong base?
- (b) 100cm^3 of 0.5M ethanoic acid solution were mixed with 100cm^3 of 0.5M sodium hydroxide solution in a plastic beaker of negligible heat capacity. The original temperature of reactions was 18.2°C and the final corrected temperature was 21.45°C . Calculate the enthalpy of neutralisation of ethanoic acid by sodium hydroxide under these conditions. Assume the specific of the solution to be that of water, i.e. $4.2\text{Jg}^{-1}\text{C}^{-1}$.

Question 10

- (a) During chemical reactions, bonds are broken (reactants) and formed (products), and the overall process may be exothermic or endothermic. Compare bond strengths in reactants and products if the overall reaction is:
- Exothermic
 - Endothermic
- (b) 50cm^3 of sodium hydroxide solution of concentration 0.400mol dm^{-3} required 20.00cm^3 of sulphuric acid of concentration 0.500mol dm^{-3} for neutralisation. A temperature rise of 3.9°C was observed if both solution and container were initially at the same temperature. Calculate the standard enthalpy of neutralisation of sodium hydroxide with sulphuric acid (the specific heat capacity of all solution is $4.2\text{Jg}^{-1}\text{K}^{-1}$ and assume no heat passes to the container).

Question 11

25cm^3 of 1.00mol dm^{-3} hydrochloric acid, at 298K was added to 50cm^3 of 1.00mol dm^{-3} sodium hydroxide also initially at 298K , in a polystyrene cup calorimeter. The specific heat capacity of water is $4.2\text{Jg}^{-1}\text{K}^{-1}$ and the density of water is 1.00g/mL .

- Calculate the value for standard enthalpy change for the reaction. If the temperature was raised by 4.6K .
- What assumptions have to be made in order to carry this calculation?

Question 12

- (a) A spirit burner containing ethanol is weighed and then used to heat up copper calorimeter containing 200cm^3 of cold water and then reweighed. The results recorded are:

Decrease in mass of ethanol = 0.4g

Rise in temperature of water = 10°C

Specific heat capacity of water = 4.2J/gK

Heat capacity of calorimeter is negligible.

Use these results to calculate the heat of combustion of ethanol.

- (b) Calculate the enthalpy change of solution of magnesium hydroxide, using the following data:

Energy or enthalpy change	Value / kJmol^{-1}
Lattice energy of $\text{Mg}(\text{OH})_2(\text{s})$	-2842
$\Delta_{\text{hyd}}(\text{Mg}^{2+}(\text{aq}))$	-1920
$\Delta_{\text{hyd}}(\text{OH}^{-}(\text{aq}))$	-460

Question 13

- (a) Given the standard enthalpy of combustion (ΔH_c^θ) of the following substances:

Hydrogen, $\Delta H_c^\theta = -286 \text{ kJ/mol}$

Carbon, $\Delta H_c^\theta = -394 \text{ kJ/mol}$

Methane, $\Delta H_c^\theta = -890 \text{ kJ/mol}$

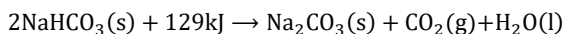
Ethene, $\Delta H_c^\theta = -1390 \text{ kJ/mol}$

Given that heat of formation of ethanol is -276 kJ/mol ; calculate in kJ/mol the heat change:

- Of formation of methane.
 - Of formation of ethene.
 - For the reaction $\text{CH}_2 = \text{CH}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(\text{l})$
 - Of combustion of 4.48 dm^3 of ethene.
- (b) By using Hess's law, calculate the standard enthalpy of formation of methane (CH_4) given that its standard heat enthalpy of combustion is 895.5 kJ/mol , the standard enthalpy of combustion of carbon graphite is 395.5 kJ/mol and the enthalpy of formation of water is 285.9 kJ/mol .

Question 14

- (a) The decomposition of baking soda is represented by the following thermochemical equation:



- Is this reaction exothermic or endothermic?
- What is the heat of reaction (ΔH) value for this reaction?
- Calculate the amount of heat required to decompose 2.24 mol of baking soda.
- Calculate the heat of formation of N_2O_5 from the following data of energy cycle.
 - $\text{NO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}); \Delta H = -57.05 \text{ kJ/mol}$.
 - $4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}_5(\text{g}); \Delta H = -110.2 \text{ kJ/mol}$.
 - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}); \Delta H = 130 \text{ kJ/mol}$.

Question 15

- (a) The standard heat of formation of methane, carbon dioxide and water are -76.2 , -394.8 and -241.6 kJ/mol , respectively. Calculate the amount of heat evolved by burning 1 m^3 of methane measured at s.t.p.
- (b) 5.93 g of CH_3CHO is combusted in 9.29 L of oxygen gas measured at 25°C and 1 atm . How much heat is produced? Given that:

$$\Delta H_f^\theta(\text{CH}_3\text{CHO}) = -166 \text{ kJ/mol}$$

$$\Delta H_f^\theta(\text{H}_2\text{O}) = -284 \text{ kJ/mol}$$

$$\Delta H_f^\theta(\text{CO}_2) = -395 \text{ kJ/mol}$$

Question 16

The following data gives the energies liberated when 1 g of each substance burned in excess oxygen. Use it to calculate the standard enthalpy of formation of ethene.

Substance	Energy liberated (kJ)
Graphite	32
Hydrogen	143
Ethene	50

Question 17

Calculate the standard of enthalpy of formation of ethyne (acetylene) from the following data:

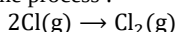
- 2g of carbon burned in excess oxygen liberated 66.1kJ
- 2 g of hydrogen burned in excess oxygen liberated 284kJ
- 2g of ethyne burned in excess of oxygen liberated 99.5 kJ

Question 18

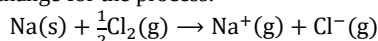
(a) Study carefully the information in the following table and then answer the questions that follow:

Process	ΔH° (kJ/mol)
$\text{Na(s)} \rightarrow \text{Na(g)}$	+108
$\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl(g)}$	+121
$\text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}$	+496
$\text{Cl(g)} + \text{e} \rightarrow \text{Cl}^-(\text{g})$	-349
$\text{NaCl(s)} \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$	+787
$\text{NaCl(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	+4

(i) Calculate the standard enthalpy change for the process :



(ii) Calculate the standard enthalpy change for the process:



(iii) Compare the difference between enthalpy change for the processes:

$\text{NaCl(s)} \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$ and $\text{NaCl(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ and then comment on the difference.

(b) Calculate the enthalpy of formation of carbon disulphide given that the enthalpy of combustion of:

Carbon disulphide = -1072 kJ/mol.

Carbon = -393.5 kJ/mol.

Rhombic sulphur = -296.1 kJ/mol.

Question 19

(a) Some enthalpy change data are shown in the table below:

Process	Enthalpy change (kJ/mol)
$\text{AgI(s)} \rightarrow \text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq})$	+112
$\text{Ag}^+(\text{g}) \rightarrow \text{Ag}^+(\text{aq})$	-464
$\text{I}^-(\text{g}) \rightarrow \text{I}^-(\text{aq})$	-293

(i) Use the data in above table to calculate the lattice energy of silver iodide.

(ii) A calculation of the lattice energy of silver iodide based on a perfect ionic model gives a smaller numerical value than the value calculated in (i) above. Explain this difference.

(b) Hydrogen chloride gas dissolves in water to form hydrochloric acid. Use standard enthalpies of formation shown below to calculate ΔH° of this reaction at 298K.

Standard enthalpies of formation at 298K in kJ/mol

HCl(g)	-92.3
$\text{H}^+(\text{aq})$	0
$\text{Cl}^-(\text{aq})$	-167.2

Question 20

- (a) Anhydrous magnesium chloride, MgCl_2 , can absorb water to form the hydrated salt, $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$.

$$\text{MgCl}_2(\text{s}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O}(\text{s})$$
- (i) Suggest **one** reason why the enthalpy change for this reaction cannot be determined directly by calorimetry.
- (ii) Some enthalpies of solution are shown in the table below:

Salt	Enthalpy of solution (kJ/mol)
$\text{MgCl}_2(\text{s})$	-155
$\text{MgCl}_2 \cdot 4\text{H}_2\text{O}(\text{s})$	-39

Calculate the enthalpy change for the absorption of water by $\text{MgCl}_2(\text{s})$ to form $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}(\text{s})$.

- (b) Given that the enthalpies of combustion of ethane, ethene and hydrogen are -1323, -1429 and -242 kJ/mol respectively. Calculate the enthalpy of hydrogenation of ethene.

Question 21

Enthalpies of combustion of some substances are given below:

Substance	$\Delta H/\text{kJ mol}^{-1}$
Hydrogen	-242
Benzene	-3302
Cyclohexene	-3746
Cyclohexane	-3940

Calculate the enthalpy of hydrogenation of benzene and cyclohexene.

Question 22

- (a) What does the first law of thermodynamics say?
- (b) Draw a well labelled Born Haber cycle for calcium fluoride and calculate atomisation energy of fluorine.

Heat of formation of calcium fluoride = -860 kJ/mol

Atomisation energy of calcium = + 174 kJ/mol

First ionisation energy of calcium = 550 kJ/mol

Second ionisation energy of calcium = +1000 kJ/mol

Electron affinity of fluorine = -363 kJ/mol

Lattice energy of calcium fluoride = -2100 kJ/mol

Question 23

Values of energy terms appearing in the Born Haber cycle for KCl are given below. The sign of each term has been deliberately omitted.

Enthalpy of atomisation of potassium is 353.2 kJ/mol

Dissociation enthalpy of chlorine gas is 507.5 kJ/mol

Ionisation enthalpy of potassium atom is 748 kJ/mol

Electron affinity of chlorine atom is 1488.1 kJ/mol

Lattice energy of potassium chloride is 2900.9 kJ/mol.

Assign either +ve or -ve sign to each energy term and calculate the enthalpy of formation of KCl(s) .

Question 24

The following are mean standard bond enthalpies

$$\text{C} = \text{O} \quad \Delta H = 743 \text{ kJ/mol}$$

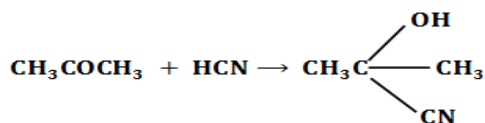
$$\text{C} - \text{H} \quad \Delta H = 412 \text{ kJ/mol}$$

$$\text{C} - \text{O} \quad \Delta H = 360 \text{ kJ/mol}$$

$$\text{C} - \text{C} \quad \Delta H = 348 \text{ kJ/mol}$$

$$\text{H} - \text{O} \quad \Delta H = 463 \text{ kJ/mol}$$

Using above information, calculate the standard enthalpy change of the reaction;

**Question 25**

Using bond energies:

$$\text{C} = \text{C} \quad 610 \text{ kJ mol}^{-1}$$

$$\text{C} - \text{C} \quad 345 \text{ kJ mol}^{-1}$$

$$\text{C} - \text{H} \quad 415 \text{ kJ mol}^{-1}$$

$$\text{H} - \text{H} \quad 435 \text{ kJ mol}^{-1}$$

And, assuming that the bonding between the carbon atoms of benzene consists of alternate double and single covalent bonds, predict a value for standard enthalpy of hydrogenation of benzene and comment on difference between this value and the experimentally determined value of approximately -210 kJ/mol .

Question 26

Benzene has a standard enthalpy of formation of 83 kJ/mol .

Calculate the standard enthalpy of formation from the following data.

Mean standard bond enthalpies are

$$\text{C} - \text{C} = 348 \text{ kJ/mol}$$

$$\text{C} = \text{C} = 615 \text{ kJ/mol}$$

$$\text{C} - \text{H} = 412 \text{ kJ/mol}$$

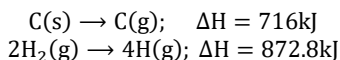
$$\Delta H^\theta \text{ for vapourisation of carbon} = 715 \text{ kJ/mol}$$

$$\Delta H^\theta \text{ for atomisation of hydrogen} = 217.5 \text{ kJ/mol}.$$

Compare the experimental value and the theoretical value for ΔH_f^θ

Question 27

- What are the four factors affecting the quantity of heat evolved or absorbed during a physical or chemical transformation?
- Using the following information and the fact that the average $\text{C} - \text{H}$ bond energy is 414 kJ/mol , estimate the standard enthalpy of formation of methane (CH_4).

**Question 28**

- What does each of the following terms implies?
 - Heat of dilution
 - Heat of solution

What is the relation between the two terms?

- (b) The reaction between peroxide and hydrazine is; $2\text{H}_2\text{O}_2 + \text{N}_2\text{H}_2 \rightarrow 4\text{H}_2\text{O} + \text{N}_2$

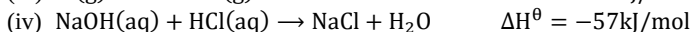
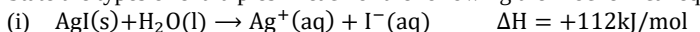
Use the values of bonds energies given below, calculate:

The enthalpy change for the above reaction in the gas phase

Bond	O – H	N – H	N – N	O – O	N $\equiv$ N
Bond energy (kJ/mol)	463	391	159	143	945

Question 29

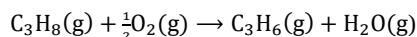
- (a) State the types of enthalpies in each of the following thermochemical equations:



- (b) The table below lists a number of mean bond enthalpies values.

Bond	Mean bond Enthalpy / kJ/mol ⁻¹
C – C	348
C = C	612
C – H	413
O – H	463

- (i) Given that the enthalpy of combustion to form carbon dioxide and water (steam) is -2102kJ/mol for propane and -1977kJ/mol for propene, determine the enthalpy change for the oxidation of 1 mole of propane to propene and steam.



- (ii) Use the mean bond enthalpies in the table above together with your answer in part (i) to calculate the bond enthalpy for the O = O bond in oxygen molecule.

Question 30

- (a) Explain briefly what is wrong with each of the following definitions:

(i) **Standard enthalpy of combustion:** *Is the heat change when one mole of an element or compound is completely burned in oxygen under standard conditions of temperature and pressure.*

(ii) **Enthalpy of neutralisation:** *Is the heat evolved when dilute solutions of acid and base react to give water under given conditions of temperature and pressure.*

(iii) **Standard enthalpy of hydrogenation:** *Is the heat evolved when an unsaturated compound is converted to the corresponding saturated compound by the reaction with one mole of hydrogen under standard conditions of temperature and pressure.*

(iv) **Ionisation energy:** *Is the energy required to remove completely any valence electron each from one mole of gaseous atom or ion at given conditions of temperature and pressure.*

- (b) The heat combustion of carbon and hydrogen are 393.5 kJ/mol and 286 kJ/mol respectively. The enthalpy of sublimation of carbon is 720kJ/mol and dissociation energy of hydrogen is 432 kJ/mol . Calculate the mean C – C bond energy of cyclopropane given the enthalpy of combustion of cyclopropane to be 2091 kJ/mol ; the mean C – H bond energy is 414 kJ/mol .

ANSWERS TO DIGGING DEEPER EXERCISES

EXERCISE 1

1. Disagree

Explanation

Amount of pressure exerted by a gas does not directly depend on the mass of the gas; it depends on the number of gas molecules (particles). With equal mass of hydrogen and oxygen, hydrogen having smaller molar mass will possess greater number of gas molecules ($n = \frac{m}{M_r}$) and hence greater pressure of hydrogen than that of oxygen despite the fact that the two have equal mass.

2. Incorrect

Explanation

For the volume of the gas to double in accordance with Charles's law the temperature in Kelvin (absolute temperature) must double too. Although the given temperature seems to double in Celsius scale but converting them to Kelvin gives 283K and 393K respectively which is clear that the latter is not twice of the former.

3. Oppose

Explanation

To be valid, Gay-Lussac's needs the temperature to be in Kelvin (absolute temperature). So in Kelvin scale the increase in temperature is from 300K to 600K from which it is clear that the latter is the twice of the former and hence the pressure should increase in accordance to Gay-Lussac's law as suggested by John.

4. No, the ideal gas law equation ($PV = nRT$) is not applicable to liquids because they are not compressible and thus they have a constant volume.

5. (i) From Boyle's law: $V \propto \frac{1}{P}$; constants: n and T

From Charles's law: $V \propto T$; constants: n and P

Avogadro's law: $V \propto n$; constants: P and T

Combining the three laws: $V \propto \frac{nT}{P}$ or $V = \frac{nRT}{P}$ (All four variables of the gaseous state are changing).

Where R is the proportionality constant; and the which is known as universal molar gas constant

Hence $PV = nRT$ (ideal gas equation).

(ii) Because it shows relationship between all variables (pressure, volume, number of molecules and temperature) of gaseous state.

6. (i) Pressure of the gas decreases as the volume increases (or pressure of the gas increases as the volume decreases).

(ii) Temperature, number of gas molecules.

7. (i) The number of molecules in the gas increases as the volume increases.

(ii) Temperature, pressure

8. Gases whose molar masses are larger than that of oxygen gas will diffuse more slowly than oxygen. These are: F_2 , N_2O , Cl_2 and H_2S

9. False

Reason

The amount of the gas which directly determine amount of pressure is the number of gas molecules and not mass. With smaller molecular mass, 2g of hydrogen possess greater number of molecules (1mol) than 4g of oxygen (0.125mol). So although the mass of oxygen is twice the mass of hydrogen the pressure exerted by hydrogen will be 8 times (greater by far) the pressure of oxygen.

10.(a) (i) The amount of pressure exerted by the gas increases as the amount of collision frequency increases.

(ii) The amount of pressure exerted by the gas increases as the amount of collision intensity increases.

(b) **Collision frequency** can be changed by one of the following ways:

- By changing temperature whereby increasing the temperature, increases the collision frequency.
- By changing pressure whereby increasing pressure by compression decreases volume of the gas and therefore increasing the collision frequency.
- By changing the volume of the container whereby using the container of smaller volume increases the collision frequency.
- By changing amount of the gas whereby adding the amount of the gas, increases the collision frequency.

Collision intensity can only be changed by changing pressure whereby increasing the temperature, increases the collision intensity.

11. The merger of Boyle's law and Charles's law is the combined gas law which can be represented as follows;

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}, \text{ where } n \text{ is constant.}$$

When volume is constant, $V_1 = V_2 = V$

Then $\frac{P_1 V}{T_1} = \frac{P_2 V}{T_2}$ or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ which is equivalent to Gay-Lussac's pressure law.

Hence the Gay-Lussac's law is contained in Gay-Lussac's law as shown above.

12. (i) Yes, the total pressure changes.

Explanation

Increasing the amount of gases, increases collision frequency between gas particles and walls of the flask and therefore increasing pressure. So adding the neon will increase pressure in the flask.

(ii) No effect.

Explanation

Neon is incapable of reacting with any gas present in the flask, so adding it in the flask will do both increase the total pressure in the flask and decrease the mole fraction of the gases by the same proportion and hence the partial pressures will remain the same.

13. According to Charles's law; hot air inside the balloon has larger volume and hence lower density than cold air outside; consequently, the balloon floats.

14. **Extreme high temperature** will cause high increase in pressure in accordance to Gay-Lussac's law and therefore the tank will burst leading to the explosion while **extreme low temperature** causes large decrease in pressure of the gas in accordance to the same law.

15. During driving, temperature of air inside car tyre increases while its volume remains constant which in turn means that the pressure in the tyre will increase in accordance to Gay-Lussac's pressure-temperature law.

16. Good flavour of chips is maintained by high pressure in the bag which ensures freshness of preservative chemicals added during the manufacture of the chips. Placing the bag in the freezer causes a reduction in pressure in accordance to Gay-Lussac's law, and hence good flavour is lost.

17. Bicycle tyre absorb heat energy from the sun raising its temperature which in turn will raise its pressure in accordance to Gay-Lussac's law. If the pressure in the tyre rises beyond its limit, the tyre will burst.

18. In the summer, the temperature is higher and therefore the pressure inside the tyre tend to increase in accordance to Gay-Lussac's law. So to prevent the bursting of the tyres, they are inflated to a slightly lower pressure.

19. (i) Avogadro's law.

(ii) Identical balloons have the same volume and therefore they both contain the same number of particles (molecules) in accordance with Avogadro's law. Since one atom of helium has smaller mass than one molecule of oxygen, with equal number of particles for each, the helium balloon will be lighter.

20. In making bakery product like bread, yeast is mixed with the dough where it releases carbon dioxide through fermentation of sugar present in the dough. Once the bread has baked, the heat causes the temperature to raise which in turn cause the carbon dioxide in the dough to increase its volume in accordance with Charles's law and hence the bread becomes fluffy.

21. In the summer, the temperature increases and therefore the pressure of the gas (CO_2) inside the bottles tend to increase in accordance to Gay-Lussac's law. So to decrease the temperature and hence to avoid the explosion of the bottles, they are kept under water.

22. A flat tyre has smaller amount of air and therefore smaller volume while inflated tyre has larger amount of air and hence greater volume in accordance with Avogadro's law.

23. Inside a pressure cooker, the food is kept in water. As the temperature of the liquid water is increased, water vapour (gaseous water) is produced. This gaseous water cannot escape the pressure cooker and therefore keeping the volume constant. Consequently, according to Amontons's law, the pressure of the gaseous water keeps rising until the temperature of the liquid water and the gaseous vapour exceed the normal boiling point of water (100°C). At this higher temperature (caused by the raise in pressure; i.e. higher pressure means higher boiling point), food can be cooked much faster.

24. Lower temperature in the outdoors, decreases the volume of gases inside the ball in accordance with Charles's law and hence the football shrinks.

25. High temperature inside of the fire increases the pressure of the gases inside the can in accordance to Gay-Lussac's law, and eventually if the pressure exceeds the pressure limit, the can will explode.

26. Boyle's law is applicable when amount of air is constant. During the inflation of the tyre, the amount of air is progressively increased in the tyre and therefore Boyle's law is inapplicable. At the initial stages of inflation, volume of the tyre will increase and pressure will remain almost constant in accordance with Avogadro's law. At later stage of the inflation, volume of the tyre remains almost constant but since amount of the gas in the tyre is still increasing, collision frequency between air molecules and the tyre's walls will increase making the pressure to increase too ($P \propto n$ at constant V and T); eventually the tyre will burst if the amount of air added is so large that the pressure exerted exceed pressure limit of the tyre.

27. (a) $P_{\text{He}} = 474\text{torr}$, $P_{\text{Ar}} = 26\text{torr}$ (b) $P_{\text{total}} = 500\text{torr}$ 28. (a) 706.896mmHg (b) 0.0418g

29. Helium: 3.16 times as fast 31. 31.79g/mol 33. 2.56 mol/min

30. 5050g/mol 32. 0.400m 34. 0.43atm

35. 4atm

Hint: O₂ is in excess (only 1atm of it will react with 2atm of H₂) so after reaction there are 2atm of unreacted oxygen and 2atm of produced gaseous water making a total of 4atm.

36. (a) 0.25atm (Hint: P_{total} stp is 1atm) (b) 0.3348mol (Hint: n_{total} = 1mol for 22.4L at stp) (c) Pressure is still 0.25atm

37. (a) 13.39g (b) 0.6049atm (c) 0.6522 (d) At s.t.p water would be frozen (and become ice). It could not behave like an ideal gas and hence the overall pressure has been overestimated.

38. (a) 1.4atm (b) 0.2atm (c) 0.857

39. 0.4atm

40. 1.8atm

41. (a) 14atm (b) 0.7 (c) 5g/L (d) X_{H₂} = 0.5 X_{Ar} = 0.167, X_{H₂O} = 0.333

Note: H₂O is included in the answer because in the given question it is given as a gas

42. (i) 739torr (ii) 3.94g

44. 787.2mmHg

43. 0.3g

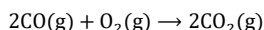
45. 2.93x seconds

46. Not correct.

Reason: CO and O₂ reacts, so direct application of Dalton's law of partial pressure is not allowed.

Calculation of correct value

At 30°C, CO reacts with O₂ According to the following equation:



From which 3atm of CO reacts with 1.5atm ($\frac{1}{2} \times 3\text{atm}$) of O₂ to give 3atm (For gases pressure ratio is equal to mole ration).

So after the reaction there are:

0atm of CO (all of it reacted)

0.5atm (2atm – 1.5atm) of unreacted O₂

3atm of produced CO₂

Then by Dalton's law of partial pressure; the total pressure in the container is given by;

$$P_T = P_{\text{O}_2} + P_{\text{CO}_2} = (3 + 0.5)\text{atm} = 3.5\text{atm}$$

Hence the correct total pressure is 3.5atm.

47. 25% CO and 75%CO₂

49. 0.25atm

48. 1.17g/dm³

50. 84.5°C.

EXERCISE 2

1. The kinetic molecular theory of gases explains how gases behave by assuming that they are made up of very fast randomly moving particles (atoms or molecules).

2. The three main components are:

- (i) The molecules of the gas have linear motion (unless they collide with something).
- (ii) No gain or loss in kinetic energy during a collision.
- (iii) The individual gas particles have negligible mass and occupy negligible space (volume) in a container.

3. The concept of pressure directly follows from the theory because each collision imparts forces on the wall it hits, and so when very large number of collisions each second hit a unit area of a container's wall, the collective force per area is just the sum of force of all the individual collisions. Since $P = \frac{\text{Force}}{\text{Area}}$, the collective force per area associated with the collisions is the pressure of the gas.

4. Kinetic gas equation is an equation for the pressure of the gas which was derived by using the postulates of kinetic molecular theory. It can be written as; $PV = \frac{Nmc^2}{3}$; where:

P is the pressure of the gas

V is the volume of the gas

N is the number of gas particles

M is the mass of one gas particle

c is the root mean square speed of the gas

5. The molecular speed is high if the molecular mass is small and hence the correct order will be as follows:

$$\frac{\text{Cl}_2 < \text{F}_2 < \text{O}_2 < \text{N}_2}{\text{Increase in molecular speed}}$$

6. 70.7g/mol

7.

- (i) Reducing the temperature of a gas reduces the average kinetic energy (or speed) of the gas molecules. This would reduce the frequency of collisions of gas molecules with the walls of the balloon and also would make those collisions less energetic. In order to maintain constant pressure against the external pressure, the volume must decrease (shrink).
- (ii) The molecules of the gas do have volume, when they are cooled sufficiently, the intermolecular forces of attraction that exist between them cause them to liquefy or solidify.

8. The molecules of gas are in constant motion, so the HCl and NH_3 diffuse along the tube. Where they meet, the solid NH_4Cl is formed. Since HCl has greater molar mass, its speed is lower, therefore, it does not diffuse as fast as the NH_3 .

9. The wind is moving molecules of air that are going mostly in one direction. Upon encountering a flag, they transfer some of their kinetic energy to it and cause it to move.

10. H_2O . Cooling slows the velocities of the He atoms, causing them to behave as though they were heavier.

11. According to the kinetic molecular theory, low temperature in the cold room implies low kinetic energy to the gas. This in turn implies low speed to the perfume gaseous ingredients leading to slow diffusion rate and hence it becomes difficult to smell.

12. 4495°C

13. 197.74°C

14. Boyle's law: $P \propto \frac{1}{V}$ At constant T and n

Justification:

A decrease in V leads to an increased gas molecules concentration and thus an increase in the number of collisions per second with the walls of the container. More frequent collisions lead to greater pressure exerted by the gases in the container.

Charles's law: $V \propto T$ at constant P and n

Justification:

Initially an increase in T leads to an increase in kinetic energy, making the speed greater and thus frequency of collision is increased and the collisions become more energetic (both collision force and frequency become high). The only way to keep P from increasing under such conditions (so as to balance with the external pressure) is to increase V, which will decrease collision frequency despite the increased speed

Avogadro's law: $V \propto n$ at constant P and T

Initially, an increase in n leads to an increased gas molecules concentration and thus an increase in number of collisions per second with the walls, and thus pressure

The only way to keep P from increasing (so as to balance with the external pressure) under these conditions is to increase the volume proportionately, which will keep the concentration constant.

15. From the first postulate of kinetic molecular theory, the gas consists of very small molecules in a random motion of which there is a collision between gas molecules themselves and the collision between gas molecules and the walls of the container. This makes the direction of the motion of the gas to be completely random whereby the gas will continue to spread out until it is evenly distributed throughout the volume of the container.

16. Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The kind of speed which is constant at constant temperature is the average velocity of all the molecules and not the molecular speed.

17. Kinetic energy (K.E) of n moles of a gas with total mass, m, moving with velocity, c, in a container of volume, V, at temperature, T, and pressure, P, is given by one of the following equations:

$$\text{K.E} = \frac{1}{2}mc^2 \text{----- (i)}$$

$$\text{K.E} = \frac{3}{2}PV \text{----- (ii)}$$

$$\text{K.E} = \frac{3}{2}nRT \text{----- (iii)}$$

- The decrease in volume and the increase in pressure occurs at the same proportion making the product PV (in (ii)) unchanged. Adding the fact that the temperature, T (in (iii)) was kept constant; no change in kinetic energy will occur and hence **the kinetic energy will remain the same.**
- Increasing T (in (iii)) clearly increases the kinetic energy. Analogously increasing P while V is kept constant, increases the value of the product PV (in (ii)) which in turn increases kinetic energy. Hence **the kinetic energy is increased** in this case.
- From (i) it is clearly understood that the increase of velocity (c) by factor of two, **increases the kinetic energy by factor of 4.**

EXERCISE 3

1.

- Real gas molecules exhibit finite volume, thus excluding some volume from compression.
- Real gas molecules exhibit intermolecular forces of attraction, thus leading to fewer and less energetic collisions with the walls of the container and hence lower pressure.

2. Kinetic theory does not recognise that; at low temperature and high pressure:

- Intermolecular forces of attraction cannot be neglected.
- Volume of gas molecules cannot be neglected compared to the volume of whole gas (container).
- Collisions between gas particles and walls of the container are not perfectly elastic.

3. SO_2 shows greatest deviation.

Reasons:

- A molecule of SO_2 has largest size (or volume)

- SO_2 molecule exhibit strongest intermolecular forces of attraction (With largest molecular weight, SO_2 has strongest Van-der-Waals dispersion forces. Also SO_2 has dipole-dipole forces in addition to the strongest dispersion forces while other gases have dispersion forces only).

4. High temperature results in high kinetic energy which overcomes intermolecular forces of attraction.

Low pressure increases distance between molecules leading to greater volume occupied and therefore molecules comprise a small part of the volume and (due to greater distance apart between molecules) the intermolecular forces of attraction become very small.

5. To be ideal the gas must obey ideal gas equation in all conditions of temperature and pressure. This requires the intermolecular forces between gas molecules and molecular size (volume) of gases to be neglected which is not possible especially at low temperature and high pressure and hence no gas is ideal; making the whole concept just imaginary.

6. (i) Smaller value.

Explanation

The smaller value means less pressure deviation and therefore the real pressure will become closer to the ideal pressure.

(ii) Not possible.

Explanation

The given constants depend on the nature of the gas. While 'a' depends on the strength of intermolecular forces 'b' depends on the molecular size all of which depend on chemical nature of the gas and hence they cannot be altered.

7. At low temperature, kinetic energy is not enough to break intermolecular forces and therefore making the molecular attraction high.

8. That statement assumes that there are no intermolecular forces between gas particles. But in reality the intermolecular forces between gas particles they do exist and thus decreasing the speed of the particles and hence the collision becomes inelastic.

9. Ammonia having intermolecular hydrogen bonding which is stronger than the Van-der-Waals dispersion forces present in the nitrogen, has stronger intermolecular forces and hence larger value of 'a' for ammonia. But larger molecular mass of nitrogen implies that nitrogen molecule has larger molecular volume and hence larger value of 'b' for nitrogen.

10.

- N_2 (Has a weakest intermolecular force of attraction. Among the non-polar, N_2 has smallest molecular weight and therefore smallest Van der Waals dispersion forces. NH_3 has a stronger intermolecular force than N_2 despite the fact that has smallest molecular weight because it is polar covalent molecule with hydrogen bond.
- CCl_4 (It has much greater molecular weight and therefore greatest size making its molecule to occupy greatest volume).

11. (i) 696K (ii) 731K

12. Liquefaction of a gas involves strengthening intermolecular forces potentially present in the gas. Ammonia having intermolecular hydrogen bonding in addition to Van-der-Waals dispersion forces has stronger intermolecular forces than fluorine which has Van-der-Waals dispersion forces only.

13. Presence of intermolecular forces as one of reasons of deviation of real gas from ideal behaviour makes liquefaction of gas possible. Since it is easier to store and transport liquid than gas, gases are usually liquefied before their storage or transportation.

14. Very low molecular mass of helium suggests that helium has very weak Van der Waals dispersion forces. The weak intermolecular forces make its liquefaction process difficult. As the result, the liquefaction of helium requires both cooling and compression equipment unlike other heavier gases like carbon dioxide which requires compression only for their liquefaction.

15. It helps to understand liquefaction process which is important in the transportation and storage of the gas.

Explanation

Gases with positive value of compressibility factor ($Z > 0$) like hydrogen and helium show positive deviation from ideal gas behaviour and thus they have very weak intermolecular forces and they are **permanent gases**. Consequently, these gases need both cooling and compression for their liquefaction.

On another hand, gases with negative value of compressibility factor ($Z < 0$) like ammonia and carbon dioxide show negative deviation and thus they have very strong intermolecular forces. This makes their liquefaction easier and they need only compression for the process.

16. The following are the two steps involved in the liquefaction of natural gas:

1. Compression

Here the pressure is increased, therefore pushing the gas molecules closer together.

2. Cooling

Here the temperature is dropped, which causes the intermolecular forces of attraction to increase.

17. The experimental molecular weight would be greater than the true value.

Explanation

Molecular weight of the vapourised liquid is calculated from the following formula:

$$M_r = \frac{mRT}{pV}$$

Significant intermolecular forces of attraction exist at temperature not far above boiling point. Therefore, the compressibility of the gas is greater and the value of PV is smaller than predicted. This would lead to a higher value of the molecular weight than the true value.

18. (a)

'a' indicates the intermolecular forces of attraction between molecules of real gases (Greater intermolecular forces, greater value of 'a').

'b' indicates actual volume of a molecule of real gas (Greater size or molecular weight of the molecule, greater value of 'b').

(b) H_2S has higher value of 'a'

Reason:

H_2S molecules exhibit stronger intermolecular forces of attraction since it has stronger Van der Waals dispersion forces (H_2S has greater molecular weight than H_2) and also has dipole-dipole forces in addition to the dispersion forces while H_2 has the dispersion forces only.

H_2S has higher value of 'b'

Reason:

Having greater molecular weight, H_2S molecule has greater size and therefore greater volume than H_2 .

(c) 'a' is correlated to boiling point. The greater value of 'a' means stronger intermolecular forces of attraction and whence higher boiling point

19. (i) 57.1atm; deviation = 14.2% (ii) 49.6atm; deviation = 0.8%

20. Agree

Explanation

Greater number of gas molecules means greater of both pressure deviation and volume deviation from their corresponding ideal results. This is because, with greater number of gas molecules the intermolecular forces will be higher with more gas molecules pulling the gas molecules backward before hitting the container's wall and hence more decrease in real pressure. Also greater number of gas molecules means greater volume occupied by gas molecules which in turn means less empty space is left compared to the volume of the container.

21. Doubling the pressure as result of doubling is the ideal behaviour which neglects presence of intermolecular forces. In real gas, doubling number of moles means more intermolecular forces which results into more pressure deviation making the increase in pressure to be less than one could expect if the gas would be ideal.

22. Kinetic energy of gas decreases as the temperature decreases toward its boiling point. At boiling point kinetic energy is so small that it is unable to break intermolecular forces to the extent that the liquefaction of the gas starts to take place.

23. **At boiling point** the kinetic energy is too small to break intermolecular forces and therefore the deviation of real pressure from ideal pressure is maximum. Also the small kinetic energy implies that gas molecules are moving with small speed in close range and therefore occupying small volume which in turn makes inappropriate to neglect the volume of individual gas molecules compared to the volume of the whole gas and thus making the volume deviation to be maximum too. Consequently, the deviation of real gas from ideal behaviour is maximum at boiling point to the extent that the liquefaction of the gas starts to take place.

At critical point the kinetic energy is high enough to break almost all intermolecular forces and therefore the pressure deviation is negligible. Also high kinetic energy implies that gas molecules are moving with very high speed with very large separation distance making them to occupy very large volume and therefore making possible to neglect the volume of individual gas molecules compared to the volume of the whole gas leading to almost zero volume deviation. Consequently, the deviation of real gas from ideal behaviour is minimum at boiling point to the extent that the gas is almost ideal such that the liquefaction of the gas is extremely difficult.

24. Smaller molecular mass of helium means that helium has smaller molecular volume and weaker Van-der-Waals intermolecular forces and therefore comparing to ideal behaviour of gases, helium has smaller volume deviation and smaller pressure deviation respectively and hence it is closer to ideal gas than chlorine.

25. **The postulate related to the constant 'a':**

Intermolecular forces of attraction are negligible in the motion of gas molecules.

Relationship: Weaker intermolecular forces means smaller value of the constant and whence the postulate becomes valid while stronger intermolecular forces leads to larger value of the constant and thus the postulate becomes invalid.

The postulate related to the constant 'b':

Volume of a gas molecule (particle) is negligible compared to the volume of the whole gas or the volume of the container.

Relationship: Smaller molecular size (volume) means smaller value of the constant and whence the postulate becomes valid while larger molecular size leads to larger value of the constant and thus the postulate becomes invalid.

26. (i) Both constants 'a' and 'b'.

Explanation

During gas liquefaction both strengthening of intermolecular forces between gas molecules and decreasing of volume of empty space (occupied by gas molecules) to zero are done simultaneously. Since the intermolecular forces is related to 'a' and the volume of empty space is related to 'b', both constants are related to the liquefaction.

(ii) Both constants 'a' and 'b'.

Explanation

Large value of 'a' means stronger intermolecular forces while large value of 'b' implies large molecular volume which means less of the empty space is left and hence easier liquefaction for gases with large value of constants, 'a' and 'b'.

27. (i) $\frac{n^2a}{V^2}$ is the pressure deviation of real pressure from ideal pressure and therefore it corrects the real pressure (P) to be ideal pressure $(P + \frac{n^2a}{V^2})$.

nb is the volume deviation of real gas from ideal gas and therefore it corrects the real volume (V) to be ideal volume $(V - nb)$.

(ii) Compressibility factor, $z = \frac{PV}{nRT}$

$$\text{From which; } V = \frac{ZnRT}{P} = \frac{0.5 \times 1 \text{ mol} \times 0.082 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 273 \text{ K}}{100 \text{ atm}} = 0.11193 \text{ dm}^3$$

But the volume of gas molecules is negligible, $b = 0$ and the given Van der Waals equation becomes:

$$\left(P + \frac{n^2a}{V^2}\right)V = nRT$$

Then substituting;

$$\left(100 \text{ atm} + \frac{1 \text{ mol}^2 \times a}{0.11193^2 \text{ dm}^6}\right) \times 0.11193 \text{ dm}^3 = 1 \text{ mol} \times 0.082 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 273 \text{ K}$$

From which $a = 1.252 \text{ dm}^6 \text{ atm mol}^{-2}$

Hence Van der Waals constants are;

$a = 1.252 \text{ dm}^6 \text{ atm mol}^{-2}$ and $b = 0$

EXERCISE 4

1. (a) Combined gas law enables conversion of the volume of the gas (formed after vapourisation of the substance) to the corresponding volume at STP by using the relation; $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ or $V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$

Avogadro's law enables calculation of molecular mass from the STP volume of the gas by using the following relation;

$$\frac{V}{22.4 \text{ dm}^3/\text{mol}} = \frac{m}{M_r} \text{ or } M_r = \frac{m \times 22.4 \text{ dm}^3/\text{mol}}{V}$$

(b) The alternative is ideal gas law by using the relation $PV = \frac{m}{M_r}RT$ or $M_r = \frac{mRT}{PV}$

(c) The most preferred alternative is ideal gas law.

Reason: No need to convert the gas volume to STP volume and therefore it is shorter alternative.

2. Abnormal results on experimentally determined molar mass are obtained when the substance undergoes dissociation or association. Dissociation splits one molecule into smaller molecules and therefore making experimental molar mass smaller than that suggested by the molecular formula while association join smaller molecules into one molecule and therefore making experimental molar mass larger than that suggested by the molecular formula.

3. Advantages:

- 1) The method is very simple to carry out.
- 2) The sample required for the experiment is very small.

Disadvantages:

- 1) This method is not applicable to non-volatile substances (with boiling point greater than 100°C).
- 2) The method cannot be used for the substance which undergoes thermal decomposition.
- 3) Due to manual handling, there is the possibility of personal error.
- 4) It is not applicable to volatile substances which are water soluble.

4. The main assumptions are:

- 1) The vapour of the substance behaves exactly as ideal gas.
- 2) The volume of bulb remains constant throughout the experiment (no volume expansion on heating).

5. 120.43g/mol

6. 89.3g/mol

7. Victor Meyer's method is compatible with volatile substances whose boiling points are below 100°C so that they can be vapourised by steam. Table salt being non-volatile substance cannot be vapourised by Victor's Meyer apparatus and hence its molar mass cannot be determined by this method.

8. This is because methanol is highly soluble in water.

9. Molecular masses obtained from the given apparatuses can be used in:

- 1) Identification of unknown substances.
- 2) Determination of molecular formula.

10. Yes, was correct.

Explanation

It is not necessary to weigh the amount of liquid initially put into the flask because a large amount of the liquid is excess. We are concerned only with the vapour that fills the flask after the excess liquid has evaporated and exited the flask. At the end of the experiment, we allowed the remaining vapour to cool and condense into a liquid. It was necessary to weigh the cooled vapour (liquid) to determine the weight of the vapor that filled the flask.

11. Finding the forgotten data:

$$\text{From; } PV = \frac{m}{M_r} RT; P = \frac{mRT}{VM_r}$$

$$\text{Substituting } P = \frac{0.292 \times 0.082 \times 295}{0.061 \times 116.56} \text{ atm} = 0.9934 \text{ atm} = 754.98 \text{ mmHg} \cong 755 \text{ mmHg}$$

Thus the forgotten data was the pressure amounted to 755 mmHg

Calculating the correct molar mass (correction):

$$\text{Volume of air displaced} = \text{volume of the sample} = 61 \text{ cm}^3 = 0.061 \text{ dm}^3$$

$$\text{Mass of the sample} = 0.292 \text{ g}$$

$$\begin{aligned} \text{Pressure exerted by the vapour of the sample} &= \text{Total pressure} - \text{Vapour pressure of water} \\ &= (755 - 22) \text{ mmHg} = 733 \text{ mmHg} \end{aligned}$$

$$\text{From the ideal gas equation, it can be shown that; } M_r = \frac{mRT}{PV}$$

$$\text{With: } m = 0.292 \text{ g, } T = 295 \text{ K, } P = 733 \text{ mmHg, } V = 0.061 \text{ dm}^3;$$

$$M_r = \frac{0.292 \times 0.082 \times 295}{\frac{733}{760} \times 0.061} \text{ or } 120.1 \text{ g/mol}$$

The correct molar mass was 120.1 g/mol.

12. The Boyle's cannot be applied when the number of gas particles has been changed; that is reason of reaching the false conclusion which is "dissociation of the gas decreases amount of the pressure".

13. (a) 58.265 (b) 116.53

14. 16.8%

15. (a) 70.72 g/mol (b) 173.6 mL.

16. (a) 0.64 atm (b) $P_{\text{PCl}_5} = 0.28 \text{ atm}, P_{\text{PCl}_3} = 0.36 \text{ atm}$

17. 53.33%

EXERCISE 5

1. (a) The term is used to represent homogenous mixture of two or more substances.

(b) There are three types

1. Gaseous solution

This is the solution in which the solvent is a gas.

In these solutions; the solute may be liquid, solid or gas. For example, a mixture of oxygen and nitrogen gas is a gaseous solution.

2. Liquid solution

This is the solution in which the solvent is a liquid.

In these solutions, the solute may be gas, liquid or solid. For example, a solution of sodium chloride in water is a liquid solution

3. Solid solution

This is the solution in which the solvent is a solid.

The solute in this solution may be gas, liquid or solid. For example, a solution of copper in zinc is a solid solution.

(c) Hydrogen in palladium (in which hydrogen gas is a solute and the solid is solvent).

2. Molarity is given by the following formula;

$$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution in dm}^3}$$

Whereas molality is given by the following formula;

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{mass of solvent in kg}}$$

But density of water is 1 kg/dm^3 . That is 1 kg of solvent is contained in 1 dm^3 .

Thus numerical value of mass of solvent in kg = numerical value of volume of the solvent in dm^3 .

It follows that: numerical value of molality = $\frac{\text{number of moles of solute}}{\text{Volume of solvent in dm}^3}$

Whereas, numerical value of molarity = $\frac{\text{number of moles of solute}}{\text{volume of solution in dm}^3}$

Where; volume of solution = volume of solvent + volume of solute

But for very dilute solution, volume of solute is negligible compared to the volume of the solvent and therefore;

$$\text{volume of solution} = \text{volume of solvent}$$

Therefore; numerical value of molarity = $\frac{\text{number of moles of solute}}{\text{volume of solvent in dm}^3}$

And hence numerical values of molality = numerical value of molarity if the solution is very dilute.

3. Molarity

Explanation:

Molarity depends on the volume which is temperature dependent unlike molality which depends on mass and the mass is not affected by temperature.

4. (a) 0.1799% (b) $4.505 \times 10^{-2}\text{m}$ (c) 8.101×10^{-4}

5. (a) 17.95m (b) 9.11M

6.

(i) **Solute:** salts. **Solvent:** water.(ii) **Solute:** ethylene glycol. **Solvent:** water.(iii) **Solute:** Oxygen (and all other minor components). **Solvent:** Nitrogen gas(iv) **Solute:** carbon dioxide. **Solvent:** water.(v) **Solute:** tin. **Solvent:** copper

7.

(i) Example: Milk in which water (liquid) is the solvent while the mixture of lactose, minerals and vitamins (solid) is the solute.

(ii) Example: Tanzania 500-shilling coin in which steel (solid) is the solvent while nickel (solid) is the solute.

(iii) Example: Soda drink in which water (liquid) is the solvent while carbon dioxide (gas) is the solute.

(iv) Example: Fog in which air (gas) is the solvent while water (liquid) is the solute.

(v) Example: Smoke in which gas particles (gases) are solvent while dust particles (solid) is the solute.

8. (i) $1.5 \times 10^{-3}\%$ (ii) $1.26 \times 10^{-4}\text{m}$

10. 3.22g

9. 4m

11. $8.764 \times 10^{-4} \text{ mol/L}$

12. Molality of the solution = 0.62m; Mole fraction of glucose = 0.011; Mole fraction of water = 0.989; Molarity of the solution = 0.67M

13. 33.57%

14. (a) 0.283L (b) 98.1% (c) 5.978m

15. $1.6 \times 10^{-4}\text{mol}$

16. 11.6M

17. 1.344M

EXERCISE 6

1.

- Boiling point is the temperature at which vapour pressure of the liquid is equal to the atmospheric pressure
- Boiling point of liquid can be changed by changing external pressure. If the external pressure is increased, the boiling point of the liquid is increased and vice-versa.

2.

(a) When a substance is in equilibrium with its own vapour. The pressure exerted by the vapour on the surface of the substance is known as the vapour pressure of the substance.

(b) Because actually the atmosphere over the liquid, which is saturated with vapour of the liquid, exerts the pressure on the liquid.

(c) The vapour pressure increases (exponentially) with increase in temperature.

3. Negative deviation from Raoult's law

Explanation

The solution being warm to touch suggests that the process of mixing A and B is exothermic. This means that the interaction created between A and B are stronger than A-A and B-B interactions which are broken in the mixing process thus making the process exothermic in overall. The exothermic nature of the mixing process is indicating a negative deviation from Raoult's law.

4. To condense a vapour of given composition to get its corresponding liquid at given pressure, lower temperature (liquid phase is below vapour phase) is needed while in condensing the vapour at given temperature, higher pressure (liquid phase is above the vapour phase) is needed.

5. No.

Explanation:

Ideal solution boils in such a way that the vapour formed is richer in one component which is more volatile. So always vapour phase has more of the component with high vapour pressure compared to liquid phase and hence vapour composition will normally be different to liquid composition.

6.

(a) Are liquids which do not mix at all so that they tend to form separating layer when they are mixed. These are liquids like water and benzene whose intermolecular forces differ much.

(b)

1. Vapour pressure

Vapour pressure of the immiscible liquid mixture is the arithmetic summation of vapour pressure of individual pure components.

2. Intermolecular forces

Intermolecular forces in pure liquids is different to intermolecular forces in the solution.

(Liquids which form immiscible mixture have different intermolecular forces).

7.

- (i) Liquid ethanol contains an extensive hydrogen bonding network, and cyclohexane is non-polar with Van-der-Waals dispersion forces. Because the cyclohexane molecules cannot interact favorably with the polar ethanol molecules, they will disrupt the hydrogen bonding. As a result, the intermolecular interactions in the solution will be weaker than those intermolecular interactions in pure ethanol and pure cyclohexane leading to a higher vapour pressure than predicted by Raoult's law and hence the solution will be non-ideal with positive deviation.
- (ii) Methanol contains an extensive hydrogen bonding network. With the polar acetone molecules, it creates intermolecular interactions in the solution which are stronger than the intermolecular interactions in pure components. This makes the real vapour of solution to be lower than that predicted by Raoult's law and hence the solution will be non-ideal with negative deviation.
- (iii) Hexane and isooctane are both non-polar molecules. Thus the predominant intermolecular forces in both liquids are London dispersion forces. So in the solution the intermolecular interactions will be similar to those intermolecular forces in the pure liquids. As result, the real vapour pressure of the solution will be almost the same as that predicted by Raoult's law and hence the solution will be approximately ideal.

8.

- (i) Ideal solution
- (ii) Non-ideal solution with negative deviation
- (iii) Non-ideal solution with positive deviation
- (iv) Non-ideal solution with negative deviation

9.

- (i) In steam distillation vapourisation is normally done by means of steam whereas direct heating is used to vapourise component in fractional distillation.
- (ii) Steam distillation is used to separate components in a heat sensitive mixture whereas the fractional distillation is a technique useful in separating the hydrocarbon fractions in crude oil.
- (iii) In steam distillation only one step of distillation and condensation is used whereas there is successive (repetition of) distillation and condensation in the fractional distillation.
- (iv) In steam distillation components are distilled at temperatures below their actual boiling points whereas in fractional distillation, the components are distilled at their boiling points.

10.

- 1) **Azeotropic distillation:** This is done by adding third component (volatile component) to the azeotrope so as to obtain new azeotrope with lower boiling point. For example, benzene may be added as third component in the ethanol-water azeotrope so as to get anhydrous alcohol.
- 2) **Chemical method:** This involve adding another substance that reacts and remove one component. For example, calcium oxide (quicklime) or concentrated sulphuric acid can be used to eliminate water from water containing azeotrope.
- 3) **Molecular sieving (adsorption):** Molecular sieves have small pores which allow to carry (adsorb) only small molecules like water leaving larger molecules like alcohol. Activated charcoal or silica gel are good examples of molecular sieves which are capable of eliminating by adsorption unwanted substances.

11. Zero heat change: This occurs when strength of intermolecular forces in pure liquid is equal to that in solution such that the energy absorbed in breaking intermolecular forces in pure liquid is equal to the energy evolved in forming intermolecular forces in the solution. As result, solution under this category are ideal solution.

Positive heat change: This occurs when strength of intermolecular forces in solution are smaller than those in pure liquid such that the energy absorbed in breaking intermolecular forces in pure liquid is greater than the energy evolved in forming intermolecular forces in the solution. As result, solution under this category are non-ideal solution with positive deviation.

Negative heat change: This occurs when strength of intermolecular forces in solution are higher than those in pure liquid such that the energy absorbed in breaking intermolecular forces in pure liquid is smaller than the energy evolved in forming intermolecular forces in the solution. As result, solutions under this category are non-ideal solution with negative deviation.

12. Ideal solution boils in such a way that, the vapour formed is richer in one component which more volatile. So on successive distillation and condensation pure component which more volatile is found in the collector as the distillate and pure component which less volatile remains in the distillation flask as the residue. Hence non-ideal solution can be separated into its pure component by fractional distillation.

13. This is because there is no solution which is exactly ideal; every solution deviates from Raoult's law to some extent at certain concentration. To be exactly ideal, the intermolecular forces of attraction in pure components must be exactly the same which is impossible (only molecules of the same substance have exactly the same intermolecular forces).

14. The intermolecular forces in pure chloroform molecules and pure acetone are dipole-dipole interactions. But on mixing, the chloroform and acetone molecules, they start forming intermolecular hydrogen bonds which are stronger than dipole-dipole interactions resulting in the release of energy and hence the increase in temperature.

15. Prediction: Small deviation from Raoult's law (The solution is almost ideal).

Explanation:

Small heat of solution means that amount of heat evolved in forming intermolecular forces in the solution is almost the same to the amount of heat absorbed in breaking intermolecular forces in pure components. This implies that the strength of

intermolecular forces in pure components is similar to strength of intermolecular forces in the solution which in turn implies that the solution is relatively ideal with almost zero deviation from Raoult's law.

16. For liquid solution to obey exactly Raoult's law, the intermolecular forces of attraction in pure components must be exactly the same which is impossible unless those components are of the same substance whose 'mixture' will no longer be a solution. So the deviation of solution from Raoult's law is compulsory.

On another hand, for gas solution to obey ideal gas law, intermolecular forces between gas molecules must be absent and size of individual gas molecules must be neglected. The two conditions are relatively easily met in small gases (gases with small molecular size) and also when there is high temperature and low pressure and hence it is easier to find gas solution which obey ideal gas law than finding the liquid solution which obeys Raoult's law.

17. Like in their respective pure component, there are dipole-dipole interactions between bromobenzene and chlorobenzene in the solution with similar strength as that acting between pure bromobenzene molecules and chlorobenzene molecules. This makes the solution nearly ideal solution unlike in chloroform-acetone solution where there are intermolecular hydrogen bonds between chloroform and acetone molecules in the solution which are stronger intermolecular forces than dipole-dipole forces in pure chloroform and acetone leading to negative deviation from Raoult's law.

18. Gas molecules in both pure form and mixture form in the solution are fast moving and are very far apart such that intermolecular forces between them are negligible and hence the solution becomes ideal.

19. The solution is ideal.

Explanation:

Ice (solid water) and liquid water have the same chemical structure of water. Their mixture is actually the one thing of pure substance which is water, and hence in solution terms the 'mixture' is exactly ideal solution.

20. Mole fraction of benzene = 0.774; Mole fraction of toluene = 0.226

21. Vapour pressure of pure A = 455.55 torr; Partial vapour pressure of A in the solution = 256.2 torr

22. Mole fraction of A is 0.47, Mole fraction of B is 0.53

23. The vapour pressure of volatile hydrocarbons is very high and therefore they get evaporated, leaving behind the system. Due to this they are not used as lubricants in automobiles unlike non-volatile hydrocarbon which have low vapour pressure.

24. Yes.

Explanation:

Limonene is high boiling liquid which decomposes at high temperature. So steam distillation is used to obtain essential oils as the distillation (boiling) of immiscible mixture of the oil and water occurs at lower temperature.

25.

- (i) Its equipment is inexpensive.
- (ii) It requires less fuel for extraction of oil.

26.

- 1) Orange oil
- 2) Eucalyptus oil
- 3) Camphor oil

27. Reason: To get high quality fatty acids in short time.

Explanation

Steam distillation is used in isolation of substances like organic compounds which decompose before boiling as their normal boiling point are above their decomposition temperature. Fatty acids being very sensitive to heat (they decompose at much lower temperature), the steam distillation is applied under reduced pressure, therefore reducing the boiling point of the mixture (operating temperature) even further. So to ensure that high quality fatty acids are obtained without any degradation of their chemical composition steam distillation is done under reduced pressure. Also since under reduced pressure, the distillation is achieved at much lower temperature, the separation is achieved much faster.

28. Positive deviation from Raoult's law.

Explanation:

The kerosene (it is hydrocarbon) being less polar, tend to weakens intermolecular hydrogen bonds in alcohol which is more polar and consequently intermolecular forces between kerosene and alcohol molecules in the solution are weaker than in pure alcohol leading to the positive deviation from Raoult's law.

29. No; the vapour pressure will not be halved.

Explanation

Vapour pressure is measured when the liquid in the container is at equilibrium with vapour. Using container of larger volume means the liquid has more surface to evaporate and therefore there are more vapour at equilibrium resulting to the same collision frequency between vapour and container's walls despite the increase in volume and hence equilibrium vapour pressure remains constant. Analogously, container of smaller volume means less surface area for liquid to evaporate resulting to the same vapour pressure despite the decrease in volume. Hence, the vapour pressure remains the same irrespective to the size of the container.

30. In the ethanol-water azeotrope, concentrated sulphuric acid would react with ethanol to give alkene (or ether in the partial dehydration) and hence the acid cannot be used to remove water in this case. In the case of the nitric acid-water azeotrope, calcium oxide would react with the nitric acid to give the calcium nitrate.

31. At room temperature, the vapour pressure of liquid ammonia is very high and thus the liquid would vigorously spew out of the bottle. But on cooling, the vapour pressure decreases and hence the liquid ammonia will not spew out.

32. Having higher boiling point than either of pure liquid means that intermolecular forces in the solution (mixture) are stronger than those present in pure liquid components suggesting negative deviation from Raoult's law. This is due to the fact that intermolecular forces in pure ethoxyethane molecules and pure trichloromethane are dipole-dipole interactions. But on mixing, the ethoxyethane and trichloromethane molecules, they start forming intermolecular hydrogen bonds which are stronger than dipole-dipole interactions resulting to higher boiling point of the solution.

33. (i) Boiling point will be above 100°C which is greater than either of the pure liquid.

Explanation:

The solution (mixture) having volume (95 mL) which smaller than the summation of individual volumes (100 mL) of pure liquids, implies that intermolecular forces in the solution are stronger than intermolecular forces in pure liquid components (X and water). The stronger intermolecular forces in the solution means that the vapour pressure of the solution is less than that predicted by Raoult's law and hence higher boiling point for the solution; suggesting that the mixture is the non-ideal solution with negative deviation.

(ii) Mineral acid like nitric acid.

34. Azeotrope is a mixture because, unlike compounds azeotropes consists of different molecules of different substances. Furthermore, components of azeotropic mixture can be separated by physical methods like azeotropic distillation. Also components of azeotropic mixture react independently; for example, only water in alcohol-water azeotrope reacts with CaO leaving alcohol unreacted.

35. The mole fraction of benzene was 0.5.

36. Azeotropes are similar to compounds in the following manner:

- They have fixed composition.
- They boil at fixed temperature without changing their composition.
- They cannot be separated into their respective pure components by simple distillation.

37. Non-ideal solution of negative solution has higher boiling point than the expected one if the solution would be ideal. Consequently, it attains azeotropic composition in **liquid phase** of which the liquid mixture has maximum boiling point. Hence the explained behaviour is the characteristic of a maximum boiling azeotrope.

38. The separation of components stopped due to formation of azeotropic mixture in the distillate. Also the formation of azeotropic mixture in the distillate suggest that the binary mixture of A and B is the non-ideal solution of positive deviation.

39. Mole fraction of benzene = 0.774; Mole fraction of toluene = 0.226

40. 80°C

Hint:

A liquid starts to boil when its vapour matches the atmospheric pressure (in this case, 1atm)

$$P_{\text{soln}} = X_{\text{Acetone}} P_{\text{Acetone}}^{\circ} + X_{\text{water}} P_{\text{water}}^{\circ} = 1\text{atm}$$

Then calculate mole fraction of each component from the given data get:

$$X_{\text{Acetone}} = \frac{1}{3}; X_{\text{water}} = \frac{2}{3}$$

$$\text{This gives: } 1\text{atm} = \frac{1}{3} P_{\text{Acetone}}^{\circ} + \frac{2}{3} P_{\text{water}}^{\circ}$$

Then by trials, you can find values of vapour pressure which satisfies above the equation where the best result is obtained by using the values at 80°C

$$\text{That is } \frac{1}{3} \times 2.12 + \frac{2}{3} \times 0.456 = 1.01\text{atm}$$

41. (a) $P_{\text{Benzene}} = 406\text{torr}$; $P_{\text{Toluene}} = 133\text{torr}$ (b) $X_{\text{Benzene}} = 0.75$; $X_{\text{Toluene}} = 0.25$

42. Raoult's law holds for an ideal solution. So the partial pressure of benzene in benzene-toluene mixture (where by both components of the mixture are non-polar, making the solution ideal) is given by the following formula: $P_{\text{benzene}} = X_{\text{benzene}} P_{\text{benzene}}^{\circ}$

Adding a polar compound (benzoic acid) to a non-polar solvent (benzene) will result in an increased intermolecular force of attraction between the polar solute and the non-polar solvent relative to the intermolecular forces of attraction between the non-polar solute and the non-polar solvent. This will reduce partial pressure of benzene, giving a negative deviation from Raoult's law.

That is in benzene-toluene mixture; $P_{\text{benzene}} < X_{\text{benzene}} P_{\text{benzene}}^{\circ}$

43. In pure alcohol and water, the molecules are held tightly by strong hydrogen bonding. Then interaction between molecules of alcohol and water is weaker than alcohol-alcohol and water-water interaction. As result, when alcohol and water are mixed, the intermolecular interactions become weaker and the molecules can easily evaporate. This increases the vapour pressure of the solution which in turn lowers the boiling point of resulting solution.

44. (a) (i) 12.45kPa

(ii) It would make no difference. The total vapour pressure will still be 12.45kPa because the vapour pressure of immiscible mixture is independent of the proportions of components.

(b) A liquid boils when its vapour pressure becomes equal to the atmospheric pressure. At 99°C, the total pressure is 100.1kPa (2.34kPa + 97.76kPa) which is slightly less than the atmospheric pressure. That means that it is close to, but below its boiling point.

- Pure water must have a vapour pressure of 101.325kPa at 100°C (normal boiling point of water)
- The combined water and ethyl benzoate vapour pressure reach 101.325kPa at temperature less than 100°C (boiling point of immiscible liquid mixture is less than either of the two components) and hence the mixture must boil somewhere between 99°C and 100°C.

45. (i) 0.84atm (ii) 33g

46. (i) 0.307 torr (ii) 0.724 (Pentane), 0.276 (Hexane)

47. 61.4g

48. 0.17

49. 48.59g/mol

50. 127g/mol

51. 0.69

EXERCISE 7

1. Vapour pressure of the solution will **decrease**.

Explanation:

As the time pass over, solvent undergoes evaporation leaving salt particles which are non-volatile. As result concentration of solute in the solution is continuously increasing leading to more lowering in vapour pressure and hence decrease in the vapour pressure of the solution over time.

2. The given compounds are electrolytes so they tend to ionise in water thereby increasing number of solute particles in the solution and hence more increase in freezing point depression. Their extent of ionisation in the solution is determined by their acidic strengths whereby fluorine being more electronegative exerts stronger negative inductive effect than chlorine making trifluoroacetic acid stronger acid than trichloroacetic acid while acetic acid having no negative inductive effect at all is the weakest acid among the three. Consequently, the degree of ionisation and hence freezing point depression will obey the given order.

3. They are both colligative properties which are determined by solute concentration in the solution and they caused by the lowering in vapour pressure of solvent in the solution. Furthermore, they both occur (bound) together in the solution; that is the solution cannot have osmotic pressure without having freezing point depression.

4. Are solutions with equal osmotic pressure. Are solutions with the same concentration and therefore the same vapour pressure at given temperature. As an example, 0.1M aqueous glucose and 0.1M aqueous urea are isotonic solutions at room temperature.

5. HCl is strong acid while acetic acid is weak acid; so the former ionises almost completely in the solution to give greater number of solute particles and hence greater depression in freezing point than the latter which ionises only partially.

6. Electrolytes undergo dissociation in solution making the observed number of particles in the solution abnormally high and hence abnormally high values of colligative properties.

7. Sucrose is non-electrolyte while sodium electrolyte is strong electrolyte. So with equimolar of their solutions, sodium chloride will ionise (dissociate) almost completely to give almost twice the sucrose concentration and hence its osmotic pressure will be almost twice too making the NaCl solution hypertonic to sucrose solution and not isotonic.

8. $0.10\text{m C}_2\text{H}_4(\text{OH})_2 > 0.10\text{m KNO}_3 > 0.10\text{m BaCl}_2 > 0.10\text{m Na}_3\text{PO}_4$

Decrease in freezing point

9. In benzene, benzoic acid undergoes association to form dimer, thus decreasing number of solute particles in the solution leading to smaller value of osmotic pressure in contrast to water in which the acid undergoes dissociation giving greater number of solute particles in the solution.

10. High lattice energy for a compound means more difficult for the compound to dissolve in the solution to give free ions. More difficult to undergo dissociation to give free ions means fewer solute particles in the solution which in turn means smaller Van't Hoff's factor. Hence compounds with high lattice energy have small Van't Hoff's factor while compounds with low lattice energy have large Van't Hoff's factor.

11.

(i) Amount of solute.

(ii) Nature of solvent.

12. 5g

14. 0.35g

13. 69.6g/mol.

15. (a) 17.95m (b) 9.1M (c) -33.4°C

16. Reason:

Mango loses water by osmosis.

Explanation

Concentrated salt solution is hypertonic with respect to mango. So when mango is placed in the solution, mango loses water to the solution by osmosis and consequently it shrivels.

17. Reason:

Water flows into flowers by osmosis.

Explanation:

Fresh water is hypotonic with respect to the flowers. So when wilted flowers are placed in fresh water, flowers will absorb water by osmosis and hence they regain their freshness.

18. The salt or sugar increases the solute concentration to a level above that present in living organisms making the food hypertonic with respect to bacteria. So any bacterial cell (which is surrounded by semi – permeable membrane) that wanders into such food will have its water drawn out by osmosis and eventually will die of dehydration.

19. Due to addition of common salt (non-volatile solute), the boiling point of the salt containing water are elevated and the egg become hard at high temperature (above normal boiling point of pure water).

20.

- (i) Salt is applied in icy road (during winter climate) to lower freezing point which in turn means melting point is lowered below ice temperature and hence the ice will melt more quickly, making driving safer.
- (ii) CaCl_2 and MgCl_2 dissociate to give greater number of solute particles (three ions) than NaCl which dissociates into two ions and hence they cause greater melting/freezing point depression making them more effective.

21. In making anti-freeze ethylene glycol is added to water and therefore doing both decreasing freezing point and raising boiling point of water. The resulted freezing point depression and boiling point elevation means that the radiator can work in extremely low temperature without freezing and extremely high temperature without boil overs and hence operating range of cooling system has been increased by colligative properties.

22. Foods with high sugar content have higher osmotic pressure than most of fluids in the body (are hypertonic with respect to body fluids). So eating them makes water to be drawn from cells by osmosis and hence thirsty feeling to the people.

23. If the soft drink is cooled to temperature that is below the freezing point of pure water, then the dissolved CO_2 lowered the freezing point of the soft drink so that it was still liquid.

But when the bottle is opened, the dissolved CO_2 escape from the solution, decreasing concentration of dissolved solute (gas) and thus raising the freezing point to the temperature above the temperature of solution and hence the solution (soft drink) freeze.

24. Seawater contains dissolved salts. So it has higher solute concentration and therefore higher osmotic pressure than most of fluids in the body (are hypertonic with respect to body fluids). So drinking seawater will make water to be drawn from cells by osmosis and hence the person will die due to dehydration.

25. (i) Not correct.

Explanation:

Isotonic solutions have equal molarity at given temperature. Solutions with equal molarity have different molality and hence different boiling point elevation and freezing point depression. Even if molarity and molality would be almost equal (for dilute solutions with water as solvent), still boiling point elevation and boiling point depression will be different because K_b and K_f values are different for different solvents.

(ii) Not correct

Explanation:

Boiling point elevation does not only depend on the molality of the solute in the solution but also on the nature of solvent which determine K_b value. So even if the molality is the same, boiling point elevation will be different to difference in the K_b values of solvents.

(iii) Not correct

Explanation:

Colligative properties do not depend on the nature of the solute (not solvent). Colligative properties like boiling point elevation and freezing point depression depend on nature of solvents which determines K_b and K_f values. Also lowering in vapour depend on the nature of solvent which determine vapour pressure of pure solvent. Only osmotic pressure does not depend on the nature of solvent.

26. 10g.

27. 269.06K

28. Atomic mass of A = 25.59amu; Atomic mass of B = 42.64amu

29. 2.33atm

Hint:

Assume density of solution is 1g/cm^3 (density of water) and then convert molality (0.01m) to molarity. After that you may continue to get the final answer.

30. 100.24°C

31. 3.42g

32. $5.27 \times 10^{-3}\text{atm}$

33. 6.45%

34. 24.6 atm

35. 0.106

EXERCISE 8

1.

- 1) Temperature
- 2) Nature of solute
- 3) Nature of solvents

2. Distribution law is not applicable when:

- 1) The temperature is not kept constant.

- 2) The molecular state of the solute in the two solvents is not the same. (If the solute undergoes either association or dissociation in one of the solvent).
- 3) The distribution of solute in the two solvents is not at equilibrium.
- 4) The solute concentration in the two solvents is high.
- 5) The solvents are miscible.

3.

- (i) Is the method of removing (extracting) a solute from a certain solvent by introducing the second solvent (extractive solvent) which is immiscible to the first one and then allowing the solute to distribute itself in the two solvents.

(ii)

First condition: The solute must be more soluble in extractive solvent than in the first solvent. That is, to ensure that greater amount of solute goes to extractive solvent, the partition coefficient between extractive solvent and first solvent, K_d should be large.

Second condition: The volume of extractive solvent should be divided into small portions (partitions) rather than using the whole large volume at once. That is, greater amount of solute is extracted by having larger number of portions of volume of extractive solvent.

4. 0.983g

5. (a) 0.0476g (b) 0.0083g

6. 3g

7.

- 1) Study of association of a solute
- 2) Study of dissociation of a solute
- 3) Study of complex ions
- 4) Study of solvent extraction
- 5) Study of distribution of indicators

8. The law is applied in solvent extraction to remove impurities; in liquid chromatography to separate solutes and also in determination of solubility of substances like solubility of drugs in water and other solvents.

9. With two polar groups (the acid has two carboxylic groups which are polar), butanedioic acid is highly polar like water and its polarity is closer to water than ether whose polarity is very low. Consequently, solubility of the acid is higher in water and hence the partition coefficient must be greater than one in favour of water.

10. Mass of X in trichloromethane layer = 18.75g

Mass of X remained in water layer = $(25 - 18.75)\text{g} = 6.25\text{g}$

$$\text{Using } K_d = \frac{\text{Concentration of X in } \text{CHCl}_3}{\text{Concentration of X in } \text{H}_2\text{O}}$$

$$\text{Substituting } K_d = \frac{18.75/100}{6.25/500} = 15 = \text{Given value}$$

Since calculation of K_d value from the result she got, gives the same value of the given K_d ; the work was correct.

11.

- (i) Carbon disulphide is purely non-polar liquid while water is highly polar liquid; so they differ much in their intermolecular forces. Since they differ much in their intermolecular forces, it becomes more difficult for their molecules to mix each other (so as to enable free distribution of iodine (solute) in the two liquids) and hence more vigorous shaking is needed for longer time.
- (ii) The time required will be less than three minutes (normal time).

Explanation

Since carbon disulphide and water differ much in their intermolecular forces, their tendency to mix is very low and hence it becomes easier to achieve separation after forcing them to mix through shaking.

(iii) The partition coefficient will be very large.

Explanation

Like carbon disulphide, iodine is purely non-polar on the contrary to water which is highly polar liquid. So the solubility of iodine in the carbon disulphide (which is on the numerator of the K_d equation) is much higher than in the water and hence the K_d value becomes large.

12.

- (i) Solvent extraction.
- (ii) Ether acts as extractive solvent to remove (separate) the organic substance from water.
- (iii)
 - 1) Ether is immiscible to water.
 - 2) Ether has greater ability to dissolve the organic substance than water.

(iv)

1) Benzene

3) Hexane

2) Chloroform

4) Acetone

13. 120

14. 29.07g/L

15. 0.082

16. 11%

17. 0.00044g/mL

18. 2.4g

19. 0.25

20. (a) 1.83 (b) More soluble in water ($K_d > 1$).**EXERCISE 9**

1. The rate of a reaction is defined as the change in concentration as a function of time. Thus, the two quantities that must be measured are:

- 1) Molarity of either a reactant or product and
- 2) Time.

2. As the reaction proceeds, concentration of reactants decreases and whence the rate of reaction decreases. So the reaction rate is unique in each particular instant of time. This makes the average rate which is taken over certain range of time less useful. To get true picture of the reaction, instantaneous rate of reaction is used.

3.(a)

- (i) Number of collisions between particles per second.
- (ii) Combined energy of the colliding particles.
- (iii) Minimum collision energy required for a collision to be successful.

(b) **Collision frequency can be changed by;**

- Changing pressure (greater pressure means more collision frequency and vice-versa)
- Changing concentration (greater concentration of reactant means more collision frequency vice-versa)
- Changing temperature (Higher temperature means more collision frequency and vice-versa)
- Changing surface area (Greater surface area of reactant means more collision frequency and vice-versa)

Collision energy can be changed by changing temperature (Higher temperature means greater collision energy and vice-versa)

Activation energy can be changed by adding or removing catalyst (in most cases, addition of catalyst, lowers activation energy and vice-versa).

4.

- (i) Greater collision frequency means greater rate of chemical reaction and vice-versa
- (ii) Greater collision energy means greater rate of chemical reaction and vice-versa.
- (iii) Greater activation energy means lower rate of reaction and vice-versa.

5.

Temperature

The increase in temperature increases both collision frequency and collision energy of reacting particles and hence the rate of chemical reaction increases with rise in temperature.

Concentration

The increase in concentration of reactants increases collision frequency and hence the reaction rate will increase as the reactants concentration increases.

Light

The increase in the light intensity increases the number of photons in light and therefore more number of reactant molecules gets energy by absorbing more number of photons and undergo chemical change. Consequently, the rate of photochemical reactions, increase with increase in the intensity of suitable light used.

Pressure

The increase in partial pressure of gaseous reactants increases collision frequency and hence the reaction rate will increase as the pressure increases.

Surface area

The greater surface area exposed, the greater chance of collisions between reacting particles leading to higher collision frequency and hence the rate of a reaction increases with increase in the surface area of solid reactant.

6. Usually the reaction rate depends on concentration of reactants. As the reaction proceed, concentration of reactants is progressively decreasing leading to the progressive decrease in the reaction rate as well.

7.

$$-\frac{1}{3} \frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{4} \frac{d[C]}{dt}$$

8. Because of the 2:1 stoichiometric ratio between NO and N₂, the NO must use 2 moles for each mole of N₂ produced. This means that the rate of consumption of NO is twice as fast as the rate of production of N₂.

9. 0.4molL⁻¹hr⁻¹10. 6.36 × 10⁻⁵M/s11. (a) 8.4 × 10⁻⁷M/s (b) 2.1 × 10⁻⁷M/s

12. Food spoilage is the chemical reaction. So low temperature of the fridge decreases the rate of the spoilage process.

13. Because the iron rusting reaction has very high activation energy which makes the reaction slow.

14. Higher temperature in hot water increases the rate of reaction that makes the light sticks to produce light.

15. For the combustion reaction to occur between woods and air, the potential energy of the reactants must be large enough to overcome activation energy. Since the activation energy for the reaction is too high to be achieved at room temperature, woods do not burn themselves unless they are ignited.

16. Coal dust has larger surface area than the coal lump. Larger surface area means more frequent collision between coal particles and oxygen molecules in air and hence higher reaction rate.

17. The activation energy of combustion of coal is so high that cannot be attained at normal temperature. When the flame is applied, part of coal and air in contact with the flame absorb heat energy from the flame and the heat is enough to overcome activation energy making the combustion to begin. The heat generated in the initial stage of combustion, liberates more heat to overcome activation energy and the combustion continues.

18. Changing magnesium from ribbon to powder increase surface area for the magnesium. The increase in the surface area increases more frequency of collisions than the increase in concentration and hence the reaction rate is increased more by changing the magnesium to powder than doubling the acid concentration.

19. Initially, the reaction rate is low because both reactants are negatively charged making to repel each other and hence high activation energy for the reaction.

Thereafter, the reaction rate increases because Mn^{2+} ions which act as autocatalyst provides an alternative route with lower activation energy.

Finally, near the end of the reaction, the reaction rate decreases because the concentration (amount) of reactants has been decreased.

20. Due to very high activation energy of reactants (H_2 and O_2), room temperature does not exert enough kinetic energy to the gases' molecules and hence collision energy between the two gases is insufficient to overcome the activation energy.

21. The average rate (which is the mean of several instantaneous rates taken over a period of time) after 60 minutes is smaller than after 30 minutes. This is due to the fact that instantaneous rates of a reaction decreases as time progresses due to decrease in concentrations of reactants. Hence the average rate taken over a longer period (60 minutes) would have a smaller value compared to that taken over a shorter period (30 min) after the reaction begins.

22. To achieve effective collision between reacting molecules, the collision must have both activation energy and proper orientation of colliding molecules. So the reaction whose most of its colliding reactant molecules have improper orientation will be slow even if those colliding molecules have attained activation energy.

23. **Hint:** Draw well labelled energy profile diagram suiting given data; from which you can easily deduce the energy values which are asked in the question.

(a) 25 kJ (b) 16 kJ (c) 6 kJ

24. (a) 0.15g/s (b) 13.3g

Hint: mass of flask and contents decrease due the loss of oxygen gas as the flask was open. So (150 – 145) g or 4.5g is the mass of oxygen produced in 30s.

25. 0.55min

EXERCISE 10

1. **Zero order:** Half-life is directly proportional to the initial concentration of reactant.

First order: Half-life remains constant even after varying initial concentration of reactant.

Second order: Half-life is inversely proportional to the initial concentration of reactant.

2. Zero order

Explanation

The rate of reaction did not change even after decreasing the concentration of reactant. This implies that, the reaction rate is independent to the concentration and hence it must be of zero order.

3. Any reaction including zero order reactions needs concentration of reactants for the reaction to take place (a reaction cannot continue if the concentration of the reactant(s) is zero). It is the **rate** of reaction that is independent and not the reaction itself.

4.

- (i) **Catalytic decomposition of HI over the surface of gold metal at high pressure** (to give hydrogen gas and iodine gas) and **photochemical combination of hydrogen gas and chlorine gas** to give hydrogen chloride gas.
- (ii) **Decomposition of hydrogen peroxide** (to give water and oxygen gas) and **radioactive decay**.
- (iii) **Thermal decomposition of hydrogen iodide** (to give hydrogen gas and iodine gas) and **thermal decomposition of nitrogen dioxide** (to give nitrogen monoxide gas and oxygen gas).
- (iv) **Acid hydrolysis of ester** (to give carboxylic acid and alcohol) and **acid hydrolysis of sucrose** (to give glucose and fructose).

5. 444s

6.

- (i) Third order.
- (ii) The reaction rate will increase by a factor of 8.

7. First order (order = 1)

9. $1.15 \times 10^{-6}\%$

8. 144 minutes

10. 8.3s

11.

(i) First order with respect to A, third order with respect to B.

(ii) $7.4 \times 10^{13} \text{L}^3 \text{mol}^{-3} \text{sec}^{-1}$

12.

(a) $5.17 \times 10^{-3} \text{s}^{-1}$.

(b) $t_{3/4}$ does not depend on the initial concentration because this is a first order reaction, which means that the time required for given fraction of reactant to react is only related to the rate constant.

13. The order with respect to BrO_3^- is 1; The order with respect to Br^- is 1; The order with respect to H^+ is 2

The overall order of reaction is 4; The value of k is $8 \text{dm}^3 \text{mol}^{-3} \text{s}^{-1}$

14. 5.68g

Assumption: the reaction is of the first order since it is decomposition reaction (Recall: most of the decomposition reactions are first order reactions).

15. A reaction takes place due to collision of reacting molecules. The chances for a large number of molecules or ions to collide simultaneously are less. Hence, the reactions of higher order are very few.

16. Disagree

Explanation

Her statement only holds with reactions with order of one and above in which reaction rate is continuously decreasing as the reaction proceeds due to decrease in concentration of reactants. However, for zero order reactions, the reaction rate does not depend on concentration of reactants and therefore the reaction rate remains constant despite the decrease in concentration.

17. For decomposition of ammonia (or hydrogen iodide) gas, the gas must be adsorbed over the metal which catalyses the reaction. Only ammonia molecules which have been adsorbed by the metal surface are capable of undergoing decomposition. If the entire metal surface has been covered by the gas (at high pressure), the rate of decomposition will remain constant regardless of concentration of the gas because for every adsorbed gas molecule which get decomposed, another unadsorbed gas molecule over the metal surface replace it, get adsorbed and thus keeping number of adsorbed gas molecules constant and the reaction rate as well.

18. **Hint:** Radioactive decay is the first order reaction.

The percentage that remains is 0.454%.

19. 116.3days

20. Don't agree.

Hint: The order of reaction can be deduced from units of rate constant. Show from units ($\text{M}^{-1} \text{s}^{-1}$) of given rate constant ($1.83 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$) that the reaction is of the second order. Then solve the question by using the integral equation of second order reaction to get the final answer which is $3.8 \times 10^{-5} \text{s}$.

21. With sufficient PH_3 , all of the catalytic sites on the tungsten surface are occupied. Thus, further increase in the amount of phosphine will not affect the reaction rate and hence the rate is independent of $[\text{PH}_3]$.

22. 16 minutes

23. First order

24. The rate would decrease to 1/8 of the initial rate.

25. First order

26. 161 minutes

27. Second order

28. 34.2 minutes

29. (a) 2

(b)(i)

The order of reaction with respect to A is 2

The order of reaction with respect to B is 0

(ii) Rate equation: $R = K[A]^2$

Units of rate constant: $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$

30.

(a) $R = K[\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2$

(b) $7.62 \times 10^{-3} \text{M}^{-2} \text{min}^{-1}$ (or $7.62 \times 10^{-3} \text{L}^2 \text{mol}^{-2} \text{min}^{-1}$)

(c) $2.6 \times 10^{-5} \text{Mmin}^{-1}$

(d) 0.514M

31.(a) The order of the reaction with respect to A = 1

The order of the reaction with respect to NaOH = 1

The initial rate in the experiment 4 = $2.4 \times 10^{-3} \text{M/s}$

(b)

(i) $R = K[A]$ (or $R = K[A][\text{NaOH}]^0$)

(ii) The value is 0.45. Its unit is s^{-1}

(iii) NaOH is so much in excess that more addition of it has no effect on the rate of the reaction.

EXERCISE 11

1.

- 1) Temperature.
- 2) Catalyst.
- 3) Chemical identity of reactants (or nature of reactants).

2. Activation energy (E_a)

3. On increasing the temperature, both collision frequency and collision energy are increased and hence the reaction rate is increased by large extent.

4. Zero activation energy means that both reaction rate and rate constant remains the same even after changing the temperature.

5. Arrhenius constant (A) and activation energy (E_a).

6.

- (a) H – H and Cl – Cl bonds are so stable that high energy is required to break the bonds and hence the activation energy for the reaction is very high.
- (b) According to Boyle's law increases in pressure (at constant temperature) decrease the volume of gases. This leads to more frequent collisions between hydrogen and chlorine molecules.
- (c) According to the kinetic theory of gases: increase in temperature increase kinetic energy of hydrogen and chlorine gas. Thus more molecules of hydrogen and chlorine will attain sufficient energy to overcome activation energy.
- (d) To increase surface area

7.(i)

Collision energy factor.

When temperature is increased kinetic energy of reacting particles is increased. This makes more reacting particles to attain activation energy and therefore the collisions between the particles become more energetic resulting to the formation of activated complex.

Collision frequency factor.

When temperature is increased, speed of reacting particles is increased thus making the particles to collide more frequently and hence the possibility of reaction between the reacting particles become higher.

(ii) Collision energy factor is more important.

8. 35.9 kcal/mol

Warning!

On your working don't insert simplified Arrhenius equation directly. Because in the question we are already given with the Arrhenius equation in the form of $k = Ae^{-E_a/RT}$, all of your working must start with this form of equation. So in this question, the simplified Arrhenius equation must be applied after showing its derivation from the given equation in the question.

9. (a) 39.4 kJ/mol (b) $2.5 \times 10^{-4} \text{ s}^{-1}$ 11. $9.25 \times 10^{14} \text{ sec}^{-1}$

10. 390.6K

12. 1715J/mol(or)1.715kJ/mol)

13.

- 1) Enzymes in the body to help metabolic activities.
- 2) Catalytic converters in exhaust system of cars to ensure proper combustion of fuel.

14.

- 1) Milk gets sour faster when it is kept at room temperature instead of being kept in the refrigerator.
- 2) Eggs tend to hard boil faster when they are at sea level in comparison to mountains or elevated levels.

15. Disagree.

Explanation

Apart from temperature and activation energy, the value of rate constant is also affected by the value of Arrhenius constant which in turn depends on a chance of having proper orientation between reacting molecules. Two reactions with identical activation energy at the same temperature, will have different rate constant even if their reactants have different chances of having proper orientation whereby the reaction whose reactants have greater chance of having proper orientation for the reaction to take place will possess greater value of Arrhenius constant and hence greater value of rate constant.

16. Rate constant increases as temperature increases. So the value of rate constant at 127°C must be greater than that of rate constant at 27°C in contrary to what she got where the rate constant at 127°C is smaller.

17. This can be done by calculating the ratio of reaction rate (which is equal to the ratio of rate constant) by using the calculated activation energy she found and then comparing it with the given ratio as follows:

$$\text{Using } \log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.30R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Since reaction rate varies directly proportional to the rate constant; $\frac{k_2}{k_1} = \frac{R_2}{R_1} = 3$ where R_2 and R_1 is the reaction rate at 20°C and 50°C respectively.

$$\text{Then } \log \left(\frac{R_2}{R_1} \right) = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\text{Substituting } \log\left(\frac{R_2}{R_1}\right) = \frac{284.24}{2.303 \times 8.314} \left(\frac{323-293}{293 \times 323}\right) = 4.7 \times 10^{-3}$$

$$\text{From which; } \frac{R_2}{R_1} = \log^{-1}(4.7 \times 10^{-3}) = 1.01 \neq 3$$

Since the calculated ratio (1.01) is not equal to the given ratio (3), Kipute got the wrong answer.

$$18. \text{ From } \log\left(\frac{R_2}{R_1}\right) = \frac{E_a}{2.303R} \left(\frac{T_2-T_1}{T_1T_2}\right); E_a = \frac{2.303RT_1T_2}{T_2-T_1} \log\left(\frac{R_2}{R_1}\right)$$

Thus the wrong value of E_a (284.24J/mol) was found after multiplying incompatible value of R (0.082) to other parameters.

So we have to eliminate it by dividing the incompatible R from the wrong answer and then the compatible R is included through multiplication.

$$\text{That is; correct } E_a = \frac{284.24\text{J/mol}}{0.082} \times 8.314 = 28819\text{J/mol or } 28.82\text{kJ/mol}$$

Hence the correct value of activation energy is 28.82kJ/mol.

19. When temperature is increased by 10°C, kinetic energy of molecules increases, number of molecules possessing activation energy become double, therefore number of effective collision double and hence the rate of reaction double even if the kinetic energy did not double (to double reaction rate, you need **number of particles** which have attained activation energy to be doubled and not kinetic energy).

20.

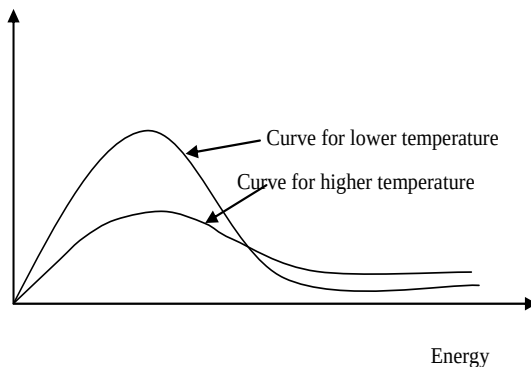
(a) Collision process

Explanation:

Collision process causes some molecules to slow down and therefore loosing 'Kinetic energy'.

(b)

Number of molecules



(c)

(i) Very few collisions have energy which is greater than activation energy

(ii) By addition of catalyst

Explanation

Catalyst lower activation energy and therefore more collisions will possess energy which is greater than activation energy.

$$21. (a) 1.76 \times 10^2 \text{kJ/mol} (b) 2.31 \times 10^{10} \text{Lmol}^{-1}\text{s}^{-1}$$

Hint for calculating the value of A in (b)

Select any pair of related rate constant and temperature, and then with the value of E_a obtained in (a) substitute in the Arrhenius equation ($k = Ae^{-E_a/RT}$ or $\ln k = \ln A - \frac{E_a}{RT}$) to get the value of A.

$$22. 24.206 \text{ kJ/mol}$$

$$23. \text{ Activation energy, } E_a = 44.027\text{kJ/mol; Arrhenius factor, } A = 1.13 \times 10^4 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}$$

$$24. 123.5\text{kJ/mol}$$

Hint:

Substitute the rate in place of the rate constant in the equation $\log\left(\frac{K_1}{K_2}\right) = \frac{E_a}{2.303R} \left(\frac{T_1-T_2}{T_1T_2}\right)$ because of the direct relationship between the rate and the rate constant.

$$25. 108.83\text{kJ/mol}$$

EXERCISE 12

1. (i) 2 (ii) 1

2. The chances that three or more particles are colliding at the same time, with proper orientation and sufficient energy, are extremely small. This makes difficult to have reactions with high molecularity.

3. Molecularity of a reaction means the number of molecules of the reactants taking place in an elementary reaction. Since at least one molecule must be present, the molecularity will be at least one (cannot be zero or negative).

4.

(a) An **activated complex** is the structure along the reaction pathway of the highest energy, which determines the activation energy for the reaction. An **intermediate** can be any structure found in the reaction path.

(b) The rate-determining step is the elementary reaction that controls the mathematical form of the overall rate law. The rate-determining step is usually the slowest elementary reaction.

(c) The slowest elementary reaction.

5.

(i) A reaction mechanism must meet two criteria.

1) The summation of all steps in the reaction mechanism must agree with the stoichiometry of the overall reaction.

2) The suggested mechanism must agree with the experimental rate law of the overall reaction.

(ii) Reaction mechanisms are considered "plausible" rather than "correct" because different sequences of elementary reactions may meet the two requirements.

6.

(a) $\text{HOOH} + 2\text{I}^- + 2\text{H}_3\text{O}^+ \rightarrow \text{I}_2 + 4\text{H}_2\text{O}$

(b) OH^- and HOI

(c) $R = k[\text{HOOH}][\text{I}^-]$

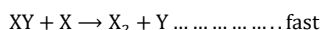
(d) Second order (or 2)

7.

(a) $R = k[\text{XY}]$

(b) $(\text{unit of time})^{-1}$

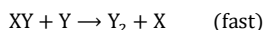
(c)

**Note:**

Any other possible mechanism is accepted provided that it satisfies the following conditions:

- Steps in the mechanism add up to the overall reaction
- One step in the mechanism must start with XY
- Rate determining step (slow step) must involve one molecule of XY

As an example, another possible mechanism is;



8. Reaction mechanism is only a logical explanation of how reaction progresses. It cannot be proven to be true. There may be more than one proposed mechanism, in which the slow elementary step is considered the rate determining step.

9. Reaction mechanism enables understanding of chemical reactions at the molecular level. This is important in the following manner:

1. Chemical reactions optimisation in industries

Through understanding of elementary reactions in the reaction mechanism, reaction rate can be understood. Good understanding of the reaction rate helps in designing and optimising chemical reactions in industrial processes where reaction speed is critical.

2. Designing new compounds

Through knowledge of reaction mechanisms products that will be formed in a reaction can be predicted. This is useful for designing new compounds with specific properties fitting daily life purposes.

3. Development of new drugs and therapeutic agents

Understanding the mechanisms of enzyme-catalysed reactions provides insights into how biological systems function, and thus can lead to the development of new drugs and therapeutic agents.

4. Development of new chemical reactions and catalyst

Understanding the reaction mechanism can provide insight into the underlying factors that govern chemical reactivity, such as bond strengths, steric effects, and electronic properties. This information can be used to design new chemical reactions and develop new catalysts which may be crucial in daily life.

10.

(i) **Mechanism:**Step 1: Hot water + tea bag $\rightarrow$ Hot water – tea bag mixtureStep 2: Hot water – tea bag mixture + sugar $\rightarrow$ tea

(ii) Taking step 1 + step 2 gives;

Overall equation: Hot water + tea bag + sugar $\rightarrow$ tea(iii) **The intermediate** is Hot water – tea bag mixture11. Overall reaction equation: $2\text{O}_3 + \text{sunlight} \rightarrow 3\text{O}_2$; Catalyst: **No** catalyst.

12.

(a) $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$ (Hint: take step 1 + step 2)

(b) Cl

Justification

Cl is used in the step 1 and regenerated in step 2 thus its amount at the end of the reaction is the same as its amount the beginning of the reaction.

(c) ClO

ClO is the product of the step 1 which is consumed as the reactant in the step 2 and therefore it does not appear in the overall reaction equation.

13. Raising the temperature will drive the fast equilibrium step (step 1) towards the left, decreasing the concentration of B which is required for step 2. The decrease in concentration of B will in turn decrease the rate of the second reaction (step 2), and hence the rate of the overall reaction ($A \rightarrow \text{products}$) will decrease as the temperature rises.

14.

(a) $R = k[\text{NO}_2][\text{CO}]$

(b)

Step 1: $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$; (Slow)**Step 2:** $\text{NO}_3 + \text{CO} \rightarrow \text{CO}_2 + \text{NO}_2$; (Fast)

15. (a)

(i) **Kinetic energy of particles.** To be effective, the colliding particles must have certain minimum energy which is known as activation energy.(ii) **The orientation of particles.** To be effective, the colliding particles must have good orientation relative to one another. Even very energetic collision (collisions with kinetic energy greater than activation energy) may not lead to reaction if the particles are not oriented properly.

(b) Decrease in temperature, would decrease the rate of reaction

Explanation

Decrease in temperature lowers the kinetic energy of molecules and therefore:

- Collisions between particles become less energetic (fewer colliding particles will attain activation energy)
- Frequency of collision will be decreased (due to decrease of the speed).

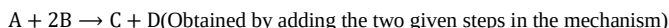
(c) Slowest step, is the rate determining step in the reaction mechanism.

In the given mechanism, the slowest step is: $\text{AB} + \text{B} \rightarrow \text{C} + \text{D}$

Thus the rate law of the above step, is the rate law of the overall reaction

That is; $R = K[\text{AB}][\text{B}]$ (i)

But the overall reaction equation of the overall mechanism is;

And the equation has no AB; so AB in $R = K[\text{AB}][\text{B}]$ must be eliminated by using the fact that:In $\text{A} + \text{B} \rightleftharpoons \text{AB}$

$$R_f = K_f [\text{A}][\text{B}] \text{ and } R_b = K_b [\text{AB}]$$

But at equilibrium: $R_f = R_b$

$$\text{That is } K_f [\text{A}][\text{B}] = K_b [\text{AB}]$$

$$\text{From which } [\text{AB}] = \frac{K_f}{K_b} [\text{A}][\text{B}] \text{ (ii)}$$

Substituting (ii) in (i) gives;

$$R = \frac{K \times K_f}{K_b} [\text{A}][\text{B}][\text{B}] = \frac{K \times K_f}{K_b} [\text{A}][\text{B}]^2$$

But $\frac{K \times K_f}{K_b}$ gives another constant, say k'

$$\text{Thus } R = k[\text{A}][\text{B}]^2$$

Hence the rate law expression for the reaction is $R = K[\text{A}][\text{B}]^2$

(d) Catalyst lower activation energy by providing alternative route for the reaction.

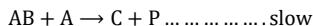
The value of k increases with temperature due to increasing number of collisions between reactants are occurring with sufficient energy to form activated complex as the temperature increases.

16.

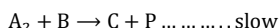
(a) $R = k[A]^2[B]$

(b) $K = 0.12$, units: $L^2 mol^{-2} min^{-1}$

(c)



Alternative possible mechanism



17.

(a) Step 2

(b) From step 2: $R = k[N_2O_2][H_2]$

Eliminating $[NO_2O_2]$ by assumption that step 1 forms rapid equilibrium;

That is $k_f [NO]^2 = k_b [N_2O_2]$

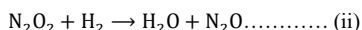
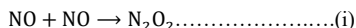
From which $[N_2O_2] = \frac{k_f}{k_b} [NO]^2$

Then $R = \frac{k \times k_f}{k_b} [NO]^2 [H_2]$

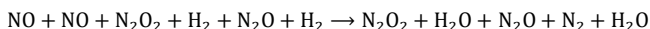
But $\frac{k \times k_f}{k_b} = k'$ (It gives modified another constant)

Thus $R = k' [NO]^2 [H_2]$ and hence the given mechanism is constant with observed rate law

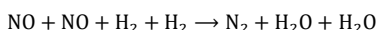
Given that:



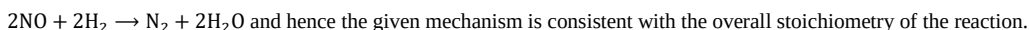
Taking (i) + (ii) + (iii)



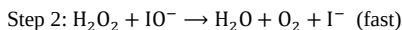
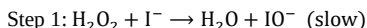
Cancelling like terms in opposite sides of the equation gives;



Or (by combining like terms)



18.



Intermediate is IO^-

19.

(i) Three

(ii) Two

(iii) Second step (has highest activation energy)

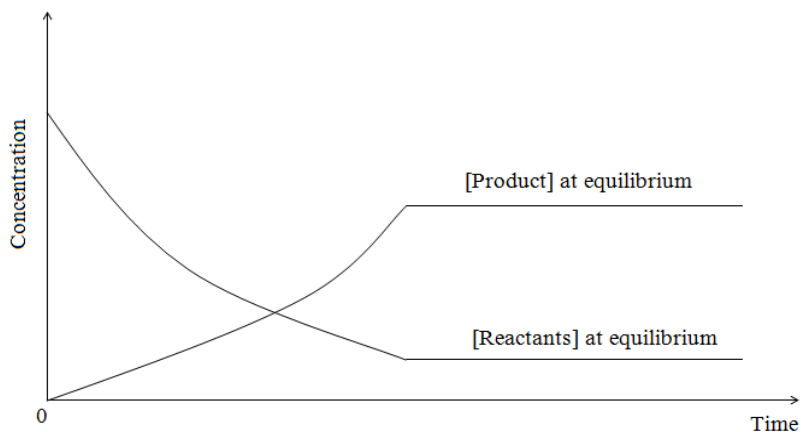
(iv) Third step (has lowest activation energy)

(v) Endothermic

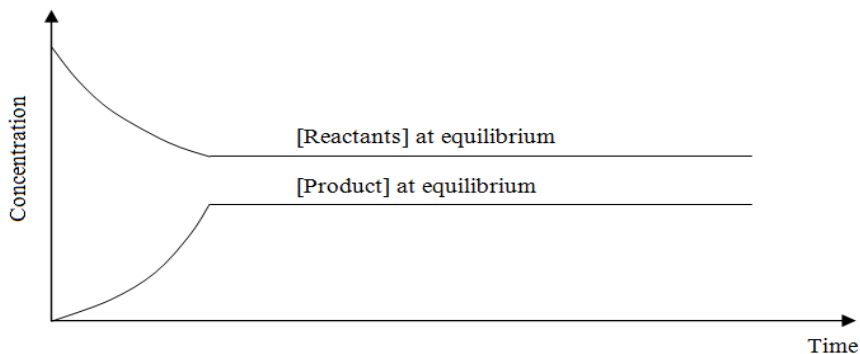
EXERCISE 13

1.

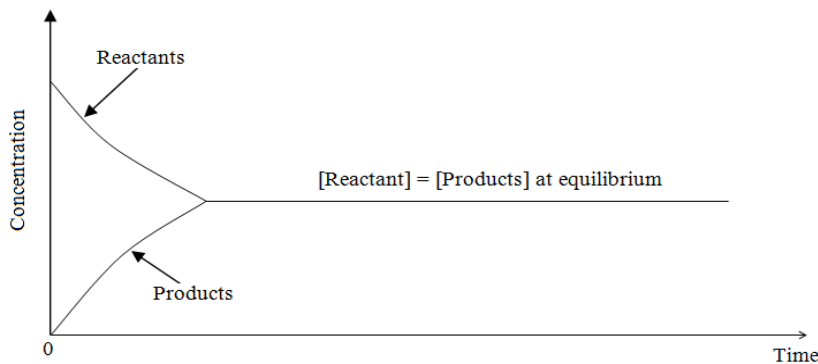
(a)



(b)



(c)

2. Only $\text{H}_2(\text{g})$

3. Forward direction

Explanation

Greater rate of forward reaction, means that there is much high concentration of reactants. So it must proceed in forward direction to decrease the concentration and the rate of forward reaction as well till the equilibrium.

4. No.

Explanation:

For the equilibrium to be established the reversible reaction must take place in a closed system. But in this case, the system is not closed as products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

5.

- At equilibrium state, the rates of forward and backward reactions are equal.
- The observable properties such as pressure, concentration, colour, density, viscosity etc., of the system remain unchanged with time once the system has attained chemical equilibrium.
- The chemical equilibrium is a dynamic equilibrium because both the forward and backward reactions continue to occur even though it appears static externally.
- The chemical equilibrium can be reached by starting the reaction either from the reactants side or from the product side.
- Both pressure and concentration affect the position of equilibrium but do not affect the equilibrium constant.
- The temperature can affect both the position of equilibrium as well as the equilibrium constant.
- A positive catalyst can increase the rates of both forward and backward reactions and thus helping the system to attain the equilibrium faster; but it does not affect the position of equilibrium and equilibrium constant.

6.

- If the reaction has greater value of K_c then the reaction is more forward. Thus the first reaction is most forward followed by the second reaction while the third reaction having lowest value of K_c is most backward (least forward).
- First reaction which involve combination of H_2 and Cl_2 to form HCl .

7. No; reactions with large equilibrium constant are not necessary to be very fast.

Reason:

Equilibrium constant is the measure of relative concentration of reactants and products at equilibrium. So even slow reactions with greater concentration of products than that of reactants have large equilibrium constants.

8. This is because, equilibrium constant is uniquely found by using concentration of reagents when the chemical system of the reversible reaction is at equilibrium and it is constant at given temperature while reaction quotient is found by using the concentrations at any time in the course of the reversible reaction and may take any value from 0 (with non-zero initial concentration of reactants and zero concentration of products) to infinitely large (with zero initial concentration of reactants and non-zero concentration of products).

9.

$$(a) \quad K_c = \frac{[CO]}{[CO_2][H_2]}$$

$$(b) \quad K_c = \frac{[CO_2]^2}{[CO]^2}$$

$$(c) \quad K_c = \frac{[Cr^{3+}]}{[Ag^+]^3}$$

$$(d) \quad K_c = \frac{[H_2]^4}{[H_2O]^4}$$

10.

$$(i) \quad K_p = \frac{(P_{N_2})(P_{H_2O})^2}{(P_{N_2H_4})(P_{O_2})}$$

$$(ii) \quad K_p = \frac{(P_{H_2})^4}{(P_{H_2O})^4} \text{ or } K_p = \left(\frac{P_{H_2}}{P_{H_2O}} \right)^4$$

$$(iii) \quad K_p = \frac{(P_{CO})}{(P_{CO_2})(P_{H_2})}$$

$$(iv) \quad K_c = \frac{[Cr^{3+}]}{[Ag^+]^3}$$

11. $[Ag(NH_3)_2]^+$ is more stable.

Reason: Large value of K_c implies that the position of equilibrium lies to the $[Ag(NH_3)_2]^+$ side (right hand side).

12.

(i) Capable of attaining equilibrium

Explanation:

$CaCO_3$ Decomposes, forming $CaO(s)$ and $CO_2(g)$ until the equilibrium pressure of CO_2 is attained (However there must be enough $CaCO_3$ to produce enough amount of CO_2 to exert equilibrium pressure).

(ii) Capable of attaining equilibrium

Explanation:

CO_2 continues to combine with CaO until the partial pressure of the CO_2 decrease to the equilibrium value.

(iii) Not capable of attaining equilibrium

Explanation:

There is no CaO present, so equilibrium cannot be attained because there is no way the CO_2 pressure can decrease to its equilibrium value (which would require some of the CO_2 to react with CaO).

(iv) Capable of attaining equilibrium

Explanation:

$CaCO_3$ decomposes until the equilibrium pressure of CO_2 is attained.

13. $K_p = 2.3 \times 10^2 \text{ atm}^2$

$$14. K_c = \frac{[\text{NO}_2][\text{O}_2]}{[\text{NO}]^2}; K_c = \frac{[\text{NO}_2][\text{O}_2]}{[\text{NO}]^2} = \frac{1}{\frac{[\text{NO}]^2}{[\text{NO}_2][\text{O}_2]}} = \frac{1}{1 \times 10^{-30}} = 1 \times 10^{30}$$

15.

- (a) Essentially goes to completion
- (b) Essentially not taking place (no reaction)
- (c) Essentially goes to completion

16. 0.308 atm (or 234 torr)

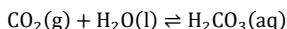
17. $K_p = 0.113 \text{ atm}$

$$18. K_c = 1.22 \text{ dm}^6 \text{ mol}^{-2}$$

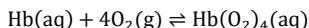
19. The equilibrium vapour pressure is $5 \times 10^{-15} \text{ atm}$.20. The value of K_p is 0.0313 atm; The value of K_c is $1.28 \times 10^{-3} \text{ mol/L}$

21.

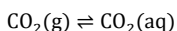
- 1) An equilibrium between gaseous carbon dioxide and dissolved carbon dioxide inside the sealed soda drink.



- 2) Interconversion between haemoglobin (Hb) and oxyhaemoglobin ($\text{Hb}(\text{O}_2)_4$) in the human body.

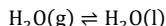


22. Because undissolved carbon dioxide and dissolved carbon dioxide are in dynamic equilibrium; that is gaseous carbon dioxide is dissolving into the liquid form at the same rate that the liquid form of carbon dioxide is being converted back to its gaseous form. So there is a constant movement of CO_2 from the liquid to the gas phase and vice versa.



23.

- (i) After evaporation of liquid vapour in the closed container, the vapour formed undergoes condensation in the upper part of the container and lid as well. So the process of evaporation is reversible physical process. At the beginning of the evaporation process, there is no enough vapour to allow water vapour to condense at high rate and thus the rate of evaporation of the liquid will be greater than the rate of condensation of vapour. As the evaporation proceeds, more vapour are formed and thus the rate of condensation increases until the rate of the condensation is equal to the rate of evaporation where the physical equilibrium between liquid water and gaseous water is said to be achieved.



- (ii) Vapour pressure

Reasons:

- 1) They are both determined when the system achieve equilibrium.
- 2) They are both independent to the amount of their corresponding substances (vapour pressure does not depend upon the amount of liquid, in this case liquid water while equilibrium constant does not depend upon the amount of reactants and products).
- 3) They both temperature dependent.
- (iii) They are similar in the following manner:
 - 1) They are both need closed system to be formed.
 - 2) They both have parameters that are constant with time.
 - 3) They are both temperature and pressure dependent.

They are different in the following manner:

- 1) Physical equilibrium is achieved when physical state of the system does not change with time while chemical equilibrium is achieved when concentrations of reactants and products do not change with time.
- 2) Physical equilibrium shows no change in physical state of matter that is involved in the equilibrium while chemical equilibrium shows no change in concentration of reactants and products that are involved in the equilibrium.
- 3) Physical equilibrium includes coexistence of two physical states inside the same closed system while chemical equilibrium includes equal rate of forward and reverse reactions.

24.

- (i) Haemoglobin-carbon monoxide bond is stronger.

Reason:

Higher equilibrium constant for the second reaction, forward reaction in the second reaction is more favoured than in the first reaction which in turn means $\text{Hb}(\text{CO})_4$ is more stable than $\text{Hb}(\text{O}_2)_4$.

- (ii) Carbon monoxide will be consumed more.

Reason:

Higher equilibrium constant for the second reaction, forward reaction in the second reaction is more favoured than in the first reaction which in turn means haemoglobin has higher affinity to carbon monoxide than oxygen.

25. By calculating K_p value from the answer she got (and other given data) and then comparing the calculated K_p value with the given K_p as follows:

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$$

$$\text{Substituting; } 1.45 \times 10^{-5} = \frac{(2.24 \times 10^{-2} \text{ atm})^2}{0.432 \text{ atm} \times (0.928 \text{ atm})^3} = 1.45 \times 10^{-3} \neq 1.45 \times 10^{-5}$$

Since the calculated K_p value is different the given K_p value, the answer was wrong.

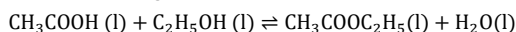
26. By calculating K_c value from the answer she got (and other given data) and then comparing the calculated K_c value with the given K_c as follows:

The least amount of acetic acid which is one of the reactants, is found when the reaction is at equilibrium. Thus, the mass of 1.8g, is the mass of acetic acid that remained at the equilibrium.

$$\text{Then at equilibrium: Number of moles acetic acid} = \frac{1.8 \text{ g}}{60 \text{ g mol}^{-1}} = 0.03 \text{ mol}$$

$$\text{Initially: Number of moles of acetic acid} = \frac{12 \text{ g}}{60 \text{ g mol}^{-1}} = 0.2 \text{ mol}$$

$$\text{Number of moles ethanol} = \frac{18.6 \text{ g}}{46 \text{ g mol}^{-1}} = 0.4 \text{ mol}$$



$$\text{Initially} \quad 0.2 \quad 0.4 \quad 0 \quad 0$$

$$\text{At equilibrium} \quad 0.2 - x \quad 0.4 - x \quad x \quad x$$

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.2-x}{V}\right)\left(\frac{0.4-x}{V}\right)} = \frac{x^2}{x^2 - 0.6x + 0.08}$$

But at equilibrium, number of moles of CH_3COOH is 0.03mol

$$\text{Then } 0.2 - x = 0.03 \quad \text{or} \quad x = 0.17$$

$$\text{Then; } K_c = \frac{0.17^2}{0.17^2 - (0.6 \times 0.17) + 0.08} = 4.2 = \text{Given } K_c \text{ value}$$

Since the calculated K_c value is equal to the given K_c value, the answer was correct.

27.

(i) Limestone undergoes thermal decomposition to give lime according to the following equation:



From which; $K_p = P_{\text{CO}_2}$

Thus P_{CO_2} at 800°C was $1.16 \text{ atm} = K_p$

From ideal gas equilibrium; $n = \frac{PV}{RT}$

Thus maximum number of moles of CO_2 will be given by;

$$n_{\text{CO}_2} = \frac{P_{\text{CO}_2}V}{RT} = \frac{1.16 \times 5}{0.082 \times 1073} \text{ or } 0.0659 \text{ mol} \quad (\text{CO}_2 \text{ is the product, so its amount at equilibrium, is the maximum amount of it which can be formed}).$$

Thus mass of CO_2 which can be produced in the reaction under given condition cannot exceed 0.0659 mol .

From the stoichiometric of the reaction, mole ratio of CO_2 to CaO (lime) is 1:1

$$\text{Thus } n_{\text{CO}_2 \text{ produced}} = n_{\text{CaO produced}} = 0.0659 \text{ mol}$$

Thus number of moles of lime produced under given conditions, also cannot exceed 0.0659 mol .

$$\text{Using } m = nM_r; \text{ mass of CaO} = 0.0659 \text{ mol} \times 56 \text{ g/mol or } 3.7 \text{ g}$$

So mass of the lime produced cannot exceed 3.7 g which is below the target amount of 5 g and hence the design was not successful.

(ii) No; the will not increase.

Reason: The solid limestone did not appear in the equilibrium constant expression (which implies that it has no effect in the equilibrium position) and hence adding its amount will not change the amount of lime produced.

(iii) Increase

Reason: From the formula of calculating number of moles of CO_2 ($n_{\text{CO}_2} = \frac{P_{\text{CO}_2}V}{RT}$) which is equal to number of moles of lime, it can be deduced that number of moles of CO_2 and hence amount of the lime increases as the volume of the container increases.

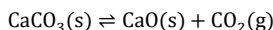
Note:

The reason that has been provided in (iii) above agrees with Le-Chatelier's principle (we will study it later); that is, the increase in volume would decrease pressure (Boyle's law) and thus the equilibrium will shift to the lime side by producing more CO_2 which exerts more pressure to keep pressure constant despite the increase in volume of the container.

28.

- (i) If the amount of limestone is so small that it produces $\text{CO}_2(\text{g})$ whose pressure is less than K_p value, no equilibrium will be achieved and the whole limestone will be converted to lime. This equilibrium-free situation, ends when the amount of limestone has been increased to the extent that it produces $\text{CO}_2(\text{g})$ whose pressure is equal to K_p . So below that limit amount of limestone (which makes $P_{\text{CO}_2} = K_p$) no equilibrium will be achieved and the whole limestone will be converted to lime (no extra work will be needed to separate the two expected solids) while above the limit amount of limestone, equilibrium will be achieved and the extra work will be unavoidable. Hence, the required maximum amount of limestone will be obtained when the amount of limestone put in the vessel is equal to the amount (of limestone) required to produce the amount of $\text{CO}_2(\text{g})$ whose pressure is equal to K_p .

Now, limestone undergoes thermal decomposition to give lime according to the following equation:



From which; $K_p = P_{\text{CO}_2}$

Thus P_{CO_2} at 800°C was $1.16\text{atm} = K_p$

From ideal gas equilibrium; $n = \frac{PV}{RT}$

Thus maximum number of moles of CO_2 will be given by;

$$n_{\text{CO}_2} = \frac{P_{\text{CO}_2}V}{RT} = \frac{1.16 \times 10}{0.082 \times 1073} \text{ or } 0.1318\text{mol}$$

Thus mass of CO_2 which can be produced in the reaction under given condition cannot exceed 0.1318mol

From the stoichiometric of the reaction, mole ratio of CO_2 to CaCO_3 (limestone) is 1:1 ($n_{\text{CO}_2\text{produced}} = n_{\text{CaCO}_3\text{reacted}}$).

Thus number of moles of limestone reacted to produce that maximum amount of CO_2 was also 0.1318mol .

To avoid presence of any unreacted limestone, its number of moles that was put in the vessel must be also 0.1318mol .

Using $m = nM_r$; mass of $\text{CaCO}_3 = 0.1318\text{mol} \times 100\text{g/mol}$ or 13.18g

Hence maximum amount of the limestone is 13.18g

- (ii) From the stoichiometric of the reaction, mole ratio of CO_2 to CaO (lime) is 1:1

Thus $n_{\text{CO}_2\text{produced}} = n_{\text{CaO produced}} = 0.1318\text{mol}$

Using $m = nM_r$; mass of $\text{CaO} = 0.1318\text{mol} \times 56\text{g/mol}$ or 7.4g

Hence mass of the lime obtained was 7.4g .

Have you noticed?

Through doubling the volume of the container (from 5L to 10L), the target of preparing at least 5g of lime (in **question 6**) has now reached.

29. Because $Q_c > K_c$, the reverse reaction is more favoured.

30. No, not at equilibrium. Forward reaction occurs ($Q_c < K_c$)

31. $[\text{CO}_2] = [\text{H}_2] = 0.69\text{M}$; $[\text{H}_2\text{O}] = [\text{CO}] = 0.31\text{M}$

32. $K_p = 0.338\text{atm}$

33.

(a) $P_{\text{CO}} = P_{\text{H}_2} = 6.13\text{atm}$, $P_{\text{H}_2\text{O}} = 2.67\text{atm}$

(b) 0.8364g

(c) 14.93atm

Hint for part (b)

Find number of moles of $\text{H}_2\text{O}(\text{g})$ reacted before reaching the equilibrium (You will get 0.0697mol).

Then from stoichiometric ratio of the given reaction equation find the corresponding number of moles of carbon required to react with this amount of $\text{H}_2\text{O}(\text{g})$ which is actually minimum number of moles of carbon required to form the equilibrium because for the equilibrium to be established $\text{H}_2\text{O}(\text{g})$ has to react with the carbon. Finally convert the number of moles of carbon (You will get also 0.0697mol) to mass by using $m = nM_r$ to get 0.8364g .

Hint for part (c)

Simply find the sum of equilibrium partial pressure of each gas to get 14.93

(That is $6.13\text{atm} + 6.13\text{atm} + 2.67\text{atm} = 14.93$)

34. The value of K_p is 0.82atm

35. The partial pressure of CS_2 changes to the maximum, its value is 1.28atm

The partial pressure of S_2 changes to the minimum, its value is 0.14atm

36. Mass of C in 100g of gases = 13.71g

Number of moles of C atoms in $\text{CS}_2 = \frac{13.71\text{g}}{12\text{gmol}^{-1}} = 1.14\text{mol}$

But 1mol of CS₂ contains 1mol of C; so number of moles of CS₂ is also 0.18mol

Also 1mol of CS₂ contains 2mol of S atoms; so number of moles of S atoms in CS₂ = 2 × 1.14mol = 2.28mol

Mass of S in 100g of gases = 86.29g

$$\text{Total number of moles of S atoms} = \frac{86.29\text{g}}{32\text{gmol}^{-1}} = 2.7\text{mol}$$

Number of moles of S atoms in S₂

= Total number of moles of S atoms – Number of moles of S atoms in CS₂

= (2.7 – 2.28)mol = 0.42mol

$$\text{Number of moles of S}_2 \text{ molecules} = \frac{0.42\text{mol}}{2} = 0.21\text{mol}$$

Then from C(s) + S₂(g) ⇌ CS₂(g);

$$K_c = \frac{[n_{\text{CS}_2}]}{[n_{\text{S}_2}]} = \frac{\frac{n_{\text{CS}_2}}{V}}{\frac{n_{\text{S}_2}}{V}} = \frac{n_{\text{CS}_2}}{n_{\text{S}_2}} = \frac{1.14\text{mol}}{0.21\text{mol}} = 5.4$$

37. The ratio of [NO] to [NO₂] is 583: 5000

38. Number of moles of HI = 1.9 moles, Number of moles of H₂ = 0.05 moles, Number of moles of I₂ = 1.15 moles

39. The pressure of hydrogen is 96695Nm⁻²; The pressure of steam is 4605Nm⁻²

40. From the given reaction equation: $K_c = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]}$

$$\text{Then } K_c = \frac{\left(\frac{n_{\text{CO}}}{V}\right)\left(\frac{n_{\text{H}_2\text{O}}}{V}\right)}{\left(\frac{n_{\text{CO}_2}}{V}\right)\left(\frac{n_{\text{H}_2}}{V}\right)} = \frac{n_{\text{CO}} \times n_{\text{H}_2\text{O}}}{n_{\text{CO}_2} \times n_{\text{H}_2}}$$

But for gases; mole ratio = volume ratio (from Avogadro's law)

$$\text{Then: } K_c = \frac{V_{\text{CO}} \times V_{\text{H}_2\text{O}}}{V_{\text{CO}_2} \times V_{\text{H}_2}}$$

Where V is the volume of each gas at equilibrium.



Initially 50 50 0 0

At equilibrium 50 – x 50 – x x x

$$\text{Then } 1.6 = \frac{x^2}{(50-x)^2} = \frac{x^2}{x^2 - 100x + 2500} = 1.6 \quad x = 27.9$$

Total volume of gaseous mixture

$$= (50 - x) + (50 - x) + x + x = 100\text{cm}^3$$

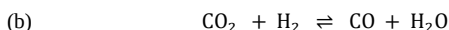
Hence:

The percentage of CO = x = 27.9%

The percentage of H₂O = x = 27.9%

The percentage of H₂ = 50 – x = 22.1%

The percentage of CO₂ = 50 – x = 22.1%



Initially 25 50 25 0

At equilibrium 25 – x 50 – x 25 + x x

$$1.6 = \frac{x(25+x)}{(25-x)(50-x)} = \frac{x^2 + 25x}{x^2 - 75x + 1250}$$

$$0.6x^2 - 145x + 2000 = 0 \quad \text{or } x = 14.68$$

Total volume of gaseous mixture at equilibrium is;

$$(25 - x) + (50 - x) + (25 + x) + x = 100\text{cm}^3$$

Hence:

The percentage of CO₂ is 10.32%

The percentage of H₂ is 35.32%

The percentage of CO is 39.68%

The percentage of H₂O is 14.68%

It should be understood that:

In above equilibrium constant expression, water is included in the expression although its normal physical state is liquid while normal physical state of other reactants are gases because the reaction is undertaken at 1000°C where water exists in gaseous state as a vapour (steam).

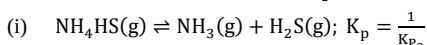
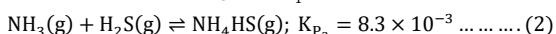
41. The value of K_p is 50, the amount of I_2 remain unreacted is 0.11 moles.

42. $[H_2] = 0.316M$, $[I_2] = 1.316M$, $[HI] = 4.368M$

43. Degree of dissociation of PCl_5 is 85%, K_p for the reaction is 2.6atm, K_c for the reaction is $0.06mol/dm^3$.

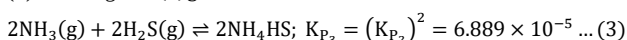
44. Percentage of dissociation of H_2S is 1.28%

45. Given that:

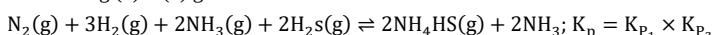


$$\text{So } K_p \text{ for the (i) above} = \frac{1}{8.3 \times 10^{-3} \text{atm}^{-1}} = 1.2 \times 10^2 \text{atm}$$

(ii) Taking $2 \times (2)$ gives;



Then taking (1) + (3) gives



$$\text{Or } N_2(g) + 3H_2(g) + 2H_2S(g) \rightleftharpoons 2NH_4HS(g); K_p = (3.1 \times 10^{-4} \text{atm}^{-2})(6.889 \times 10^{-5} \text{atm}^{-2}) \\ = 2.13559 \times 10^{-8} \text{atm}^{-4}$$

Hence the K_p value for the reaction (ii) is $2.13559 \times 10^{-8} \text{atm}^{-4}$

EXERCISE 14

1.

- (i) No effect on position of the chemical equilibrium.
- (ii) The position of equilibrium will shift to the left.
- (iii) The position of the equilibrium will shift to the right.
- (iv) The position of the equilibrium will shift to the left.
- (v) The position of the equilibrium will shift to the left.

2.

- (a) The equilibrium shifts to the right.

Reason

The system will adjust to decrease the concentration of the added N_2O_4 by shifting to the NO_2 side.

- (b) The equilibrium shifts to the right.

Reason

The system will adjust to the removal of NO_2 by shifting to the side that produces more NO_2 .

- (c) No shift to the position of the equilibrium.

Reason

Although adding N_2 will increase the total pressure of the system, N_2 is not involved in the reaction. The partial pressures of NO_2 and N_2O_4 are therefore unchanged and hence there is no shift to the position of the equilibrium.

- (d) The equilibrium shifts to the right.

Reason

If the volume is increase, the pressure of the system is decreased in accordance to Boyle's law and therefore the equilibrium will shift in the direction that has more gas molecules.

- (e) The equilibrium shifts to the left.

Reason

The reaction is endothermic, so we can imagine heat as a reagent on the reactant side of the question. Decreasing the temperature, will shift the equilibrium in the direction that produces heat, that is in the N_2O_4 side.

3.

- 1) Adding amount of P_4
- 2) Adding amount of H_2
- 3) Increasing temperature
- 4) Increasing pressure

4. Catalyst lowers the activation energy of both forward reaction and backward reaction by the same magnitude. This makes K_f and K_b to increase by the same proportion and hence the K_c value remains unchanged.

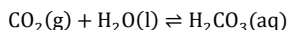
5.

- (i) When a reaction has (almost) zero heat of the reaction.
- (ii) No scenario.
- (iii) **First scenario:** When the reaction does not involve gas.

Second scenario: When reaction (even if it is involving gases) is not accompanied with change of number of gas particles.

- (iv) Any scenario.

6. In the coca cola soda, carbon dioxide is dissolved at high pressure and form the following equilibrium:



Opening the bottle decreases the pressure in the bottle, shifts the equilibrium position to $\text{CO}_2(\text{g})$ side, thereby the solubility of the gas is decreased and hence gas bubbles are suddenly escaping the bottle with the hissing sound.

7. In the Haber process, ammonia is produced as per equation:



The following conditions are applied to increase the yield of ammonia:

- 1) Very high pressure in the range of 200atm to 500atm

This shifts the position of equilibrium to the ammonia side (right hand side) as the production of ammonia per above equation is accompanied with significant reduction of volume.

- 2) Relative low temperature of 450°C .

The reaction is exothermic. So applying low temperature shifts the position of equilibrium to the ammonia side. However below 400°C no ammonia is produced.

- 3) Catalyst based on finely divided reduced iron promoted by alumina.

The low temperature favours production of ammonia but at very slow rate. So it is necessary to introduce catalyst which gives sufficient reaction rate in spite of relatively low temperature.

8.

- Once equilibrium has been attained the concentration of carbon dioxide gas (CO_2) remain unchanged and hence the pressure become constant.
- The current of blown air displace $\text{CO}_2(\text{g})$ from the line kiln thus removing the carbon dioxide and hence the position of chemical equilibrium will shift to the right by producing more quick lime.

9.

- (i) Exothermic

Explanation

If the temperature is lowered the system must respond in accordance to Le-Chatelier's principle by producing heat (exothermic process) to compensate the amount of the heat lowered. Since the low temperature also favour the formation of sulphur trioxide, the conversion must be exothermic too.

- (ii) **Name:** Vanadium(V) oxide.

Effect on the yield: No effect.

Effect on the rate: It increases the rate of both forward and backward reaction by equal amount.

- (iii) **Advantage:** High yield of sulphur trioxide is obtained.

Disadvantage: Slow rate of producing sulphur trioxide.

10.

- (i) Sufficient oxygen shifts equilibrium position to the oxyhaemoglobin side by producing more oxyhaemoglobin.
- (ii) At high altitude the air pressure is lowered and the decrease in pressure shifts equilibrium position to the free oxygen side by producing more oxygen gas in accordance with Le-Chatelier's principle. This decreases the amount of oxyhaemoglobin and hence the person feels bad.
- (iii) According to Le-Chatelier's principle, more haemoglobin means the position of equilibrium will shift to the oxyhaemoglobin side by producing more oxyhaemoglobin. This will ensure sufficient amount of oxyhaemoglobin in the body despite the decrease in the air pressure at high altitudes.

11. No.

Explanation:

Adding the amount of certain component in the chemical equilibrium will only shift the equilibrium position if it either changes concentration of reagents present in the equilibrium or changes their partial pressures.

Adding pure liquid or solid in the chemical equilibrium does not change the equilibrium position because they neither change the concentration nor appear in the equilibrium constant expression.

Also adding a gas like noble gas which does not react with gases (reagents) present in the equilibrium does not shift equilibrium position because the gas does not affect partial pressures of gases present in the equilibrium.

12.

(i) Increase

Explanation:

Low pressure gives higher yield.

(ii) Endothermic

Explanation:

Increase in temperature at given pressure increases the yield.

13.

- (a) The solution will be yellow because addition of acid increase concentration of H^+ thus shifting the position of equilibrium to the left.
- (b) The solution will be colourless because the alkaline solution neutralises an acid which is equivalent to removal of H^+ and hence the equilibrium will shift to right.
- (c) The solution will be yellow because NaBr being strong ionic salt ionises completely yielding Br^- ; so there is an increase in concentration of Br^- , the factor which shifts the position of chemical equilibrium to left.
- (d) The solution will be colourless because the silver nitrate solution reacts with Br^- to give AgBr thus decreasing the concentration of Br^- and hence equilibrium shifts to the right.

14. Let:

 E_{afu} and E_{abu} be activation energy for uncatalysed forward and backward reaction respectively. E_{afc} and E_{abc} be activation energy for catalysed forward and backward reaction respectively. K_{fu} and K_{bu} be the rate constants for uncatalysed forward and backward reaction respectively. K_{fc} and K_{bc} be the rate constant for catalysed forward and backward reaction respectively.

For uncatalysed reaction:

From Arrhenius equation; $(K = Ae^{-E_a/RT})$

$$K_{fu} = Ae^{-E_{afu}/RT} \text{ and } K_{bu} = Ae^{-E_{abu}/RT}$$

For catalysed reaction:

From the Arrhenius equation;

$$K_{fc} = Ae^{-E_{afc}/RT} \text{ and } K_{bc} = Ae^{-E_{abc}/RT}$$

Then, the increasing factor for forward reaction rate;

$$\frac{R_{\text{catalysed}}}{R_{\text{uncatalysed}}} = \frac{K_{fc}}{K_{fu}} = \frac{Ae^{-E_{afc}/RT}}{Ae^{-E_{afu}/RT}} = e^{\frac{E_{afu}-E_{afc}}{RT}}$$

And the increasing factor for backward reaction rate;

$$\frac{R_{\text{catalysed}}}{R_{\text{uncatalysed}}} = \frac{K_{bc}}{K_{bu}} = \frac{Ae^{-E_{abc}/RT}}{Ae^{-E_{abu}/RT}} = e^{\frac{E_{abu}-E_{abc}}{RT}}$$

But;

$$E_{afu} - E_{afc} = E_{abu} - E_{abc} = \Delta E_a$$

Thus;

$$\text{The forward reaction factor} = \text{The backward reaction factor} = e^{\frac{\Delta E_a}{RT}}$$

Hence the catalyst increases the rates of both forward and backward reactions by the same factor.

15. Let: K_{cu} and K_{cc} be equilibrium constant for uncatalysed and catalysed reaction respectively.

Then using;

$$K_c = \frac{K_f}{K_b} = \frac{Ae^{-E_{af}/RT}}{Ae^{-E_{ab}/RT}} = e^{\frac{-(E_{af}-E_{ab})}{RT}}$$

But; $-(E_{af} - E_{ab}) = -\Delta H$; where ΔH is the heat of reaction

$$\text{Thus; } K_c = e^{\frac{-\Delta H}{RT}}$$

$$\text{For uncatalysed reaction; } K_{cu} = e^{\frac{-H_u}{RT}}$$

$$\text{For catalysed reaction; } K_{cc} = e^{\frac{-H_c}{RT}}$$

Then finding the ratio of K_c values for catalysed and uncatalysed reaction

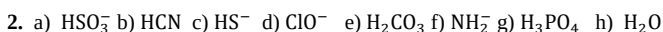
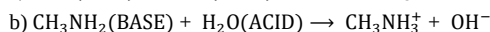
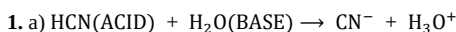
$$\frac{K_{cu}}{K_{cc}} = \frac{e^{-H_u/RT}}{e^{-H_c/RT}} = e^{(H_c - H_u)/RT}$$

But $H_c = H_u$ and therefore; $H_c - H_u = 0$

Thus; $\frac{K_{cu}}{K_{cc}} = e^0 = 1$

Hence $K_{cu} = K_{cc}$ (catalyst does not change value of equilibrium constant).

EXERCISE 15



3.

(i) Conjugate acid: H_2O ; conjugate base: O^{2-}

(ii) Conjugate acid: H_3O^+ ; conjugate base: OH^-

(iii) Conjugate acid: NH_4^+ ; conjugate base: NH_2^-

(iv) Conjugate acid: H_2CO_3 ; conjugate base: CO_3^{2-}

4. (b) White fumes (c) HCl being gaseous is removed from the equilibrium system and thus the position of equilibrium shifts to the right.

5. **Hint:** Ammonia is the weak base, hydrochloric acid is the strong acid, and ethanoic acid is the weak acid.

6. Since the colour of the indicator depends upon the relative concentration of ionised indicator to that of unionised indicator, the colour change is gradual and does not occur suddenly at a specific pH value.

7. Acidity can be neutralised by a base. Hence, we should choose baking soda solution because it is a weak base and will react with excess acid produced in the stomach due to hyperacidity and will neutralise it.

8. The pH of the pond water lies between 7 and 8.3 exclusive.

9. As the aqueous solution of A turns phenolphthalein solution pink, hence A is basic in nature. On adding an acidic solution, the pink colour disappears indicating that B neutralises A. Hence, B is acidic in nature.

10. (i) On adding phenolphthalein to NaOH solution, the colour becomes pink.

(ii) On adding dilute HCl solution dropwise to the same test tube, the pink colour disappears and the solution again becomes colourless.

(iii) On again adding NaOH to the above mixture, pink colour reappears due to presence of unreacted NaOH which was in excess, thus making the solution basic.

11.

(i) Yes.

Reason: Because their **colour change** occurs at **narrow range**.

(ii) Yes.

Explanation:

The equivalence point of reaction between acetic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) which is weak acid and caustic soda (NaOH) which is strong base occurs when the solution is basic. Since the end point of the given spices occurs at basic solution too, they are suitable indicators for the given reaction.

(iii) The following are the reasons for preferring synthetic indicators to natural indicators in scientific settings:

1) Precision

Natural indicators are generally less precise and less reliable than synthetic indicators.

2) Stability

Natural indicators are less stable and have shorter life than synthetic indicators.

3) Range

Natural indicators can be used to measure pH over narrower range than synthetic indicators.

4) Availability

Natural indicators may be more difficult to obtain and may vary in quality while synthetic indicators are more readily available and consistent.

12.

(i) No. For an indicator to be suitable for detecting acid and base, its end point must occur at pH that is close to 7. But for blueberry, the end point occurs at pH far below the neutral point (pH of 7). This means that it is possible for two acidic solutions (one with pH below the end point, e.g. pH of 2 and another with pH above the end point, e.g. pH of 4) to give different colours (of blue and red respectively) or one acidic solution and another basic solution, both with pH above the

end point (e.g. the acid with pH of 4 and the base with pH of 10) to give the same colour of red and hence the indicator cannot detect acid and base with certainty.

(ii) No.

Explanation:

The equivalence point of reaction between methanoic acid which is weak acid and potassium hydroxide which is strong base occurs when the solution is basic. Thus the equivalence point diverges from the end point of blueberries which occurs at acidic solution and hence the indicator becomes unsuitable for the titration.

(iii) Possible reasons are:

- 1) To reduce environmental pollution accompanied with production and usage of synthetic indicators.
- 2) To avoid high cost of producing synthetic indicators.

13. (a) (i) pipette (ii) burette (b) Everything with distilled water (c) Pink to colourless, the first drop of excess acid removes the pink alkaline colour of phenolphthalein. (d) 0.00625 mol (e) 0.00625 mol HCl (f) 0.278 mol/dm³

14. (a) 0.50M (b) 0.0125 mol (c) 0.025 mol (d) 1.014M

15. (a) 0.025 mol (b) 0.625M (c) 12.5M

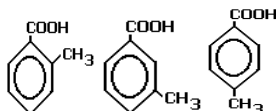
16. (a) 0.20 mol (b) 0.00394 mol (c) 0.196 mol (d) 0.098 mol, 3.92 g (e) 96.55% MgO

(f) Mg(OH)₂ from MgO + H₂O and MgCO₃ from the original mineral source, both of these compounds react with acid and would lead to a false titration value.

17. (a) 0.00205 mol (b) 0.00205 (c) 136 g/mol

(d) The simplest aromatic carboxylic acid is benzoic acid C₆H₅COOH, M_r = 122

136 – 122 = 14, which suggests an 'extra' CH₂ (i.e. -CH₃ attached to the benzene ring instead of a H), so, since the COOH is attached to the ring, there are three possible positional/chain isomers of CH₃C₆H₄COOH (M_r = 136) which are 2-, 3- or 4-methylbenzoic acid.



18. (a) 0.00475 mol (b) 0.399 g, 99.75%

19. (a) 27.7% (b) (i) 56.2% (ii) 16.1%

20. 4.24 g/L (Na₂CO₃) and 5.04 g/L (NaHCO₃)

EXERCISE 16

1. (a) 3 (b) 9 (c) 9 (Hint for part (b): The concentration given is of H⁺ and not for an acid)

2. A (pH = 4.41) is more acidic, B is more basic.

3. pH = 1.19, pOH = 12.81

4. 1.8 g

5. 34

6. pH = 13.1

8. (a) Presence of lone pair on the N

(b) pH = 11.13

9. pH = 2.6 (Hint: Treat the solution with pH of 7 as pure water, then use dilution principle to find [H⁺] in the mixture. Finally, the pH is easily found from the [H⁺] as usual).

10. 1.7

11. pH calculation involve K_a, K_b and K_w all of which are equilibrium constants whose values vary significantly as temperature change.

12. Disagree.

Explanation

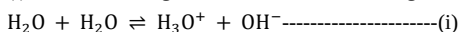
The neutrality of water is due to the equality of concentration of hydronium ion and hydroxide ion in self-ionisation and not pH. The equality comes from stoichiometry of self-ionisation of water which is not affected by temperature change; so even at 100°C, [H₃O⁺] = [OH⁻]. Temperature affects the pH at which the equality occurs; at 25°C the equality occurs when the pH is 7 whereas at 100°C, the equality occurs when pH is 6.

13. 2200 mL

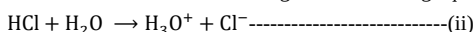
14. pH = 2.4

15.

(i) Water undergoes self-ionisation according to the following equation:



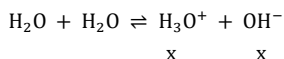
HCl dissolves in water according to the following equation:



So the introduction of HCl disturbs the equilibrium and thus the ionisation of water (in (i)) because it gives H₃O⁺ which is also present in the equilibrium.

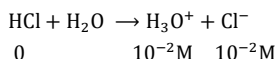
Therefore the increase in $[\text{H}_3\text{O}^+]$ by the acid is going to shift the equilibrium position to the left and hence the concentration of water ionised will decrease from 10^{-7}M to x .

So from water:



At equilibrium

And from HCl:



After ionisation:

Then by considering ions present in the equilibrium:

$$[\text{H}_3\text{O}^+] = x + 10^{-2} \text{ and } [\text{OH}^-] = x$$

It follows that: $K_w = [H_3O^+][OH^-]$

Substituting $10^{-14} = (x + 10^{-2})x$; $x^2 + 10^{-2}x - 10^{-14} = 0$

Solving above quadratic equation gives practical value of x which is 10^{-12}

$$\text{So } [\text{H}_3\text{O}^+] = x + 10^{-2} = 10^{-12} + 10^{-2} = 10^{-2}\text{M} = [\text{HCl}]$$

Here the contribution of water on $[\text{H}_3\text{O}^+]$ is extremely small, such that the whole $[\text{H}_3\text{O}^+]$ comes from HCl and hence it was correct for Kipute to ignore completely self-ionisation of water.

Then $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 10^{-2}\text{M} = 2$

(ii) In 10^{-8}M HCl , the acid is very dilute and thus the $[\text{H}_3\text{O}^+]$ from the acid is comparable to that from water and hence it is incorrect to ignore self-ionisation of water which in turn leads to incorrect negligence of $[\text{H}_2\text{O}^+]$ from water.

Thus Total $[\text{H}_3\text{O}^+] = [\text{H}_3\text{O}^+] \text{ from HCl} + [\text{H}_3\text{O}^+] \text{ from H}_2\text{O}$

Let $[\text{H}_3\text{O}^+]$ from $\text{H}_2\text{O} = x$

Then from ionisation of water, $[\text{OH}^-]$ is also x

And $[\text{H}_3\text{O}^+]$ total = $1 \times 10^{-8} + x$

Using; $K_w = [\text{OH}^-] [\text{H}_3\text{O}^+]$; $1 \times 10^{-14} = (1 \times 10^{-8} + x)x$

$$\text{Or } x^2 + (1 \times 10^{-8})x - 1 \times 10^{-14} = 0$$

Solving above equation gives $x = 9.5 \times 10^{-8} \text{M}$

$$\text{So } [\text{H}_3\text{O}^+] = (1 \times 10^{-8} + 9.5 \times 10^{-8})\text{M} = 1.05 \times 10^{-7}\text{M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.05 \times 10^{-7}) = 6.98$$

Hence the pH of the solution is 6.98

16.

- 1) **Water is a weak electrolyte.** This is indicated by the reversibility sign ($\rightleftharpoons$) in the equation.
- 2) **Water is amphoteric.** This is indicated by presence of both H_3O^+ and OH^- in the equation.
- 3) **Water is neutral.** This is because mole ratio of H_3O^+ to OH^- is 1:1, implying that water gives equal concentration of H_3O^+ and OH^- in the ionisation.

17. (a) $K_a = \frac{[\text{CH}_3\text{CH}_2\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}]}$ (b) $\text{pH} = 2.73$ (c) Concentration of H_3O^+ should decrease tenfold but the dilution will also move equilibrium to the right thus increasing degree of dissociation of the acid and hence the decrease of the concentration of H_3O^+ become less than expected.

18. (a) Endothermic because an increase in value of K_w as temperature increases suggest that position of equilibrium shift to the right as the temperature increases and hence according to Le-Chatelier's principle the reaction must be endothermic.

(b) $[\text{H}^+]$ from water itself become dominant and cannot be neglected and pH of the solution becomes very close to 7 (Just slightly below 7).

19. (a) 0.01M, pH = 2 (b) 0.1M (c) 0.0316M, 0.1316M (d) $[H^+]$ of 0.105M < 0.1316M because reaction II suppress reaction I by common ion effect.

20. 0.65°C

21. Van't Hoff factor = 1.0753; Dissociation constant = 2.73×10^{-3}

22. $[F^-] = 0.02M$, $pH = 1.5$

23. pH=12.53 (**Hint:** The solution with pH of 2 is acidic while that of 13 is basic. So the question involves acid-base reaction. To solve; convert pH of 13 into corresponding $[\text{OH}^-]$, then use it with $[\text{H}^+]$ from the acidic solution to deduce the excess reactant. You will find that $[\text{OH}^-]$ was in excess; then continue to find pOH and hence pH of the mixture).

24. 302mL (or 0.302L)

25. $K_w = 1 \times 10^{-13}$

EXERCISE 17

1. The buffer solution consists of a weak acid and its conjugate base. If acid is added to the solution, it is consumed by the conjugate base and if base is added to the solution, it is consumed by the weak acid, keeping the pH almost constant.

2.

- (i) Dilution decreases concentrations of both weak acid (or base) and its conjugate base (or acid) by the same factor and thus keeping their ratio in their molar concentration unchanged and hence the pH remains constant.
- (ii) Dilution decreases concentrations of components of buffer solution and hence it decreases buffer capacity.

3. pH will decrease (more acidic solution), since the position of equilibrium will shift to unionised NH_3 , resulting in lower $[\text{OH}^-]$.

4. $\text{pH} = 4.46$, $[\text{H}^+] = 3.5 \times 10^{-5} \text{M}$

5. $\text{pH} = 4.53$

6. $\text{pH} = 5.48$

7. $\text{pH} = 5.06$

8. 12g

9. The three buffer systems of the human body are:

- 1) Carbonic acid/bicarbonate buffer system,
- 2) Phosphate buffer system, and
- 3) Protein buffer system.

10.

In the real life it is difficult the acid with pK_a which exactly meet with our targeted pH of the buffer. So we have to adjust concentration ratio of the buffer components so as to achieve the intended pH. The adjustment we will demand us to apply the Henderson-Hasselbalch equation.

Furthermore, even if occasionally we can succeed to get the acid with pK_a that is exactly equal to the intended pH, an addition of strong acid or base to the buffer will alter the equality in concentration slightly and thus the pH will deviate slightly from the pK_a value and hence we will be demanded to perform pH calculation to know the new pH after the deviation.

11. The answers are:

- (i) Buffer 4 because it has highest ratio.
- (ii) Buffer 3 because it has highest concentration of acetate and acetic acid.
- (iii) Strong acid because the addition of acid decreases pH and buffer 2 has smaller pH than buffer 1.
- (iv) Strong base because the addition of base increases pH and buffer 4 has larger pH than buffer 3.
- (v) Buffer 1 and buffer 3 because they have the same concentration ratio of their components.
- (vi) Buffer 3 because has **highest and equal** concentrations of acetate and acetic acid.

12. The most efficient buffer is found when the pK_a value of the buffer solution is equal to the targeted pH. Among the given acids, chlorous acid has pK_a (1.95) which is closest to the target (pH of 2) and hence Mr. Akilikubwa should use chlorous acid.

13.

(i) Acidic buffer solution.

(ii) Possible buffers are:

- 1) Mixture of CH_3COOH and CH_3COONa
- 2) Mixture of CH_3COOH and NaOH
- 3) Mixture of CH_3COONa and HCl

(iii) The amount of each should be as follows:

- 1) For $\text{CH}_3\text{COOH} | \text{CH}_3\text{COONa}$ mixture: The amount should be taken in such a way that **there is an equal concentration of the two components in the mixture.**
- 2) For $\text{CH}_3\text{COOH} | \text{NaOH}$ mixture: The amount should be taken in such a way that **the concentration of CH_3COOH in the mixture is twice the concentration of NaOH .**
- 3) For $\text{CH}_3\text{COONa} | \text{HCl}$ mixture: The amount should be taken in such a way that **the concentration of CH_3COONa in the mixture is twice the concentration of HCl .**

14. Dissociation constant of weak acid or weak base present in the buffer system tend to increase as the temperature increases. This means that the weak acid and base dissociate more at higher temperature leaving smaller concentration of undissociated acid or base which in turn decreases reserve acidity or reserve basicity respectively and hence buffer capacity is decreased.

15.

- 1) **Concentrations of salt and acid:** The pH will be high if the ratio, $\frac{[\text{Salt}]}{[\text{Acid}]}$ is high too. Thus if $[\text{Salt}]$ is high compared to $[\text{Acid}]$, the pH will be high whereas high $[\text{Acid}]$ compared to $[\text{Salt}]$ leads to low pH of the solution.
- 2) **The magnitude of K_a value:** The pH will be high if the magnitude of pK_a value is large. So if the **nature of acid** allows it to have large K_a value due to its high strength, the pK_a value will be small and hence its pH will be small as well. Also **high temperature**, makes K_a value high too and hence (as result of small value of pK_a) low pH.

16. Salt: acid = 6.93: 1

17. 36mL

18. (a) Acidic buffer (b) $\text{pH} = 4.87$

19. (a) 0.96gdm^{-3} . **Assumption:** Ionisation of the acid to give anions is negligible and hence all propanoate ions (anions) come from sodium propanoate (salt). (b) 0.85gdm^{-3}

20. (a) pH = 13 (b) (i) 0.05M (ii) 0.05M (iii) 4.74 (iv) The pH remain virtually constant because ethanoate ions from the salt react (combine) with added hydrogen ions and the solution mixture to become a buffer.

21. pH = 4.2

23. (a) pH = 4.45 (b) pH = 4.13 (c) pH = 1.52

22. pH = 9.26

24. pH = 8.97

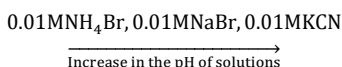
EXERCISE 18

1.

- (i) The solution would be **neutral** since the conjugate base of a strong acid is a weaker base than water, so the major species (conjugate base of strong acid and cation of strong base) remaining in solution are neutral.
 (ii) The solution would be **basic** since the conjugate base of a weak acid is a stronger base than water, so it hydrolyses in water to produce hydroxide ions.
 (iii) The solution would be **acidic** since the conjugate acid of a weak base being strong acidic hydrolyses in water to produce H^+ ions.

2. a) basic b) neutral c) neutral d) acidic e) acidic f) basic

3. The pH of the given solutions is determined by hydrolysis. NaBr being strong ionic salt, does not hydrolyse in water and thus its pH is 7. KCN contains strong base anion and thus it undergoes anionic hydrolysis to give basic solution with pH which is above 7 while NH_4Br having strong acid cation undergoes cationic hydrolysis with pH which is below 7. Hence the arrangement is as follows:

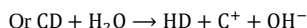
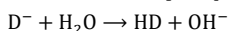


4. $0.1MNa_2CO_3$

Reason:

The basic salt has the highest pH and among the given salts only Na_2CO_3 is the basic salt.

5. Since the salt was made from strong base and weak acid, its cation (C^+) is weak acid while anion (D^-) is strong base. Thus the compound undergoes anionic hydrolysis to give basic solution as per equation;



6. In the aqueous solution, the salt having strong acid cation, undergoes cationic hydrolysis yielding enough concentration of free ions (H^+ (aq) and Cl^- (aq) from HCl (aq) which are responsible for doing electrolytic conduction.

i.e. $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3H^+(aq) + 3Cl^-(aq)$

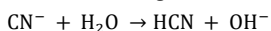
7. In aqueous solution, NH_4^+ in the salt being strong acid cation, undergoes cationic hydrolysis yielding acidic solution which reacts with $NaHCO_3$ to evolve carbon dioxide gas which appears as effervescence of colourless gas that turns lime water milky.

That is $NH_4^+ + H_2O \rightarrow NH_4OH + H^+$

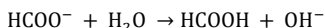
(From NH_4Br)

Then $H^+ + HCO_3^- \rightarrow CO_2 + H_2O$

8. Potassium cyanide contains cyanide ion which is strong base anion (it is conjugate base of HCN which is weak acid) and therefore it undergoes anionic hydrolysis to give basic solution and hence the litmus paper turns blue.



9. Sodium methanoate contains methanoate ion which is strong base anion and thus it undergoes anionic hydrolysis to give basic solution and the anion is odourless in basic solution.



10. $(NH_4)_2SO_4$ contains strong acid cation (NH_4^+) and therefore in aqueous solution it undergoes cationic hydrolysis yielding acidic solution which is responsible of evolving hydrogen gas (which produced the 'pop' sound) when magnesium (metal) is introduced in the solution.

That is $NH_4^+ + H_2O \rightarrow NH_4OH + H^+$

Then $2H^+ + Mg \rightarrow Mg^{2+} + H_2$

11. pH = 5.274

13. pH = 8.96

15. pH = 8

12. pH = 5.784

14. pH = 5.13

16. (a) $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$

A1 B2 B1 A2

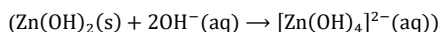
(b) $K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$ (c) pH = 5.1 (d) By adding ammonia solution to make basic buffer solution.

EXERCISE 19

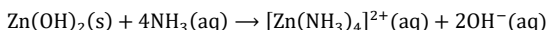
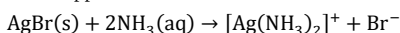
1.

a) Greater: $\text{Zn(OH)}_2(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ (b) Lower: increased $[\text{Zn}^{2+}]$ decreases the amount of dissolved Zn(OH)_2 by common ion effect.(c) It depends on the relative amount of NaOH to that of Zn(OH)_2 :

In small amount become lower due to common ion effect while when NaOH present in excess become greater due to formation of soluble complex.

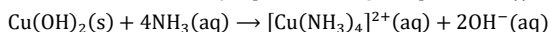
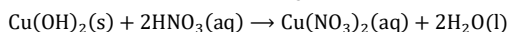


(d) Greater: this is due to the formation of soluble complex;

2. $K_{\text{sp}} = 6.25 \times 10^{-9} \text{mol}^3 \text{dm}^{-9}$ 3. $1.28 \times 10^{-35} \text{M}$ 4. $Q_{\text{sp}} = 7.5 \times 10^{-5} \text{M}^2$, so precipitate will form since $Q_{\text{sp}} > K_{\text{sp}}$ 5. $Q_{\text{sp}} = 5 \times 10^{-7} \text{M}^2$, so no precipitate will form since $Q_{\text{sp}} < K_{\text{sp}}$ 6. (a) $2.24 \times 10^{-5} \text{mol dm}^{-3}$ (b) $5 \times 10^{-9} \text{mol dm}^{-3}$ 7. $4.87 \times 10^{-5} \text{M}^3$ 8. AgBr being highly covalent in character as result of very large polarising power of Ag^+ , does not dissolve in water which is polar solvent (it readily form yellow precipitate in water). However, in aqueous ammonia, it tends to form soluble complex which appears to dissolve.

Insoluble

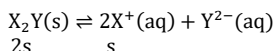
Soluble

9. Cu(OH)_2 contains strong base anion which is capable of reacting with the acid, HNO_3 , to form soluble products. It also contain strong acid cation which is capable of reacting with Lewis base, NH_3 , to form soluble complex.

10. Calcium sulphate is sparingly soluble electrolyte whose solubility decreases as the temperature decreases because its dissolution is endothermic. So cooling its saturated solution, lowers its solubility and the solution becomes supersaturated.

On another hand, carbon dioxide is a gas whose solubility decreases as the temperature increases due to high kinetic energy of gas molecules which makes them to escape from the solution. So heating its saturated solution, lowers its solubility and the solution becomes supersaturated.

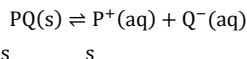
11. Carbonate ion in calcium is the conjugate base of weak acid and thus it is strong base. Consequently, calcium carbonate is basic salt that react with acids like hydrochloric acid to give clear solution.

That is opposite to Cl^- which is the conjugate base of strong acid (HCl). Apart from that, the added hydrochloric acid being strong electrolyte with the same ion (Cl^-) as that present in AgCl, it decreases solubility of the silver chloride by common ion effect, leading to the formation of precipitate.12. Disagree because the two compounds have different number of ions per formula unit; so their K_{sp} values will be different even if their molar solubility product is the same.**Calculation of the solubility product**

$$K_{\text{sp}} = [\text{X}^+]^2[\text{Y}^{2-}] = s(2s)^2 = 4s^3 \text{ or } s = \sqrt[3]{\frac{K_{\text{sp}}}{4}}$$

$$\text{Substituting } s = \sqrt[3]{\frac{1.08 \times 10^{-7}}{4}} = 3 \times 10^{-3} \text{M}$$

Then;



$$\text{From which; } K_{\text{sp}} = [\text{P}^+][\text{Q}^-] = s^2 = (3 \times 10^{-3})^2 = 9 \times 10^{-6}$$

The solubility product of PQ is 9×10^{-6} .13. (a) $6.08 \times 10^{-4} \text{g cm}^{-3}$ (b) 0.8mol dm^{-3}

14. pH = 12.35

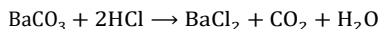
15. (a) $K_{sp} = [Mg^{2+}][OH^{-}]^2$; Units: $\text{mol}^3\text{dm}^{-9}$ (b) $1.7 \times 10^{-4} \text{mol dm}^{-3}$ (c) 99.7%

16. (a) $8.7 \times 10^{-4} \text{M}$ (b) $5.8 \times 10^{-4} \text{M}$ (c) (i) SrF_2 precipitates first (Hint: solve for $[\text{Sr}^{2+}]$ required for precipitation of each salt then compare; whereby the salt with smaller value of the concentration precipitates first) (d) 50%

17. (a) $2.6 \times 10^{-13} \text{M}^3$ (b) $1.61 \times 10^{-6} \text{M}$ (c) $[\text{IO}_3^-] = 0.21 \text{M}$, $[\text{Pb}^{2+}] = 5.8 \times 10^{-12} \text{M}$

18. (a) $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$; Units: $\text{mol}^2\text{dm}^{-6}$ (b) $1.14 \times 10^{-5} \text{mol dm}^{-3}$

(c) BaCO_3 can react with HCl in the stomach thus easily dissolves in it according to the following equation:



EXERCISE 20

1. (a) Reducing agent (b) Reducing agent (c) Oxidising agent (d) Oxidising agent

2. **Hint:** Chlorate(I) ion is ClO^-

3. $\text{Sn}^{2+}(\text{aq}) < \text{Ag}^+(\text{aq}) < \text{Au}^{3+}(\text{aq})$

4. (i) $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$

Oxidant is potassium dichromate. Reductant is iron (II) sulphate.

(ii) $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$

Oxidant is potassium iodate. Reductant is potassium iodide.

(iii) $2\text{Cu}^{2+} + 4\text{I}^- \rightarrow \text{Cu}_2\text{I}_2 + \text{I}_2$

Oxidant is copper (II) sulphate. Reductant is potassium iodide.

(iv) $2\text{Cl}_2 + 6\text{OH}^- \rightarrow \text{ClO}_3^- + 5\text{Cl}^- + 3\text{H}_2\text{O}$

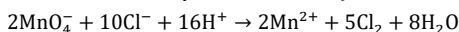
Oxidant is chlorine gas. Reductant is chlorine gas.

5. (a) +5 and +7 respectively (b) Does not involve only one iodine containing specie as the reactant. It involves two iodine species as reactants, giving only one iodine containing specie as product; this is opposite to disproportionation reaction and hence the reaction is **comproportionation reaction**. (c) On addition of starch, the solution turns blue (d) $\text{IO}_4^-(\text{aq}) + 7\text{I}^-(\text{aq}) + 8\text{H}^+(\text{aq}) \rightarrow 4\text{I}_2(\text{s}) + 4\text{H}_2\text{O}(\text{l})$

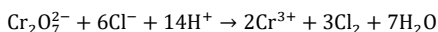
6. This is because, unlike $\text{K}_2\text{Cr}_2\text{O}_7$:

- KMnO_4 cannot be obtained pure enough.
- KMnO_4 readily reacts with traces of organic material or other reducing substances in water.
- KMnO_4 decomposes in sunlight.

7. Potassium permanganate (KMnO_4) is so strong oxidising agent that can oxidise Cl^- from HCl thus interfering the measurement of volume of KMnO_4 which was exactly used to oxidise Fe^{2+} in the titration.



8. This is due to oxidation of Cl^- (reducing agent) in NaCl to Cl_2 by potassium dichromate (VI), $\text{K}_2\text{Cr}_2\text{O}_7$ (oxidizing agent) while itself becomes reduced to Cr^{3+} which is detected by its green colouration.



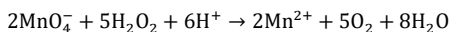
9. This is because:

- It ensures that the reaction occurs at reasonable high rate.
- It enables complete reduction of MnO_4^- to $\text{Mn}(\text{II})$ and not to $\text{Mn}(\text{III})$ which would be formed at lower temperature.
- CO_2 is soluble in water, thus heating removes all dissolved CO_2 out of the solution, driving the reaction in forward direction.

10.

(i) Number of moles of $\text{KMnO}_4 = \frac{20.25}{1000} \times 0.02 \text{mol} = 4.05 \times 10^{-4} \text{mol}$

KMnO_4 reacts with H_2O_2 according to the following equation:



From which mole ratio of MnO_4^- to H_2O_2 reacted = $\frac{5}{2} \times 4.05 \times 10^{-4} \text{mol}$

= $1.0125 \times 10^{-3} \text{mol}$ in 25cm^3 of its solution

Then $[\text{H}_2\text{O}_2] = \frac{n}{V} = \frac{1.0125 \times 10^{-3}}{25 \times 10^{-3}} \text{M} = 0.0405 \text{M}$

Using dilution principle: $M_c V_c = M_d V_d$

Then substituting $M_c \times 50 = 0.0405 \times 1000$; $M_c = 0.81 \text{M}$.

Hence original concentration of H_2O_2 was 0.81mol dm^{-3}

(ii) NaMnO_4 is hygroscopic.

The titre volume would be larger than the obtained one.

Concentrated H_2SO_4 is good oxidizing agent; so it would oxidize H_2O_2 as KMnO_4 does.

The titre volume would therefore be less than the obtained one.

11. $0.810 \text{ mol dm}^{-3}$

12. (a) $2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{S}_4\text{O}_6^{2-}(\text{aq}) + 2\text{I}^-(\text{aq})$ (b) 0.0358 g (c) $0.0504 \text{ mol dm}^{-3}$, 12.8 g dm^{-3}

13. (i) 1.72 g dm^{-3} (ii) **Starch indicator** is used for the titration, when the last of the iodine reacts with the thiosulphate, the blue colour from the starch-iodine mixture is discharged and the solution becomes colourless.

14. 0.090 M Fe^{2+} , 0.060 M Fe^{3+}

15. (a) 89.4% (b) Potassium manganate(VII) is not used for this titration because it is strong enough to oxidise chloride ions (from the hydrochloric acid) to form chlorine, thus interfering measurement of correct volume of the permanganate which is exactly used to oxidise Fe^{2+} in the titration.

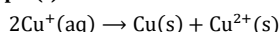
16. 14%

17. (a) 0.002 mol of $\text{Na}_2\text{S}_2\text{O}_3$, 0.001 mol of iodine (b) 0.000333 mol (c) 0.0980 g (d) 0.98 g , 97.0%

EXERCISE 21

1. 0.5603 V

2. (a) **Equation for disproportionation of copper(I) ions**



The cell diagram corresponding to the above disproportionation reaction is $\text{Cu}^+(\text{aq}) \mid \text{Cu}^{2+} \parallel \text{Cu}^+(\text{aq}) \mid \text{Cu}(\text{s})$

From which $E_{\text{cell}}^0 = E_{\text{R}}^0 - E_{\text{L}}^0 = 0.52 - 0.34 = +0.18 \text{ V}$

Since e.m.f of a cell corresponding to the above reaction is positive, the reaction is spontaneous and hence Cu^+ ions disproportionate in aqueous solution.

Equation for disproportionation of silver(I) ions

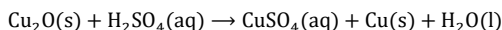


The cell diagram corresponding to the above disproportionation reaction is $\text{Ag}^+(\text{aq}) \mid \text{Ag}^{2+}(\text{aq}) \parallel \text{Ag}^+(\text{aq}) \mid \text{Ag}(\text{s})$

From which $E_{\text{cell}}^0 = E_{\text{R}}^0 - E_{\text{L}}^0 = 0.8 - 1.98 = -1.18 \text{ V}$

Since e.m.f of a cell corresponding to the above reaction is negative, the reaction is not spontaneous and hence Ag^+ ions do not disproportionate in aqueous solution.

(b) Blue solution of CuSO_4



Or ionically $\text{Cu}_2\text{O}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s}) + \text{H}_2\text{O}(\text{l})$

3. $1.47 \times 10^{-9} \text{ M}$

4. 0.56 V

5. 0.0591 V

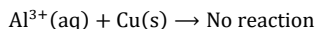
6. (i) Kinetic factors (ii) Non-standard conditions (iii) Very small difference in E^0 values.

7. Zinc having more negative E^0 , undergoes oxidation in preference to iron to form Zn^{2+} while iron undergoes oxidation in preference to tin because it has more negative E^0 than tin. Hence zinc prevents the initiation of iron corrosion (rusting) by preventing the oxidation of iron, $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$, which is necessary for the corrosion to occur.

8. Yes; can be used.

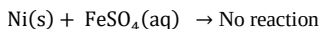
Explanation

Al having smaller value of reduction potential, is more reactive than copper. Therefore, Al cannot be reduced by Cu from the solution and hence the solution of aluminium can be safely stirred by using the copper spoon.



9. (i) Having lower reduction potential, nickel is stronger reducing agent and more reactive than copper and therefore it displaces the copper from copper sulphate solution (nickel spatula appears to dissolve in solution) and hence nickel spatula should not be used to stir $\text{CuSO}_4(\text{aq})$. $\text{Ni}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Ni}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

(ii) Having larger reduction electrode potential, nickel is weaker reducing agent and less reactive than iron thus making it incapable of displacing iron from the salt and hence ferrous sulphate can be stored in a nickel container.



10. The salt bridge connects the two half-cell solutions and thus completes the circuit of electrochemical cell. Therefore:

- Potassium chloride is used because it is strong electrolyte and hence it enables conduction of electricity in the two half-cells.
- Agar-gel is used to mix with potassium chloride so that they remain semi-solid and thus do not mix with the half-cell solutions, and also the semi-solid state prevents the diffusion of the electrolytes from one half – cell to the other, maintaining the charge balance in the two half cells.

11. (a) Positive **Reasons:** (i) K_c is large (greater than 1) (ii) The reaction occurs (It is spontaneous) (b) The oxidising agent is Mg^{2+} (c) Would increase Hint: To justify use Nernst equation (d) Would increase (Again you may use Nernst equation to explain by considering effect of change of value of Q_c on the cell potential) (e) 0V.

12. (a) $Cd(s) + 2Ag^+(aq) \rightarrow Cd^{2+}(aq) + 2Ag(s)$; $E^\theta = +1.2V$ (b) Anions (NO_3^- ions) will flow from the Ag^+ solution to the Cd^{2+} solution to balance the positive charges of new produced Cd^{2+} . (c) **The cell voltage will increase.** Ag^+ is a reactant, so increasing $[Ag^+]$ will increase the driving force for the forward (spontaneous) reaction and hence the cell potential will increase (Alternatively, you may use Nernst equation by considering the change in value of Q_c). (d) **The cell voltage will decrease.** Adding NaCl will have no effect on the Cd half-cell, but will cause AgCl to precipitate in the Ag half-cell ($Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$). Thus $[Ag^+]$ decreases, and since Ag^+ is a reactant, decreasing $[Ag^+]$ causes a decrease in voltage. (e) **The cell voltage will decrease.** $R_Q = \frac{[Cd^{2+}]}{[Ag^{2+}]^2}$, so diluting solution in both half-cells by the same amount make the value of Q_c to increase and hence according to Nernst equation; $E_{cell} = E_{cell}^\theta - \frac{RT}{nF} \ln Q_c$, if Q_c increases, cell voltage decreases.

13. 1.96×10^{37}

14. 9.247×10^{57}

15. $1.2 \times 10^{-12}M$

16. (a) (i) Mg (ii) Cl_2 (b) Cl_2 and Br_2 (c) (i) $Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(l)$; $E^\theta = +0.29V$

Reason: The overall e.m.f is positive and hence the reaction is feasible (ii) Extraction of bromine from sea water.

EXERCISE 22

1. $3.0367 \times 10^5 C$

2. 635.3 min

3. 56.18 g per equivalent weight

4. 8.04 hours

6. $1.106cm^{-1}$

8. $25.73 \Omega^{-1}cm^2mol^{-1}$

5. 0.0252A

7. $419.04\Omega^{-1}cm^2mol^{-1}$

9. $400 \Omega^{-1}cm^2eq^{-1}$

10. $104.16\Omega^{-1}cm^2eq^{-1}$

11. $4.6 \Omega^{-1}cm^2eq^{-1}$

12. Because in the solid form, ions are not free to move.

13.

- Non-ideality of conditions:** Faraday's second law assumes ideal conditions such as constant temperature, concentration of electrolyte, and absence of side reactions and impurities in the electrolyte. These ideal conditions are difficult to achieve in practice, and as such, the law may not hold in real life situations.
- Limited to single-electrode reactions:** Faraday's second law applies only to reactions that involve a single electrode, meaning that only one substance is being deposited or liberated. In more complex electrochemical systems, where multiple species may be involved, Faraday's law becomes less applicable.
- Does not account for overpotential:** Overpotential is the additional voltage required to drive a reaction at an electrode due to the activation energy barrier. Faraday's second law does not take into account the effect of overpotential, which can lead to deviations from the expected amount of substance deposited or liberated.
- Variation of current:** Faraday's second law assumes that the current passing through the electrolyte is constant, which is not always the case in practical systems. Variations in current can affect the deposition or liberation of substances and lead to deviations from Faraday's law.
- Concentrated solutions:** Faraday's second law of electrolysis is applicable only to dilute solutions of electrolytes. This is because, in concentrated solutions, the ions tend to interact with each other, which makes the electrolyte behave differently from the predictions of the law.

14. Hydrochloric acid being strong electrolyte, it is almost full ionised even at 0.1M concentration. So the dilution does not increase number of ions significantly, it only increases mobility of ions and hence the increase in the molar conductivity is small. This is different to acetic acid which is a weak electrolyte. For the weak electrolyte, the dilution increases both number of ions (due to an increase on degree of dissociation in accordance with Ostwald's dilution law) and their mobility, leading to greater increase in the molar conductivity.

15. Don't agree

Explanation

It is true that a strong electrolyte is completely dissociated in solution and thus, furnishes all ions for conductance. However, at higher concentrations, the dissociated ions are close to each other and thus, the inter-ionic attractions (ion-ion interactions) are greater. These forces reduce mobility of the ions and thus, conductivity is low. With a decrease in concentration (dilution), the ions move far away from each other thereby decreasing inter-ionic forces of attractions. This results to a slight increase in molar conductivity on dilution.

16. (a) solution A and solution E (b) solution B and solution C (c) solution A, solution B, solution C and solution E (all solutions except solution D) (d) solution D (e) not possible: the conductivity is determined by the ability of compounds to ionise in the solution (not by the solution pH which could be used to distinguish acid base). So both strong acid and base will give the same observation but different to those of weak acid and base which will also give the same observation on their side.

17. (a) 1F (b) 4F (c) 1F

18. 118g

19. (a) $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ (b) $FeCl_2$ (You must deduce this from calculations of given data)

(c) $Fe^{2+}(aq) + 2Cl^-(aq) \rightarrow Fe(s) + Cl_2(g)$ (d) 0.231L (e) 2.27A

20. $0.00238\Omega^{-1}\text{cm}^{-1}$, $238\Omega^{-1}\text{cm}^2\text{mol}^{-1}$

21. $0.528\text{Scm}^2\text{mol}^{-1}$

22. $1.84 \times 10^{-5}\text{mol dm}^{-3}$

23. 0.039

EXERCISE 23

1. (a) Exothermic, reactants (b) Endothermic, products (c) Endothermic, products

(d) Exothermic, reactants (e) Exothermic, reactants (f) Exothermic, reactants

2.

(a) $\Delta H_f^\theta(\text{Br}_2(\text{g})) > 0$; Elemental bromine is liquid at standard conditions; to convert it to gas heat must be added.(b) $\Delta H_f^\theta(\text{Br}_2(\text{l})) = 0$; Diatomic liquid state is the pure elemental form of bromine.(c) $\Delta H_f^\theta(\text{I}_2(\text{g})) > 0$; Elemental iodine is solid at standard conditions; to convert it to gas, heat must be added.(d) $\Delta H_f^\theta(\text{I}_2(\text{s})) = 0$; Diatomic solid state is the pure elemental form of iodine.3. $\text{Cl}(\text{g})$ has higher (more positive) enthalpy.**Reason:**

The enthalpy of reaction, ΔH_r , is $\Delta H_f(\text{product}) - \Delta H_f(\text{reactant})$. The change being negative means reactant is at a higher potential than the product. When the reaction occurs, heat is released, stabilising the system and the system moves to a lower energy potential.

4. -56.848kJ/mol

5. 46.4K (or $^\circ\text{C}$)

6. -1390kJ/mol

7.

(i) Exothermic

(ii) Exothermic

(iii) Endothermic

8. Diluting a concentrated acid with water is a highly exothermic process. So, when water is added to concentrated acid, large amount of heat is liberated which changes some water to steam explosively which can splash the acid and even the glass apparatus may break due to excessive heating.

9. From the definition of heat of solution;

$$\text{Heat of solution of NaOH, } \Delta H_{\text{soln}} = \frac{\text{Heat change } \Delta H}{\text{Number of moles of NaOH, } n}$$

$$\text{From which; } \Delta H = n \times \Delta H_{\text{soln}} = V_{\text{soln}} \times [\text{NaOH}] \times \Delta H_{\text{soln}} = \frac{500}{1000} \text{L} \times 7\text{mol L}^{-1} \times -42000\text{J mol}^{-1} = -147000\text{J}$$

But also; heat change, $\Delta H = -mc\Delta T$ (negative sign is introduced because the process is exothermic)

$$\text{Where } m = \rho_{\text{soln}} V_{\text{soln}}$$

$$\text{Thus; } \Delta H = -\rho_{\text{soln}} V_{\text{soln}} c\Delta T \text{ (where } \Delta T \text{ represents temperature that increased in making the solution)}$$

$$\text{It follows that: } -\rho_{\text{soln}} V_{\text{soln}} c\Delta T = -147000\text{J}$$

$$\text{Substituting } \Delta H = -1\text{g cm}^{-3} \times 500\text{cm}^3 \times 4.18\text{J g}^{-1}\text{C}^{-1} \times \Delta T = -147000\text{J}$$

$$\text{From which, } \Delta T = 70^\circ\text{C}$$

Thus the temperature of the solution = Initial temperature + $\Delta T = (21 + 70)^\circ\text{C} = 91^\circ\text{C}$ which is far above the temperature required to cause the burn injury and hence Mr. Akilikubwa got serious burn injury.

10. Reaction equation: $\text{NaOH} + \text{HNO}_3 \rightarrow \text{NaNO}_3 + \text{H}_2\text{O}$ **Incorrect determination:**

$$n_{\text{NaOH}} = \frac{100}{1000} \text{dm}^3 \times 0.3 \text{mol dm}^{-3} = 0.03\text{mol}$$

$$n_{\text{HNO}_3} = \frac{115}{1000} \text{dm}^3 \times 0.305 \text{mol dm}^{-3} = 0.030575\text{mol}$$

Since $n_{\text{HNO}_3} > n_{\text{NaOH}}$ and the mole ratio of the reaction equation is 1:1, HNO_3 was in excess and limited reactant is NaOH .

$$\text{Thus } n_{\text{NaOH}} = n_{\text{H}_2\text{O}} \text{ produced} = 0.03\text{mol}$$

$$\text{Using } \Delta H = mc\Delta T; \text{ Where } m = \rho V \text{ and}$$

$$\text{Heat released in the reaction, } \Delta H = -\rho V c\Delta T$$

$$\text{Where: } \rho = 1\text{g cm}^{-3}; V = (100 + 115)\text{cm}^3 = 215\text{cm}^3; C = 4.2\text{J g}^{-1}\text{C}^{-1}; \Delta T = (39 - 35)^\circ\text{C} = 4^\circ\text{C}$$

$$\text{Then } \Delta H = -1\text{g cm}^{-3} \times 215\text{cm}^3 \times 4.2\text{J g}^{-1}\text{C}^{-1} \times 4^\circ\text{C} = -43612\text{J} = -3.612\text{kJ}$$

$$\text{Then using } \Delta H_n = \frac{\Delta H}{n_{\text{H}_2\text{O}}} = \frac{-3.612\text{kJ}}{0.03\text{mol}} = -120.4\text{kJ/mol}$$

Hence incorrectly determined enthalpy of neutralisation is -120.4kJ/mol .

Correct determination:

Adding water to the container with NaOH does not change the number of moles of NaOH (n_{NaOH})

So n_{NaOH} and hence $n_{\text{H}_2\text{O}}$ produced remained to be 0.03 mol. The only variable that will change is, V

That is correct $V = (100 + 115 + 20)\text{cm}^3 = 235\text{cm}^3$

(The temperature rise of 4°C occurred in 235cm^3 of solution and not in 215cm^3).

Correct $\Delta H = -1\text{gcm}^{-3} \times 235\text{cm}^3 \times 4.2\text{Jg}^{-1}\text{C}^{-1} \times 4^\circ\text{C} = -3948\text{J} = -3.948\text{kJ}$.

Then correct $\Delta H_n = -\frac{3.948\text{kJ}}{0.03\text{mol}} = -131.6\text{kJ/mol}$

Absolute error = $(131.6 - 120.4) = 11.2\text{kJ/mol}$

Percentage error = $\left(\frac{\text{Absolute error}}{\text{Real value}}\right) \times 100\% = \frac{11.2}{131.6} \times 100\% = 8.5\%$

Hence the percentage error is 8.5%

11. (a) -54.3kJ/mol

(b) The two possible reasons which made the determined value of enthalpy of neutralisation to be smaller than the actual value are:

- 1) **Heat loss to the surroundings** (to calorimeter wall, to air or to thermometer) due to imperfections of calorimeter or mixing the two solutions slowly, causing an underestimation of the heat released which in turn makes the enthalpy to appear smaller than the actual value.
- 2) **Incomplete mixing** due to incomplete transfer of acid or base from graduated cylinder or spattering of some of the acid or base leading to overestimation of amount of water produced and hence the enthalpy appears to be smaller than the actual value

12. (a) Exothermic because the temperature increases confirming that heat was released in the process.

(b) To make all the heat is given out rapidly so that heat loss becomes as small as possible.

(c) -58.5kJ/mol

(d) Since the number of moles of each reactant is the same and both are used up in the reaction (there is no limiting reagent) doubling the concentration of HCl would not change the temperature because it would become the excess reagent and KOH the limiting reagent.

13. 18.54kJ is absorbed.

14. (a) 1.7mol (b) 255kJ (c) 10g

15. The temperature change is directly proportional to the molarity of the substance. Therefore:

Even though the volume has doubled, the molarity of acid and alkali has remained the same so the temperature rise remains to be 6°C .

When the concentration is doubled, the temperature change doubles, and hence the temperature rise and become 12°C .

16. -90kJ

17. -605.7kJ/mol

18. (a) 12.6kJ (b) 0.015mol (c) -840kJ/mol

(d) 1. Heat lost to surroundings 2. Heat absorbed by the apparatus due to its heat capacity 3. Incomplete combustion.

EXERCISE 24

1. -394kJ/mol

2. -10.94kJ/mol

3. -83.5kJ/mol

4. -1.9kJ/mol

5. (a) $\text{C}_2\text{H}_6(\text{g}) + \frac{7}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}); \Delta H_c^\ominus = -1560\text{kJ/mol}$

Don't forget to include **state symbols** and the **value of enthalpy change** whenever you are asked to give thermochemical equation.

(b) 84.4kJ/mol

6. (a) Lattice enthalpy/energy (b) -670kJmol^{-1}

7. (a) **A** is enthalpy of formation, **B** is lattice enthalpy (b) -883kJ/mol ; Hydration (or solvation) enthalpy.

8. -296kJ/mol

9. 0

10. 253kJ/mol

11.

- (i) It is impossible to get isolated constituent ions of a compound which would then combine and measure amount of heat evolved.
- (ii) This is due to presence of covalent characters in ionic compounds.

Explanation:

Calculations of lattice energy by Born-Haber cycle assumes the bonds in the compounds are hundred percent ionic while in reality there are some covalent characters which go together with a degree of polarisation of the ionic bonds. The covalent nature makes the bond to be stronger than the prediction made by the lattice energy.

(iii) **Strongly** ionic compounds like halides of alkali metals, for example; KCl and NaF.

12. Using bond energy to calculate heat of reaction is the least accurate method for determining heat of reactions due to the following reasons:

- 1) The bond energy values are given as average values and hence their calculations just give estimations of heat of reactions.

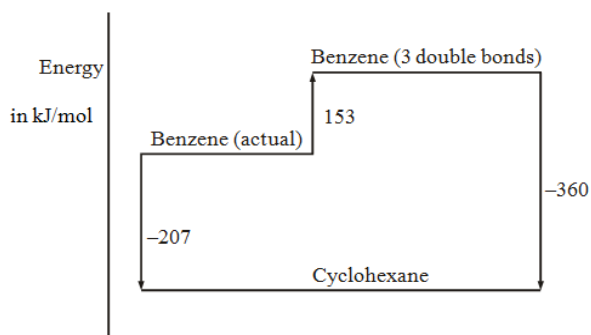
- 2) The calculation from bond energy is for gaseous reactants and products only hence the calculated heat of reactions that involve solids and liquids will be even less accurate.
13. Such transition reactions have so small heat change accompanying them that cannot be measured directly.
- 14.
- It is difficult to control hydration of anhydrous copper (II) sulphate. Any attempt to form hydrated copper (II) sulphate by mixing anhydrous copper (II) sulphate and water in the calorimeter will give a solution of copper (II) sulphate instead of hydrated copper (II) sulphate.
 - Methods which can be applied are:
 - Hess's law cycle method.
 - Combining thermochemical equation method.

15. **Hint:** Calculate enthalpy of reaction when ethenol is formed and when ethanal is formed and you will find that in forming ethanal the reaction is more exothermic and hence more thermodynamically favoured.

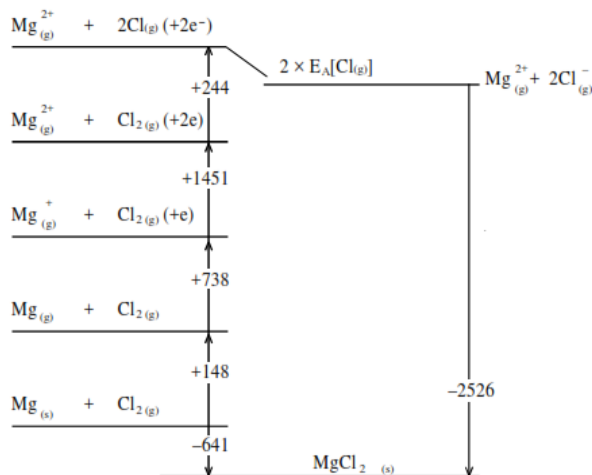
16. (a) -160kJ/mol (b) Highly exothermic enthalpy change of solution.

17. (a) -120kJ/mol (b) $3 \times (-120\text{kJ/mol}) = -360\text{kJ/mol}$ (c) Benzene is more stable because unlike in cyclohexene where π bond is localised, π bonds in benzene are stabilised by delocalisation of the electrons through mesomerism and the difference between actual and calculated value amounted to $+153\text{kJ/mol}$ is the energy required to break mesomerism/resonance before doing addition of hydrogen atoms.

Illustration



18. (a)



$E.A = -348\text{kJ/mol}$

(b) Theoretical value assumes the compound is 100% ionic while in reality the compound has some covalent character which corresponds to its degree of polarisation. So the difference is due to presence of covalent bond character because Mg^{2+} polarises Cl^{-} .

19. (a) ΔH_f (b) First ionisation energy of calcium (c) $+697\text{kJ/mol}$ (d) -147kJ/mol

20. (a) $\text{S}^{-}(\text{g})$ (b) Before the addition of second electron, energy is absorbed to overcome repulsion of the first electron in step E. (For more detail refer to the book for Inorganic chemistry in the series) (c) (i) Atomisation enthalpy of S (ii) Second ionisation enthalpy of Ca (iii) Second electron affinity of S (d) To remove second electron in step D requires

more energy because fewer electrons which remain after removing first electron in step C experience weaker screening effect **OR** simply fewer remaining electrons are more strongly attracted nearer to nucleus (due to decreased repulsion) and stronger nuclear attractive force per electron (Again you may refer to the Inorganic book in the series for more discussion) (e) $+539\text{kJ/mol}$

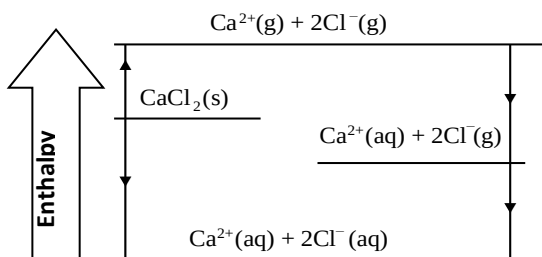
21. (a) (ii)

Second ionisation energy is required for formation of CaCl_2 while only first ionisation energy is required for CaCl .

Dissociation energy of Cl_2 is required for formation of CaCl_2 while a half of the dissociation energy is required for CaCl .

Twice the electron affinity of Cl is required for formation of CaCl_2 while only single electron affinity is required for CaCl .

(b) (i)



Use above cycle to get enthalpy of solution of $\text{CaCl}_2 = -163\text{kJ/mol}$

(ii) Decrease. **Reason:** Dissolving CaCl_2 is exothermic (as negative sign of its enthalpy of solution obtained in (i) suggests), so according to Le-Chatelier's principle when temperature is increased the position of equilibrium shifts to the left by forming more undissolved CaCl_2 .

22. (a) -82.8kJ/mol (b) (i) -1442kJ/mol (ii) The bigger source of error is that the calculation in (i) does **not** take into account the enthalpy of vapourisation of water. Extra energy would be released from the condensation of water, giving a more exothermic value which is closer to -1560 kJ/mol .

Digging deeper!

Since the enthalpy of vapourisation of water is 40.7kJ/mol , $3 \times 40.7\text{kJ}$ would be released when the water condenses, giving an enthalpy of combustion of $-1442 - (3 \times 40.7) = -1564\text{ kJ/mol}$, which is very close to the standard value.

23. (a) -3915.6kJ/mol (b) -3720kJ/mol (c) -3934.2kJ/mol **Hint:** To correct value obtained in (b); cyclohexane being at reactants side, apply (add to the answer obtained in (b)) its **endothermic** enthalpy of vapourisation for one mole while for water which is at products side, apply its **exothermic** enthalpy of condensation for six moles keeping in the mind that the enthalpy of condensation is of equal magnitude but opposite in sign to the enthalpy of vapourisation.

(d)

- Apart from (a) none of the answers can be considered as a standard enthalpy values at $298\text{K}/1\text{atm}$, since bond enthalpy calculations can only involve gaseous species and the fact that bond energies are based on average values for similar molecules.
- The value of -3720 kJ/mol , ignoring state changes, has an error of 195.6 kJ/mol compared to the standard enthalpy value based on standard enthalpy changes calculated in (a).
- When corrections are applied to take into account state changes with respect to $298\text{K}/1\text{atm}$, the error is reduced to 18.6 kJ/mol , which implies there are not bad results from average bond enthalpies in organic molecules.

SOLUTIONS TO EXAMINATION QUESTIONS

PART ONE

Questions 1

- (a) Above critical temperature, gas (vapour) particles are very fast moving with very high kinetic energy which breaks any attempt of forming intermolecular forces through application of high external pressure. Consequently, liquefaction of the substance becomes impossible and hence its liquid state cannot exist.

- (b) Given that:

$$v = 140\text{cm}^3 = \frac{140}{1000}\text{dm}^3; T = 150^\circ\text{C} = 423\text{K}$$

$$P = 755\text{mmHg} = \frac{755}{760}\text{atm}, m = 0.071\text{g}$$

$$\text{From } PV = \frac{m}{M_r} RT$$

$$M_r = \frac{mRT}{PV} = \frac{0.071 \times 0.082 \times 423 \times 760 \times 1000}{755 \times 140} = 17.7\text{g/mol}$$

Thus the measured molar mass of water is approximately 18g/mol

But the molecular formula H_2O suggests molecular mass of water to be 18g/mol

Hence the given figures are in accordance with the formula H_2O for steam

Question 2

- (a) Enclosing the gas in the larger container at the same temperature (room was the same) means that each individual gas particle has to move greater distance before hitting the container's wall leading to smaller collision frequency and consequently the pressure will decrease after changing the container.

- (b) If the oxidation number of Beryllium (Be) in the compound is x, then the molecular formula of its chloride will be BeCl_x

Where $x = \text{oxidation number of Be} = \text{number of moles of chlorine atoms in the compound}$

But percentage of Be in the Compound is 11.3%

So the percentage of chlorine atoms in the compound is $(100 - 11.3)\% = 88.7\%$

And molar mass of the compound $(\text{BeCl}_x) = \text{Relative vapour density} \times 2 = 40 \times 2 = 80$

Thus mass of chlorine atoms in the compound $\frac{88.7}{100} \times 80 = 70.96\text{g}$

Therefore number of moles of chlorine atoms in the compound $= \frac{70.96}{35.5}\text{mol} = 2\text{mol}$

So oxidation number of Be in the compound is 2

The molecular formula of the compound is then become BeCl_2

It follows that $y + 71 = 80$; where y is atomic mass of Be

From which $y = 9$

Hence the relative atomic mass of Be is 9

It should be noted that:

In the question it was asked to find the relative atomic mass of Be from the result of its oxidation number and not otherwise.

Question 3

- (a) Pressure-volume gas law is Boyle's law which can be stated as follows: Volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature.
- (b) From Graham's of diffusion

$$\frac{t_x}{t_{O_2}} = \sqrt{\frac{M_x}{M_{O_2}}} \text{ or } M_x = M_{O_2} \left(\frac{t_x}{t_{O_2}} \right)^2$$

Where $M_{O_2} = 32\text{g/mol}$

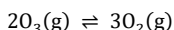
$t_{O_2} = 240\text{ seconds}, t_x = 3\frac{3}{4}\text{ minutes} = 225\text{ seconds}$

Then $M_x = 32 \times \left(\frac{225}{240} \right)^2 = 28\text{g/mol}$

Hence the relative molecular mass of X is 28

Question 4

- (a) Temperature of negative Kelvin would imply that the gas has negative volume and it is impossible to have negative volume.
- (b) Ozone always exists in a mixture with oxygen as result of its dissociation according to the following equation:



So if the percentage of O_3 is 10%

Then the percentage of O_2 will be $(100 - 10)\% = 90\%$

So average molecular mass of gases

$$= \frac{10}{100} M_{O_3} + \frac{90}{100} M_{O_2}$$

$$= \left(\frac{10}{100} \times 48 \right) + \left(\frac{90}{100} \times 32 \right) = 33.6 \text{ g/mol}$$

If M_m and t_m is the average molecular mass of the mixture and time taken by mixture to diffuse respectively;

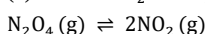
Then by Graham's law of diffusion: $\frac{t_m}{t_{H_2}} = \sqrt{\frac{M_m}{M_{H_2}}}$ or $t_m = t_{H_2} \sqrt{\frac{M_m}{M_{H_2}}}$

So, $t_m = 1 \sqrt{\frac{33.6}{2}} = 4.1 \text{ minutes} = 246 \text{ seconds}$

Hence the time required for ozonide oxygen is 246 seconds

Questions 5

- (a) They are similar in a manner that they both involve movement of gas particles from region of higher gas concentration to that of lower concentration.
They are different in a manner that, while in effusion gas particles pass through aperture, in diffusion gas particles move through an open space.
- (b) Since NO_2 and N_2O_4 are at equilibrium according to the following equation:



It follows that:

Observed molar mass of N_2O_4 = observed molar mass of NO_2

But $M_r = 2 \text{ g/mol} \times \text{Relative vapour density} = 2 \times 24 = 48 \text{ g/mol}$

Using $i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}}$

Then Vant' hoff factor for $N_2O_4 = \frac{92}{48} = 1.92$

Using $\alpha = \frac{i-1}{N-1}$ where $N = 2$

Then $\alpha = \frac{1.92-1}{2-1} = 0.92$ or 92%

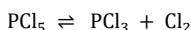
Hence degree of dissociation of the gas is 92%

Question 6

- (a) Nitrogen liquefies first.

Reason: Intermolecular forces are higher for gases with higher critical temperature, making easier to perform liquefaction process.

- (b) PCl_5 (Phosphorous pentachloride) dissociates according to the following equation:



$N = 2$

Using $\alpha = \frac{i-1}{N-1}$

Where $\alpha = 20\% = 0.2$

So $0.2 = \frac{i-1}{2-1}$ or $i = 1.2$

But $i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}}$

From which Observed molar mass = $\frac{\text{Expected molar mass}}{i} = \frac{208.5}{1.2} = 173.75 \text{ g}$

But relative vapour density = $\frac{\text{Molar mass}}{2 \text{ g/mol}} = \frac{173.75}{2} = 86.875$

Hence the relative vapour density for dissociated mixture is 86.875.

Questions 7

- (a)
- Is the temperature at and above which a gas cannot be liquefied, no matter how much pressure is applied.
 - Is the volume occupied by one mole of a gas at critical temperature and pressure.
 - Is the pressure required to liquefy a gas at its critical temperature
- (b) Iodine dissociates according to the following equation: $I_2 \rightleftharpoons 2I$; $N = 2$

$M_r = 2 \text{ g/mol} \times \text{relative vapour density}$

So the observed molar mass of iodine = $2 \times 87 = 174 \text{ g/mol}$

$i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{254}{174} = 1.46$

$$\alpha = \frac{i-1}{N-1} = \frac{1.46-1}{2-1} = 0.46 \text{ or } 46\%$$

Hence the percentage dissociation of I_2 is 46%

Questions 8

(a)

- (i) 'a' indicates the intermolecular forces of attraction between molecules of real gases (Greater intermolecular forces, greater value of 'a').

'b' indicates actual volume of a molecule of real gas (Greater size or molecular weight of the molecule, greater value of 'b').

H_2S has higher value of 'a'

Reason:

- (ii) H_2S molecules exhibit stronger intermolecular forces of attraction since it has stronger Van der Waals dispersion forces (H_2S has greater molecular weight than H_2) and also has dipole-dipole forces in addition to the dispersion forces while H_2 has the dispersion forces only.

H_2S has higher value of 'b'

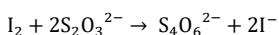
Reason:

Having greater molecular weight, H_2S molecule has greater size and therefore greater volume than H_2 .

- (iii) 'a' is correlated to boiling point. The greater value of 'a' means stronger intermolecular forces of attraction and whence higher boiling point.

- (b) Hydrogen iodide (HI) dissociate according to the following equation: $2HI \rightleftharpoons H_2 + I_2$

The liberated iodine reacts with sodium thiosulphate according to the following equation:



Where mole ratio of I_2 to $Na_2S_2O_3$ is 1:2

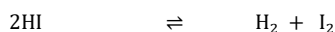
But number of moles of $Na_2S_2O_3$ in 15cm^3 of its solution

$$= \frac{15}{1000} \times 0.1 \text{ moles} = 1.5 \times 10^{-3} \text{ moles (using } n = MV)$$

$$\text{So number of moles of liberated } I_2 = \frac{1.5 \times 10^{-3}}{2} \text{ moles} = 7.5 \times 10^{-4} \text{ moles}$$

$$HI \text{ contain } 1/128 \text{ moles} = 7.8125 \times 10^{-3} \text{ moles}$$

Thus 7.8125×10^{-3} moles of HI dissociates to give 7.5×10^{-4} moles of I_2



$$\text{After dissociation } 7.8125 \times 10^{-3} - 2x \qquad \qquad x \qquad x$$

Where $x = 7.5 \times 10^{-4}$ moles

$$\begin{aligned} \text{Degree of dissociation} &= \frac{\text{Number of moles dissociated}}{\text{Original number of moles before dissociation}} = \frac{2x}{7.8125 \times 10^{-3}} \\ &= \frac{2 \times 7.5 \times 10^{-4}}{7.8125 \times 10^{-3}} = 0.192 \text{ or } 19.2\% \end{aligned}$$

Since $n = \frac{m}{M_r}$ and for given element, M_r is constant and hence percentage by mass of HI = percentage by moles

So percentage by mass of HI which remain undissociated is

$$(100 - 19.2)\% = 80.8\%$$

Question 9

(a)

- (i) N_2 (Has a weakest intermolecular force of attraction. Among the non-polar, N_2 has smallest molecular weight and therefore smallest Van der Waals dispersion forces. NH_3 has a stronger intermolecular force than N_2 despite the fact that has smallest molecular weight because it is polar covalent molecule with hydrogen bond.

- (ii) CCl_4 (It has much greater molecular weight and therefore greatest size making its molecule to occupy greatest volume).

- (b) From $PV = nRT$, $n = \frac{PV}{RT}$

$$\text{Thus } n_{CO_2} \text{ evolved} = \frac{200 \times 850}{760 \times 1000 \times 0.082 \times 1073} \text{ moles} = 2.54227 \times 10^{-3} \text{ moles}$$

$CaCO_3$ Decompose according to the following equation:



From which mole ratio of CO_2 to $CaCO_3$ is 1:1

Thus number of moles of $CaCO_3$ decomposed is also 2.54227×10^{-3} moles

And mass of $CaCO_3$ decomposed is $2.54227 \times 10^{-3} \times 100g = 0.254227g$ (Using $m = nM_r$)

$$\text{Hence the percentage of } CaCO_3 \text{ decomposed} = \frac{0.254227}{2.5} \times 100\% = 10.17\%$$

Hence 10.17% of CaCO_3 decomposed

Question 10

(a) From the kinetic equation: $PV = \frac{Nmc^2}{3}$

But the kinetic energy of N molecules $= \frac{1}{2}Nmc^2$

Where m is the mass of one molecule and Nm is the total mass of N molecules.

So from K.E $= \frac{1}{2}Nmc^2$, $Nmc^2 = 2K.E$

Then substituting $Nmc^2 = 2K.E$ to the above kinetic equation gives: $PV = \frac{2}{3}K.E$

Thus $K.E = \frac{3}{2}PV$

But from ideal gas equation: $PV = nRT$

So $K.E = \frac{3}{2}nRT$ for n moles of gas

If n = 1 (for one mole of the gas): $K.E = \frac{3}{2}RT$

Since R is constant, $\frac{3}{2}R$ is also constant and therefore $K.E = \text{constant} \times T$ or $K.E \propto T$.

Hence the result of kinetic energy the kinetic energy of gas molecules varies directly proportional to the absolute temperature.

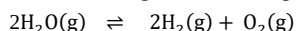
(b) Mass of water original present $= 1\text{cm}^3 \times 1\text{g/cm}^3 = 1\text{g}$ ($m = \rho V$)

At 2500°C , 3.98% of water dissociated;

That is mass of water dissociated $= \frac{3.98}{100} \times 1\text{g} = 0.0398\text{g}$

Number of moles of water dissociated $= \frac{0.0398}{18\text{gmol}^{-1}} = 2.2111 \times 10^{-3}\text{mole}$

Water vapour dissociated according to the following equation



From which mole ratio of H_2O to H_2 is 1:1

Thus number of moles of hydrogen produced was also 2.2111×10^{-3} moles

And also mole ratio of H_2O to O_2 is 2:1

Thus number of moles of O_2 produced is $\frac{2.2111 \times 10^{-3}}{2}$ moles $= 1.10555 \times 10^{-3}$ moles

Percentage by mass of water which remain undecomposed $= (100\% - 3.98)\%$ or 96.02%

Thus mass of water vapour (gas) which remain undecomposed

$$= \frac{96.02}{100} \times 1\text{g} = 0.9602\text{g}$$

Number of moles of the vapour $= \frac{0.9602}{18} = 0.0533$ moles

Total number of moles of gases

$=$ Number of moles of water vapour + number of moles of $\text{H}_2(\text{g})$ + number of moles of $\text{O}_2(\text{g})$

$= 2.2111 \times 10^{-3} + 1.10555 \times 10^{-3} + 0.0533 = 0.0566$ moles

Using $PV = nRT$

From which $V = \frac{nRT}{P} = \frac{0.0566 \times 0.082 \times 2773 \times 760}{760} = 12.87\text{dm}^3$

Hence the gases should occupy 12.87dm^3

Question 11

(a)

(i) The law that govern the breathing process is **Boyle's law** which state that: *The volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature.*

(ii) Boyle's law is obeyed by the gases at **high temperature** and **low pressure**.

(b) Mass of HI dissociated $= \frac{16}{100} \times 3\text{g} = 0.48\text{g}$

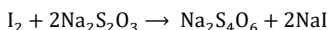
Number of moles of HI dissociated $= \frac{0.48}{128}$ moles $= 3.75 \times 10^{-3}$ moles

HI dissociated according to the following equation: $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$

From which mole ratio of HI to I_2 is 2:1

Thus number of mole of I_2 produced $= \frac{1}{2} \times 3.75 \times 10^{-3}$ moles $= 1.875 \times 10^{-3}$ moles

Iodine reacts with $\text{Na}_2\text{S}_2\text{O}_3$ according to the following equation:



From which mole ratio of I_2 to $\text{Na}_2\text{S}_2\text{O}_3$ 1:2

Thus number of moles of $\text{Na}_2\text{S}_2\text{O}_3$ required was $2 \times 1.875 \times 10^{-3}$ moles or 3.75×10^{-3} moles

But $[\text{Na}_2\text{S}_2\text{O}_3] = 0.165\text{M}$

$$\text{And } V = \frac{n}{c}$$

$$\text{Thus volume of } \text{Na}_2\text{S}_2\text{O}_3 = \frac{3.75 \times 10^{-3}}{0.165} = 0.0227\text{dm}^3 \text{ or } 22.7\text{cm}^3$$

Hence volume of sodium thiosulphate required is 22.7cm³

Since mole ratio of H_2 to I_2 is 1:1; number of moles of H_2 produced was also

$$1.875 \times 10^{-3} \text{ moles}$$

Using $m = n\text{Mr}$

So mass of hydrogen gas (H_2) which would remain uncombined

$$= 1.875 \times 10^{-3} \times 2\text{g} = 3.75 \times 10^{-3}\text{g}$$

Hence mass of uncombined hydrogen gas is $3.75 \times 10^{-3}\text{g}$

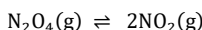
Question 12

- (a) The temperature, at which volume or pressure of any gas reduces to zero, is referred to as absolute zero temperature. Its value is equal to 0K or -273°C . The absolute zero temperature is just hypothetical temperature because practically all gases become liquefied before reaching -273°C .

- (b) For gases, volume ratio = moles ratio (Avogadro's law)

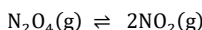
Thus we can treat volume in similar way as mole in stoichiometric ratio

N_2O_4 (Nitrogen tetraoxide) decompose partially into NO_2 according to the following equation:



If initial volume of N_2O_4 (before its decomposition at 27°C) is V_1

Then after decomposition at 27°C



$$V_1 - \frac{20}{100}V_1 = 0.8V_1 \quad \frac{2 \times 20V_1}{100} = 0.4V_1$$

$$\text{Total volume of gaseous mixture} = 0.8V_1 + 0.4V_1 = 1.2V_1$$

But it is given that, the volume of the gaseous mixture = 1dm^3

$$\text{Then } 1.2V_1 = 1 \quad \text{or } V_1 = \frac{5}{6}\text{dm}^3$$

Thus the initial volume of undecomposed N_2O_4 at 27°C was $\frac{5}{6}\text{dm}^3$

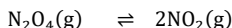
Since pressure is kept constant at 760mmHg; Charles law is applicable.

$$\text{That is from Charles law } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\text{From which } V_2 = \left(\frac{T_2}{T_1}\right)V_1$$

$$\text{Thus the volume of undecomposed } \text{N}_2\text{O}_4 \text{ at (a) } 100^\circ\text{C} = \frac{373}{300} \times \frac{5}{6}\text{dm}^3 = \frac{373}{360}\text{dm}^3$$

So at 100°C (373K)



$$\text{After Decomposition} \quad \frac{373}{360} - x \quad 2x$$

$$\text{Total volume of gaseous mixture} = \frac{373}{360} - x + 2x = \frac{373}{360} + x$$

$$\text{But } x = \frac{90}{100} \times \frac{373}{360} \text{ (At } 100^\circ\text{C } \text{N}_2\text{O}_4 \text{ is 90\% decomposed)}$$

$$x = 0.9325$$

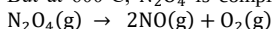
$$\text{So total volume} = \frac{373}{360} + x = \frac{373}{360} + 0.9325 = 1.969\text{dm}^3$$

Hence the gases will occupy 1.969dm^3 at 100°C

$$\text{Also from } V_2 = \left(\frac{T_2}{T_1}\right)V_1$$

$$\text{The volume of undecomposed } \text{N}_2\text{O}_4 \text{ at (ii) } 600^\circ\text{C} = \frac{873}{300} \times \frac{5}{6}\text{dm}^3 = 2.425\text{dm}^3$$

But at 600°C , N_2O_4 is completely dissociated into nitrogen oxide and oxygen, so the equation for the reaction becomes:



From which mole ratio of N_2O_4 to NO is 1:2

And mole ratio of N_2O_4 to O_2 is 1:1

Thus:

$$\text{Volume of NO produced} = 2 \times 2.425 = 4.85 \text{ dm}^3$$

$$\text{Volume of } O_2 \text{ produced} = 2.425 \text{ dm}^3$$

So total volume of the gaseous mixture = $(2.425 + 4.85) \text{ dm}^3 = 7.275 \text{ dm}^3$

Hence the gases will occupy 7.275 dm^3 at 600°C

Question 13

- (a) Both association and dissociation lead to abnormal result of experimental determination of molar mass of volatile substances as explained below:

Dissociation

Dissociation is splitting of a large molecule into two or more smaller molecules. It leads to increase in number of gas molecules and whence the increase in volume of the gas. So from the ideal gas equation which can be written as $PV = \frac{m}{M_r} RT$; it is clearly understood that the volume (V) of the gas varies inversely proportional to its molar mass (M_r). So the increase in volume of the gas as the result of dissociation leads to decrease in molar mass of the gas. Hence dissociation makes the measured molar mass of volatile substance to be smaller than that suggested by its normal molecular formula.

Association

Association is the combining of more than one small molecule to form one larger molecule. It leads to decrease in number of gas molecules and whence decrease in volume of the gas. So from the ideal gas equation; $PV = \frac{m}{M_r} RT$ where volume of the gas varies inversely proportional to its molar mass, the molar mass of the gas must increase as result of association. Hence association makes the measured molar mass of volatile substance to be greater than suggested by its normal molecular formula.

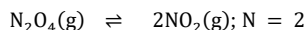
- (b) By Graham's law of diffusion: $\frac{V_{O_2}}{V_{N_2O_4}} = \sqrt{\frac{M_{N_2O_4}}{M_{O_2}}}$

$$\text{From which: } M_{N_2O_4} = M_{O_2} \left(\frac{V_{O_2}}{V_{N_2O_4}} \right)^2 = 32 \times \left(\frac{3}{2} \right)^2 = 72 \text{ g/mol}$$

Thus the observed molar mass of N_2O_4 is 72g/mol.

But the expected molar mass of N_2O_4 is 92g/mol. (as calculated from its molecular formula).

And N_2O_4 dissociated according to the following equation



$$\text{Using } i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{92}{72} = 1.28$$

$$\text{So from } \alpha = \frac{i-1}{N-1}$$

$$\text{Degree of dissociation of } N_2O_4 = \frac{1.28-1}{2-1} = 0.28 \text{ or } 28\%$$

Hence the degree of dissociation of N_2O_4 is 28%

Question 14

- (a) From the kinetic equation of gases: $PV = \frac{1}{3} mc^2$; but $K.E = \frac{1}{2} Nmc^2$ or $Nmc^2 = 2K.E$

$$\text{Then } PV = \frac{2}{3} K.E$$

From one of the assumption of kinetic theory of gases; $K.E \propto T$

Thus $K.E = kT$ where k is the constant for proportionality

$$\text{Therefore; } PV = \frac{2}{3} kT \dots \dots \dots (i)$$

If T is constant:

$$\frac{2}{3} kT = \text{Constant and therefore (i) becomes: } PV = \text{Constant or } V = \frac{\text{Constant}}{P}$$

Hence $V \propto \frac{1}{P}$ which is Boyle's law.

If P is constant:

$$\frac{2k}{3P} = \text{Constant and therefore the equation (i) above becomes: } V = \text{Constant} \times T$$

Hence $V \propto T$ which is Charles's law.

Since both laws can be derived from the kinetic equation of gases as shown above, the two laws are contained in the equation.

(b) Let $x\text{cm}^3$ of methane is mixed with $y\text{cm}^3$ of ethane

Then $x + y = 24$ (i)

Equation for combustion of methane: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

From which mole of ratio and hence volume ratio of CH_4 to CO_2 is 1:1

Thus the volume of CO_2 produced by combustion of CH_4 was $x\text{cm}^3$

Equation for combustion of ethane: $\text{C}_2\text{H}_6 + \frac{7}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$

From which mole ratio and hence volume ratio of C_2H_6 to CO_2 is 1:2

Thus the volume of CO_2 produced from combustion of C_2H_6 was $2y\text{cm}^3$

So total volume of CO_2 produced from combustion = $(x + 2y)\text{cm}^3$

When KOH is introduced into the gases, the strong alkaline solution absorb $\text{CO}_2(\text{g})$ according to the following equation:
 $2\text{KOH}(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$

So the decrease in volume after introduction of KOH ; is the volume of CO_2 which was formed from combustion of the two gases.

That is $x + 2y = 32$(ii)

Solving (i) and (ii) simultaneously gives: $x = 16$ and $y = 8$

Hence there are 16cm^3 of methane and 8cm^3 of ethane in the mixture.

Question 15

(a) From kinetic equation of gases: $PV = \frac{N}{3}mc^2$

But Nm is the total mass for N molecules of the gas, m_g ;

It follows that: $PV = \frac{m_g c^2}{3}$

From which $P = \frac{m_g c^2}{3V}$

But $\frac{m_g}{V}$ density of the gas, ρ_g

Thus $P = \frac{\rho_g c^2}{3}$ or $c^2 = \frac{3P}{\rho_g}$

Whence $c = \sqrt{\frac{3P}{\rho_g}}$

If pressure P , is constant, $\sqrt{3P} = \text{constant}$

Then it becomes; $c = \frac{\text{constant}}{\sqrt{\rho_g}}$ or $c \propto \frac{1}{\sqrt{\rho_g}}$

Since the speed of the gas is directly proportional to the rate of diffusion (or effusion) of the gas, it can be concluded that:

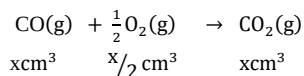
Rate of diffusion $\propto \frac{1}{\sqrt{\rho_g}}$ which is the mathematical form of Graham's law of diffusion.

Since the Graham's law can be derived from kinetic equation of gases, the validity of the kinetic equation confirms the validity of the Graham's law.

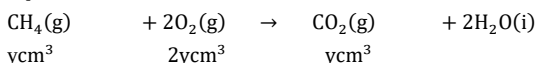
(b) Let volume of carbon monoxide, methane and hydrogen be $x\text{cm}^3$, $y\text{cm}^3$ and $z\text{cm}^3$ respectively

Then $x + y + z = 32$ ----- (i)

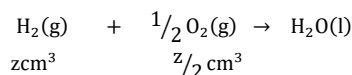
Equation for combustion of carbon monoxide



Equation for combustion of methane



Equation for combustion of hydrogen



Volume of CO_2 reduced volume after introducing $\text{KOH}(\text{aq}) = 22\text{cm}^3$

Thus $x + y = 22$ (ii)

Volume of oxygen reacted = $(50 - 16)\text{cm}^3 = 34\text{cm}^3$

Then $\frac{x}{2} + 2y + \frac{z}{2} = 34$

or $x + 4y + z = 68$ (iii)

Solving (i), (ii) and (iii) simultaneously gives: $x = 10, y = 12$ and $z = 10$

Hence the composition of the mixture was carbon monoxide, 10cm^3 , methane, 12cm^3 and hydrogen, 10cm^3 respectively

Question 16

(a) **Statement 1:** Correct.

Statement 2: Incorrect

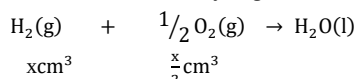
Reason:

For one mole of the gas to occupy the volume of 22.4L , the room pressure (1atm) must be accompanied with temperature of 0°C (and not the room temperature which is 25°C). At room temperature and pressure volume of one mole of the gas will be greater than 22.4L .

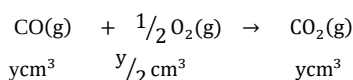
(b) Let volume of hydrogen, carbon monoxide and nitrogen be $x\text{cm}^3, y\text{cm}^3$ and $z\text{cm}^3$ respectively

Then $x + y + z = 65$ (i)

Equation for combustion of hydrogen



Equation for combustion of carbon monoxide



Nitrogen does not combust easily in oxygen

Volume of CO_2 = Reduced volume after introducing $\text{KOH} = (55 - 25) = 30\text{cm}^3$

Then $y = 30$(ii)

The gases which remain after introducing KOH are nitrogen and unreacted oxygen

Thus volume of unreacted oxygen + volume of nitrogen = 25cm^3

But volume of reacted oxygen = $\left(\frac{x}{2} + \frac{y}{2}\right)\text{cm}^3$

So the volume of unreacted oxygen = $50 - \left(\frac{x}{2} + \frac{y}{2}\right)$

And volume of nitrogen = $z\text{cm}^3$

It follows that: $50 - \left(\frac{x}{2} + \frac{y}{2}\right) + z = 25$

or $x + y - 2z = 50$(iii)

Solving (i), (ii) and (iii) simultaneously gives

$x = 30, y = 30$ and $z = 5$

$\%\text{H}_2 = \frac{30}{65} \times 100\% = 46.15\%$

$\%\text{CO} = \frac{30}{65} \times 100\% = 46.15\%$

$\%\text{N}_2 = \frac{5}{65} \times 100\% = 7.7\%$

Hence the percentage by volume of each gas in the original mixture was:

Hydrogen gas 46.15%

Carbon monoxide gas 46.15%

Nitrogen gas 7.7%

Question 17

(a) From the kinetic equation of gases: $PV = \frac{1}{3} Nmc^2$

If $N = N_A = 6.02 \times 10^{23}$ molecules, $n = 1$ (n is the number of moles of the gas)

And $Nm = N_A m = M_r$ (M_r is the molar mass of the gas)

Then $PV = \frac{M_r c^2}{3}$ but for $n = 1$, $PV = RT$

Then $RT = \frac{M_r c^2}{3}$ or $c^2 = \frac{3RT}{M_r}$

Hence $c = \sqrt{\frac{3RT}{M_r}}$

Where c is the root mean square (r.m.s) speed of gas molecules.

The kinetic energy (K.E) can also be deduced from the above equation for the root mean square speed as follows:

$$\text{From } c = \sqrt{\frac{3RT}{M_r}}$$

But kinetic energy (K.E) of the gas = $\frac{1}{2}mc^2$ where m is the given mass of the gas.

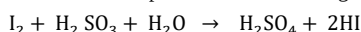
$$\text{But } c = \sqrt{\frac{3RT}{M_r}}$$

$$\text{Then K.E} = \frac{1}{2}m \left(\sqrt{\frac{3RT}{M_r}} \right)^2 = \frac{3mRT}{2M_r}; \text{ But } \frac{m}{M_r} = n;$$

$$\text{Hence K.E} = \frac{3}{2}nRT \text{ for } n \text{ moles of the gas}$$

$$(b) \text{ Number of moles of iodine in } 11.2\text{cm}^3 \text{ of its solution} = \frac{11.2}{1000} \times 0.05 = 5.6 \times 10^{-4} \text{ moles}$$

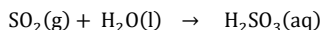
Iodine reacts with sulphurous acid according to the following equation:



From which mole ratio of I_2 to H_2SO_3 is 1:1

Thus number of H_2SO_3 in 100cm^3 of its solution is also 5.6×10^{-4} moles

H_2SO_3 is formed by mixing SO_2 and water according to the following equation



Thus number of moles of SO_2 in 100cm^3 of acid solution was also 5.6×10^{-4} moles

Hence number of moles of SO_2 per 1dm^3 (1000cm^3) of the acid solution

$$= 5.6 \times 10^{-4} \times 10 \text{ moles} = 5.6 \times 10^{-3} \text{ moles}$$

Volume of the gas (dissolved SO_2) can be found by using ideal gas equation as follows:

$$\text{From } PV = nRT; V = \frac{nRT}{p} = \frac{5.6 \times 10^{-3} \times 0.082 \times 288 \times 760 \text{dm}^3}{742} = 0.1355 \text{dm}^3 \text{ or } 135.5 \text{cm}^3$$

Hence the volume of dissolved sulphur dioxide per dm^3 of the acid was 135.5cm^3

Question 18

(a) Duma's method works with volatile substances only. Glucose being non-volatile substance cannot be vapourised by Duma's apparatus and hence the method is not suitable in determining its molar mass.

(b) Given that:

Volume of sample of air = 200dm^3

Mass of CO_2 in the air sample = 0.157g (potassium hydroxide bulb adsorbs CO_2 component only from the air components so the increase in mass of the bulb must be the mass of CO_2 in the air sample).

Temperature, $T = 14^\circ\text{C} = 287\text{K}$

$$P_{\text{air}} = 753 \text{ mmHg} = \frac{753}{760} \text{ atm}$$

From ideal gas equation: $PV = nRT$

$$\text{So } n_{\text{air}} = \frac{P_{\text{air}}V}{RT} = \frac{753 \times 200}{760 \times 0.082 \times 287} = 8.42 \text{ moles}$$

$$\text{Using } n = \frac{m}{M_r}$$

$$\text{Then } n_{\text{CO}_2} = \frac{m_{\text{CO}_2}}{M_{\text{CO}_2}} = \frac{0.157\text{g}}{44\text{gmol}^{-1}} = 3.5682 \times 10^{-3} \text{ moles}$$

$$\text{But } \frac{n_{\text{CO}_2}}{n_{\text{air}}} = \frac{V_{\text{CO}_2}}{V_{\text{air}}} \text{ (From Avogadro's law)}$$

$$\text{So percentage by volume of } \text{CO}_2 \text{ in the air} = \frac{n_{\text{CO}_2}}{n_{\text{air}}} \times 100\% = \frac{3.5682 \times 10^{-3}}{8.42} \times 100\% = 0.0424\%$$

Hence the percentage of CO_2 in the air is 0.0424% by volume.

Question 19

Mass of H_2SO_4 in 100kg of 98% $\text{H}_2\text{SO}_4 = \frac{98}{100} \times 100\text{kg} = 98\text{kg} = 98000\text{g}$

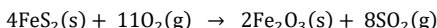
Using $n = \frac{m}{M_r}$

$$\text{Number of moles of } \text{H}_2\text{SO}_4 = \frac{98000\text{g}}{98\text{gmol}^{-1}} = 1000 \text{ moles}$$

But 1 mole of SO_2 produce 1 mole of H_2SO_4

Thus 1000moles of H_2SO_4 are produced by 1000moles of SO_2

But from;



Mole ratio of FeS_2 to SO_2 is 4:8 or 1:2

Thus number of moles of FeS_2 required to produce 1000moles of SO_2 is $\frac{1000}{2}$ moles = 500moles

Using $m = nMr$

Mass of iron pyrites, $\text{FeS}_2 = 500 \times 120\text{g} = 60000\text{g}$ or 60kg

(a) Hence 60kg of iron pyrites would be required

Form the given equation: Mole ratio of FeS_2 to O_2 is 4:11

So number of moles of O_2 required to complete combustion = $\frac{11}{4} \times 500\text{moles} = 1375$ moles

If n_{air} is the number of moles of air containing 1375 moles of O_2

Then $\frac{21}{100} n_{\text{air}} = 1375$ moles (For gases, percentage by volume is equal to the percentage by moles)

So $n_{\text{air}} = \frac{1375 \times 100}{21}$ moles = $\frac{137500}{21}$ moles

From $PV = nRT$

$$V_{\text{air}} = \frac{n_{\text{air}}RT}{P_{\text{air}}} = \frac{137500 \times 0.082 \times 288 \times 760}{21 \times 750} \text{dm}^3 = 156690 \text{dm}^3 \text{ or } 156.69 \text{m}^3$$

(a) Hence 156.69m^3 of air would be required for complete combustion of the pyrites.

Question 20

(a) Real gases fails to obey Charles's and Boyle's law at:

- Low temperature
- High pressure

(b) By Graham's law of diffusion: $\frac{V_{\text{O}_2}}{V_{\text{inert}}} = \sqrt{\frac{M_{\text{inert}}}{M_{\text{O}_2}}}$

$$\text{So } M_{\text{inert}} = M_{\text{O}_2} \left(\frac{V_{\text{O}_2}}{V_{\text{inert}}} \right)^2 = 32 \times \left(\frac{50}{141.4} \right)^2 = 4 \text{gmol}^{-1}$$

Hence the relative atomic mass of an inert gas is 4

Question 21

(a)

- Intermolecular forces of attraction between gas molecules in motion is negligible.
- The volume of individual gas molecules is negligible compared to the volume of the whole gas.

(b)

Composition by element	C	H	O
Percentage by mass of each	37.21	7.8	55
Mass of each in 100g of the compound	37.21g	7.8g	55g
Number of moles of each using $n = \frac{m}{Mr}$	$\frac{37.21\text{g}}{12\text{gmol}^{-1}} = 3.1\text{mol}$	$\frac{7.8\text{g}}{1\text{gmol}^{-1}} = 7.8\text{mol}$	$\frac{55\text{g}}{16\text{gmol}^{-1}} = 3.4375 \text{ mol}$
Divide by the smallest to get simpler ratio	$\frac{3.1 \text{ mol}}{3.1 \text{ mol}} = 1$	$\frac{7.8 \text{ mol}}{3.1 \text{ mol}} = 3$	$\frac{3.4375 \text{ mol}}{3.1 \text{ mol}} = 1$

So empirical formula of the compound is CH_3Cl if the molecular formula of the compound is $(\text{CH}_3\text{Cl})_n$

Then $12n + 3n + 35.5n = M_r$

or $50.5n = M_r$

$$\text{But } M_r = \frac{nRT}{PV} = \frac{2.4 \times 0.082 \times 298 \times 760 \times 1000}{740 \times 934} = 64$$

Then $50.5n = 64$ or $n = 1$

Hence the molecular formula of the compound is CH_3Cl

Question 22

- (a) At high temperature and low pressure.
 (b) From Van – der – Waals equation: $\left(P + a \left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$

Substituting given values: $\left(11 + a \left(\frac{2}{4}\right)^2\right)(4 - (2 \times 0.05)) = 2 \times 0.082 \times 300$

$$a = 6.46 \text{atmL}^2 \text{mol}^{-2}$$

Hence the value of 'a' for the gas is 6.46atmL²mol⁻²

Question 23

- (a)
- Temperature must be kept constant.
 - If there is no chemical reaction between gases.
- (b) By Dalton's law of partial pressure total pressure (P_T) in the vessel is given by:

$$P_T = P_{N_2} + P_u = \frac{n_{N_2}RT}{V} + \frac{n_uRT}{V}$$

$$P_T = (n_{N_2} + n_u) \frac{RT}{V}; \text{ From which } n_u = \frac{P_TV}{RT} - n_{N_2} = \frac{4.18 \times 3}{0.082 \times 300} - 0.4 = 0.1 \text{ moles}$$

$$\text{From Graham's law of diffusion: } \frac{V_{N_2}}{V_u} = \sqrt{\frac{M_u}{M_{N_2}}}$$

$$\text{But from Avogadro's law it can be shown that: } \frac{V_{N_2}}{V_u} = \frac{n_{N_2}}{n_u}$$

$$\text{Thus } \frac{n_{N_2}}{V_u} = \sqrt{\frac{M_u}{M_{N_2}}}$$

$$M_u = M_{N_2} \left(\frac{n_{N_2}}{n_u}\right)^2 = \left(\frac{0.4}{0.1}\right)^2 \times 28 \text{g/mol} = 448 \text{g/mol}$$

Hence molar mass of unknown gas is 448g/mol

Question 24

- (a)
- Boyle's law describes relationship between pressure and volume of ideal gas when temperature and amount of the gas are kept constant.
 - Charles's law describes relationship between volume and temperature of ideal gas when pressure and amount of the gas are kept constant.
 - Gay-Lussac's law describes relationship between pressure and temperature of ideal gas when volume and amount of the gas are kept constant.
 - Avogadro's law describes relationship between amount of ideal gas and its volume when pressure and temperature are kept constant.
- (b) When another flask is immersed in the hot oil bath, the pressure in the hot flask will be greater than the pressure in the cold flask. So gas (hydrogen) molecules will start to move from the hot flask to the cold flask until the pressure in the two flasks balance; i.e. until Pressure in the cold flask = Pressure in the hot flask.

Let number of molecules moved from the hot flask be y.

Then number of moles of hydrogen molecules in the hot flask = $0.35 - y$

And number of moles of hydrogen molecules in the cold flask = $0.35 + y$

So when the pressure at the two flask are at equilibrium (balance each other)

$$\frac{(0.35-y)RT_2}{V} = \frac{(0.35+y)RT_1}{V}$$

Where T_1 is the temperature of the cold flask = $27^\circ\text{C} = 300\text{K}$

T_2 is the temperature of the hot flask = $127^\circ\text{C} = 400\text{K}$

(It should be noted that: In this calculation; the expansion of volume of the flask due to rise in temperature has been neglected, that is why the volume of the two flasks, V remains the same).

Substituting the given values: $(0.35 - y) 400 = (0.35 + y) 300$

From which, $y = 0.05$ moles

Hence

- Number of hydrogen gas in the hot flask is $(0.35 - y)$ moles = $(0.35 - 0.05)$ moles = 0.3 moles.
- Number of moles of hydrogen gas in the cold flask is $(0.35 + y)$ moles = $(0.35 + 0.05)$ moles = 0.4 moles

$$\text{From } V = \frac{nRT}{P}$$

Where $n = 0.35$, $R = 0.082$, $T = 300\text{K}$ (27°C), $P = 0.5\text{atm}$

$$\text{So volume of each flask} = \frac{0.35 \times 0.082 \times 300}{0.5} \text{ dm}^3 = 17.22 \text{ dm}^3$$

Then the final pressure in each flask can be found from either cold or cold flask and will give the same result by using;

$$P = \frac{nRT}{V}$$

$$\text{So for cold flask: } P = \frac{0.4 \times 0.082 \times 300}{1.722} \text{ atm} = 5.7 \text{ atm}$$

Hence the final pressure of the system is 5.7atm in each flask

Question 25

(a) (i) It is completely **elastic**.

(ii) Pressure

(iii) Under presence of intermolecular forces, the collision will not be elastic. This is because, the intermolecular forces lower speed as well as kinetic energy making the collision inelastic as some kinetic energy are transformed into intermolecular energy. Also the intermolecular forces, lowers the observed pressure. This is because as result of decrease in speed, both collision frequency and collision force (intensity) are decreased resulting to decrease in pressure of the gas.

(b)

Composition by element	C	H	N
Percentage by mass of each	75.92	6.37	17.71
Mass of each in 100g of the compound	75.92g	6.37g	17.71g
Number of moles of each using, $n = \frac{m}{M_r}$	$\frac{75.92\text{g}}{12\text{gmol}^{-1}} = 6.33\text{mol}$	$\frac{6.37\text{g}}{1\text{gmol}^{-1}} = 6.37\text{mol}$	$\frac{17.71\text{g}}{14\text{gmol}^{-1}} = 1.265\text{mol}$
Divide by smallest to get simpler ratio	$\frac{6.33\text{mol}}{1.265\text{mol}} = 5$	$\frac{6.37\text{mol}}{1.265\text{mol}} = 5$	$\frac{1.265\text{mol}}{1.265\text{mol}} = 1$

The empirical formula of the compound is $\text{C}_5\text{H}_5\text{N}$

$$\text{From } M_r = \frac{mRT}{PV}$$

$$\text{But } \frac{m}{V} = \text{density, } \rho$$

$$\text{Then } M_r = \frac{\rho RT}{P} = \frac{2.12 \times 0.082 \times 383 \times 760}{630} = 80 \text{ g/mol}$$

Let molecular formula of the compound be $(\text{C}_5\text{H}_5\text{N})_n$

$$\text{Then } 60n + 5n + 14n = 80 \text{ or } 79n = 80 \text{ or } n = 1$$

Hence the molecular formula of the compound is $\text{C}_5\text{H}_5\text{N}$

Question 26

(a)

(i) This describes relationship between pressure and temperature of an ideal gas when volume and amount of the gas are kept constant. The law states that: Pressure of given mass of a gas varies directly proportional to its absolute temperature provided that the volume of the gas is constant.

Mathematical equation:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

(ii) This describes the relationship between volume, pressure and temperature of an ideal gas when amount of the gas is kept constant. The law states that: Volume of fixed mass of a gas varies directly proportional to absolute temperature and inversely proportional to its pressure.

Mathematical equation:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

(b)

Composition by element	C	H
Percentage by mass of each	46.1	53.9
Mass of each in 100g of the compound	46.1g	53.9g
Number of moles of each, $n = \frac{m}{M_r}$	$\frac{46.1\text{g}}{12\text{gmol}^{-1}} = 3.84\text{mol}$	$\frac{53.9\text{g}}{1\text{gmol}^{-1}} = 53.9\text{mol}$
Divide by smallest to get simpler ratio	$\frac{3.84}{3.84} = 1$	$\frac{53.9}{3.84} = 14$

So the empirical formula of the compound is CH_{14}

By Graham's law of diffusion: $\frac{t_X}{t_{\text{O}_2}} = \sqrt{\frac{M_X}{M_{\text{O}_2}}}$

$$M_X = M_{\text{O}_2} \left(\frac{t_X}{t_{\text{O}_2}} \right)^2 = 32 \left(\frac{20}{15.7} \right)^2 = 52 \text{ g/mol}$$

If the molecular formula of the compound is $(\text{CH}_{14})_n$

$$\text{Then } 12n + 14n = M_r = 52$$

$$26n = 52 \text{ or } n = 2$$

Hence molecular formula of the compound is C_2H_{28}

$$\frac{V_{\text{CO}_2}}{V_X} = \sqrt{\frac{M_X}{M_{\text{CO}_2}}} \text{ or } V_{\text{CO}_2} = V_X \sqrt{\frac{M_X}{M_{\text{CO}_2}}}$$

$$V_{\text{CO}_2} = 50 \sqrt{\frac{52}{44}} = 54.4 \text{ cm}^3$$

Hence 54.4 cm^3 of CO_2 would diffuse in 20 seconds

Question 27

$$\text{Using } n = \frac{PV}{RT}$$

Before opening the cock:

$$\text{Number of moles of } \text{SO}_2 = \frac{0.75 \times 2.125}{0.082 \times 353} \text{ moles} = 0.055 \text{ moles}$$

$$\text{Number of moles of } \text{O}_2 = \frac{0.5 \times 1.5}{0.082 \times 353} \text{ moles} = 0.02591 \text{ moles}$$

After opening the cock:

The two gases mix together then:

- Total number of moles of gaseous mixture, $n_T = (0.055 + 0.02591) \text{ moles} = 0.08091 \text{ moles}$
- Total volume of the gaseous mixture = total volume of the two chambers = $(2.125 + 1.5) \text{ L} = 3.625 \text{ L}$

$$X_{\text{SO}_2} = \frac{n_{\text{SO}_2}}{n_T} = \frac{0.055}{0.08091} = 0.68$$

Thus mole fraction of SO_2 was 0.68

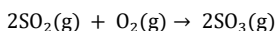
$$P_T = \frac{n_T RT}{V} = \frac{0.08091 \times 0.082 \times 353}{3.625} = 0.646 \text{ atm}$$

The total pressure is 0.646 atm

$$\text{Partial pressure of } \text{SO}_2, P_{\text{SO}_2} = X_{\text{SO}_2} P_T = 0.68 \times 0.646 \text{ atm} = 0.43928 \text{ atm}$$

If the mixture is allowed to react after passing through catalyst:

SO_2 reacts with O_2 according to the following equation (Assuming reaction reach to completion i.e. it is irreversible):



From which mole ratio of SO_2 to O_2 is 2:1

Thus 0.02591 moles of O_2 reacts with $0.02591 \times 2 = 0.05182$ moles of SO_2

So SO_2 present in excess and $(0.055 - 0.05182) \text{ moles} = 0.00318 \text{ moles}$ of it remain unreacted at the end of the reaction

Also from the above reaction equation; mole ratio of O_2 (**limited reactant**) to SO_3 is 1:2

Thus number of moles of SO_3 produced was $0.02591 \times 2 = 0.05182 \text{ moles}$

So at the end of the reaction there are 0.00318 moles and 0.05182 moles of SO_2 and SO_3 respectively.

Therefore; the total number of moles of the final gaseous mixture = $(0.05182 + 0.00318) \text{ moles} = 0.055 \text{ moles}$

$$\text{Then } X_{\text{SO}_3} = \frac{n_{\text{SO}_3}}{n_T} = \frac{0.05182}{0.055} = 0.9422$$

Thus mole fraction of SO_3 in the final mixture was 0.9422

$$P_T = \frac{n_T RT}{V} = \frac{0.055 \times 0.082 \times 353}{3.625} \text{ atm} = 0.4392 \text{ atm}$$

The total pressure in the final mixture is 0.4392 atm

Question 28

(a) The four (main) postulates are:

1. The gas particles are so small compared with the distances between them that the volume of the individual particles can be neglected.
2. The gas particles are in constant motion of which they collide the walls of the container, therefore exerting pressure.
3. There is no intermolecular forces (neither attraction nor repulsion) between gas particles.
4. The average kinetic energy of a collection of gas particles is directly proportional to the absolute temperature of the gas.

(b) By Graham's law of diffusion: $\frac{V_{\text{NH}_3}}{V_{\text{HCl}}} = \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}}$

(Time taken for diffusion of each solution is constant because the two ends of the tube were immersed in the solutions at the same time)

But volume of solution diffused varies directly proportional to the distance travelled by the solution.

It follows that: $\frac{l_{\text{NH}_3}}{l_{\text{HCl}}} = \sqrt{\frac{36.5}{17}} = 1.465$

$$l_{\text{NH}_3} : l_{\text{HCl}} = 1.465 : 1$$

If total length of the tube is l , then the distance traveled by NH_3 before forming a white cloud of

$$\text{NH}_4\text{Cl} = \left(\frac{1.465}{1 + 1.465} \right) l = \frac{293}{493} l$$

Hence a white cloud of NH_4Cl (s) forms at $\frac{293}{493}$ of the total length of the tube from the ammonia.

Question 29

(a)

(i) "Volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature."

(ii) "The volume of the gas varies directly proportional to its number of molecules or moles at constant temperature and pressure."

(iii) "The total pressure exerted in the container of the mixture of two or more gases is equal to the summation of their partial pressures provided that the gases do not react."

(Have you noticed the difference between 'say about' (question 26) and 'say' (in this question) in the approach of answering questions?)

(b) From $PV = \frac{m}{M_r} RT$ then $P = \left(\frac{m}{V} \right) \frac{RT}{M_r}$ but $\frac{m}{V} = \rho$

$$P = \frac{\rho RT}{M_r} \text{ or } \rho = \frac{PM_r}{RT}$$

If P_B and P_T are density of air at the bottom and the top of the mountain respectively

$$\text{Then } \rho_T = \frac{P_T M_r}{RT_T} \text{ and } \rho_B = \frac{P_B M_r}{RT_B} \text{ So } \frac{\rho_T}{\rho_B} = \frac{P_T T_B}{P_B T_T} = \frac{710 \times 303}{760 \times 273} = 1.0369$$

$$\text{Hence } \rho_T = 1.0369 \rho_B$$

Where ρ_T is the density of air at the top of the mountain and ρ_B is the density of air at the bottom of the mountain

Question 30

(a) Volume of all gases varies directly proportional to their number of moles and absolute temperature and inversely proportional to their pressure.

$$(b) P_{N_2} = \frac{n_{N_2} RT}{V} = \frac{m_{N_2} RT}{M_{N_2} V}$$

Where $m_{N_2} = 5.65\text{g}$, $R = 0.082$, $T = 300\text{K}$

$M_{N_2} = 28\text{g/mol}$, $V = (15\text{L} + 6\text{L}) = 21\text{L}$

$$P_{N_2} = \frac{5.65 \times 0.082 \times 300}{28 \times 21} = 0.2364 \text{ atm}$$

Partial pressure of nitrogen gas is 0.2364atm

$$P_{O_2} = \frac{n_{O_2} RT}{V} = \frac{m_{O_2} RT}{M_{O_2} V}$$

Where $m_{O_2} = 5\text{g}$ and $M_{O_2} = 32\text{g/mol}$

$$P_{O_2} = \frac{5 \times 0.082 \times 300}{32 \times 21} = 0.183 \text{ atm}$$

Partial pressure of oxygen gas 0.183atm

By Dalton's law of partial pressure: $P_T = P_{O_2} + P_{N_2} = (0.2364 + 0.183)\text{atm} = 0.4194 \text{ atm}$

The total pressure is 0.4194atm

Question 31

(a) The law is Dalton's law of partial pressure.

It states that: The total pressure exerted in the container of the mixture of two or more gases is equal to the summation of their partial pressure provided that the gases do not react.

(b) By Graham's law of diffusion: $\frac{\text{Rate of diffusion of oxygen gas}}{\text{Rate of diffusion of unknown gas}} = \sqrt{\frac{M_U}{M_{O_2}}}$

But rate of diffusion varies directly proportional to the rate of pressure change then $\frac{\frac{\Delta P_{O_2}}{t_{O_2}}}{\frac{\Delta P_U}{t_U}} = \sqrt{\frac{M_U}{M_{O_2}}}$

$$\frac{\Delta P_{O_2} t_U}{\Delta P_U t_{O_2}} = \sqrt{\frac{M_U}{M_{O_2}}} \quad \text{or} \quad \frac{(2000 \times 1500)85}{(2000 \times 1500)55} = \sqrt{\frac{M_U}{32}} \quad \text{or} \quad M_U = 76 \text{ g/mol}$$

Hence molar mass of unknown gas is 76g/mol

Question 32

(a) From the kinetic equation of gases; $PV = \frac{Nmc^2}{3}$

But $K.E = \frac{1}{2} mc^2$ (for one molecule of the gas)

Or $mc^2 = 2K.E$; Then $PV = \frac{2}{3} N \times K.E$

But from one of the assumptions of kinetic theory of gases: $K.E \propto T$

Then $K.E = kT$ where k is constant for proportionality and $PV = \frac{2}{3} NkT$

But $\frac{N}{N_A} = n$ or $N = nN_A$ where n is the number of moles of the gas

Substituting $N = nN_A$ to $PV = \frac{2}{3} NkT$ gives $PV = \frac{2}{3} nN_A kT$

Since N_A is constant, $\frac{2}{3} N_A k$ gives another constant, R

Hence **$PV = nRT$** this is ideal gas equation

(b) $K.E = \frac{3}{2} RT$ for one mole of a gas

$$K.E = \frac{3}{2} \times 8.314 \times 300 = 3741.3 \text{ J}$$

Hence kinetic energy for one mole of the gas is 3.7413kJ

Question 33

$$n_{He} = \frac{P_{He} V}{RT} = \frac{187.1 \times 0.25}{0.082 \times 300 \times 760} = 2.5 \times 10^{-3} \text{ moles}$$

(i) There were 2.5×10^{-3} moles of Helium in the original vessel.

$$n_{CO_2} = \frac{P_{CO_2} V}{RT} = \frac{561.3 \times 0.25}{0.082 \times 300 \times 760} = 7.5 \times 10^{-3} \text{ moles}$$

(ii) Thus 7.5×10^{-3} moles of carbon dioxide gas was produced

(iii) If n_{ea} and n_{ee} represent number of moles of ethane and ethene respectively (which are originally present in the vessel)

Then from given equation for combustion:

Number of moles of CO_2 produced by combustion of ethane = $2n_{ea}$

And number of moles of CO_2 produced by combustion of ethene = $2n_{ee}$

It follows that: $2n_{ea} + 2n_{ee} = 7.5 \times 10^{-3}$ moles

From which: $n_{ea} + n_{ee} = 3.75 \times 10^{-3}$ moles

So total number of moles of gases present in the original vessel is:

$$n_{ea} + n_{ee} + n_{He} = (3.75 + 2.5) \times 10^{-3} \text{ moles} = 6.25 \times 10^{-3} \text{ moles}$$

But total pressure present in the original vessel, $P_T = 680 \text{ mmHg}$

$$\text{And } P_{He} = P_{He} = \left(\frac{n_{He}}{n_T} \right) \times P_T = \frac{2.5 \times 10^{-3}}{6.25 \times 10^{-3}} \times 680 \text{ mmHg} = 272 \text{ mmHg}$$

Hence the partial pressure of Helium in the original vessel was 272mmHg

(iv) Using $V = \frac{nRT}{P}$

Substituting the value of partial pressure of Helium obtained in (iii) above;

$$V = \frac{2.5 \times 10^{-3} \times 0.082 \times 300 \times 760}{272} = 0.11718 \text{ dm}^3 \text{ or } 171.8 \text{ cm}^3$$

Hence the volume of the original vessel was 0.11718 dm^3 or 171.8 cm^3

Question 34

- (a) **a** is the coefficient of attraction reflecting the strength of intermolecular force of attraction between gas particles (molecules).
b is the effective volume reflecting the molecular size of the gas.
- (b) From Van der Waals equation for real gases: $\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$

$$\text{Substituting given values } \left(P + 1.34\left(\frac{0.02}{1.6}\right)^2\right)(1.6 - (0.02 \times 0.32)) = 0.02 \times 0.082 \times 293$$

$$P = 0.3 \text{ atm}$$

Hence the pressure of real gas is 0.3 atm

Question 35

$$\text{Using } M_r = \frac{mRT}{PV}$$

At 110°C (383K)

$$M_r = \frac{0.11 \times 0.082 \times 383 \times 760 \times 1000}{454 \times 63.7} = 91 \text{ g/mol}$$

Molar mass of ethanoic acid at 100°C is 91 g/mol

At 156°C (429K)

$$M_r = \frac{0.081 \times 0.082 \times 429 \times 760 \times 1000}{458 \times 66.4} = 71 \text{ g/mol}$$

Molar mass of ethanoic acid at 110°C is 71 g/mol

Interpretation of the results:

Measured molar mass of CH_3COOH is greater than its expected molar mass of 60 g/mol , because molecules of the acid are capable of undergoing association as result of strong hydrogen bonding formed between its molecules. Degree of association of the acid decrease with an increase in temperature as the high temperature weakens the strength of hydrogen bonding and hence molar mass of CH_3COOH at 156°C become smaller than that measured at 110°C .

Question 36

- (a) HCl and NH_3

Explanation

HCl and NH_3 being polar, they are highly soluble in water; so they will dissolve in it to make a solution and hence they would not come out the other end.

$$(b) \text{ By Dalton's law of partial pressure: } P_T = (n_{\text{O}_2} + n_{\text{H}_2}) \frac{RT}{V} = \left(\frac{m_{\text{O}_2}}{M_{\text{O}_2}} + \frac{m_{\text{H}_2}}{M_{\text{H}_2}}\right) \frac{RT}{V}$$

$$P_T = \left(\frac{86.2}{32} + \frac{1.5}{2}\right) \frac{0.082 \times 361}{3.2 \times 10^3} \text{ atm} = 0.032 \text{ atm}$$

Hence the total pressure in the vessel is 0.032 atm

Question 37

- (a) It is describing the relationship between the total pressure of a mixture of non-reacting ideal gases and the partial pressures of each individual component.

$$(b) \frac{t_J}{t_A} = \sqrt{\frac{M_J}{M_A}} \text{ or } M_J = M_A \left(\frac{t_J}{t_A}\right)^2 = 120 \times \left(\frac{300}{580.8}\right)^2 \text{ g/mol} = 32 \text{ g/mol}$$

Hence relative molecular mass of J is 32 g/mol

Question 38

- (a)

- (i) From its definition, compressibility factor (Z) is given by:

$$Z = \frac{\text{Real volume}}{\text{Ideal volume}}$$

If V represents real volume, the formula becomes: $Z = \frac{V}{\text{Ideal volume}}$

But ideal volume can be calculated from ideal gas equation with measured (actual) P , T and n

$$\text{That is } V = \frac{nRT}{P} \quad (\text{From } PV = nRT)$$

Where V is the ideal volume.

Then the formula $Z = \frac{V}{\text{ideal volume}}$ becomes $Z = \frac{V}{\frac{nRT}{P}} = \frac{PV}{nRT}$

Thus the compressibility factor, $Z = \frac{PV}{nRT}$

Where:

P is the measured (real) pressure

V is the measured (real) volume

n is the measured number of moles

(ii) For ideal behaviour, $Z = 1$

For the positive deviation, $Z > 1$

For the negative deviation, $Z < 1$

(b) From $PV = \frac{m}{M_r}RT$ or $m = \frac{PVM_r}{RT} = \frac{0.12 \times 3 \times 207}{0.082 \times 353} = 2.57\text{g}$

Hence mass of the vapour is 2.57g

Question 39

(a)

(i) Is the gas which obeys ideal gas equation ($PV=nRT$) in all conditions of temperature and pressure.

(ii) Ideal gas equation can be derived by combining Boyle's law, Charles's law and Avogadro's law as shown below:

From Boyle's law: $V \propto \frac{1}{P}$; constants: n and T

From Charles's law: $V \propto T$; constants: n and P

Avogadro's law: $V \propto n$; constants: P and T

Combining the three laws: $V \propto \frac{nT}{P}$ or $V = \frac{nRT}{P}$

Where R is the proportionality constant; and the constant is known as universal molar gas constant

Hence $PV = nRT$ and the result is known as ideal gas equation.

(b) At = s.t.p. $T = 273\text{K}$, $P = 101300\text{Pa}$

So taking: $T_1 = 18^\circ\text{C} = 291\text{K}$, $V_1 = 267\text{cm}^3$, $P_1 = 100400\text{Pa}$, $T_2 = 273\text{K}$,

$P_2 = 101300\text{Pa}$, $V_2 = ?$

From general gas equation: $\frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1}$

$$V_2 = \left(\frac{T_2}{T_1}\right)\left(\frac{P_1}{P_2}\right)V_1 = \frac{273 \times 100400 \times 267}{291 \times 101300} \text{cm}^3 = 248\text{cm}^3$$

Thus volume of the gas at s.t.p = 248cm^3

Normal density, $\rho = \frac{m}{V} = \frac{0.162}{248} = 6.532 \times 10^{-4}\text{g/cm}^3$

(i) Normal density of the gas is $6.532 \times 10^{-4}\text{g/cm}^3$ or 0.6532g/dm^3

Using $M_r = \frac{nRT}{PV} = \frac{\rho RT}{P} = \frac{0.6532 \times 0.082 \times 273 \times 101300}{101300} = 14.6\text{g/mol}$

Relative density of the gas = $\frac{M_r}{2\text{g/mol}} = \frac{14.6}{2} = 7.3$

(ii) Relative density of the gas is 7.3

Question 40

(a)

(i) Separation of gases having different densities by diffusion.

Others:

1. In determination of densities and molar masses of unknown gases by comparing the rates of diffusion with known gases.
2. In separation of isotopes of some of the elements.
- (ii) During the preparation of gases by downward displacement of water.
- (iii) In determination of molecular formula of gases.

Others:

1. In determination of atomicity of gases.
2. In establishing the relationship between relative molecular mass and vapour density.

From Graham's law of diffusion: $\frac{t_{O_2}}{t_{O_2}} = \sqrt{\frac{M_u}{M_{O_2}}}$ or $M_u = \frac{32\text{g}}{\text{mol}} \times \left(\frac{177}{250}\right)^2 = 16\text{g/mol}$

The relative molecular mass of unknown gas is 16

Question 41

- (a) Only two postulates are free from error which are:
1. A gas consists of very small particles (molecules) in a random motion of which there is a collision between gas particles themselves and the collision between gas particles and the walls of the container, thus exerting a pressure.
 2. Kinetic energy of gas particles varies directly proportional to the absolute temperature.
- (b) Number of moles of H_2 reacted after t seconds = $(1 - 0.8)\text{moles} = 0.2\text{moles}$

H_2 and I_2 React according to the following equation: $H_2 + I_2 \rightarrow 2HI$

From which mole ratio of H_2 to HI is 1:2

Hence number of moles of HI formed after t seconds was $2 \times 0.2\text{moles} = 0.4\text{moles}$

Question 42

- (a) The four factors are:
1. **Density (or molar mass) of the gas:** High density (or molar mass) means small rate of diffusion.
 2. **Pressure:** High pressure of the gas means small rate of diffusion.
 3. **Temperature:** High temperature of the gas means high rate of diffusion.
 4. **Concentration difference (concentration gradient):** Large concentration difference from one point to another, means high rate of diffusion

- (b) From Graham's law of diffusion: $\frac{R_{H_2}}{R_{Ne}} = \sqrt{\frac{M_{Ne}}{M_{H_2}}} = \sqrt{\frac{20.18}{2.02}} = 3.16$

If t_{H_2} represents the time for $\frac{2}{3}$ of H_2 to diffuse and t_{Ne} represents the time for $\frac{2}{3}$ of Ne (the same amount as that of H_2) to diffuse: and because rate of diffusion varies inversely proportional to the time taken for the diffusion to take place, it follows that: $\frac{R_{H_2}}{R_{Ne}} = \frac{t_{Ne}}{t_{H_2}} = 3.16$

Substituting $\frac{t_{Ne}}{6\text{hr}} = 3.16$: $t_{Ne} = 3.16 \times 6\text{hr} = 18.96\text{ hr}$

Thus 18.96 hours is required for $\frac{2}{3}$ of Ne to diffuse

Then (by cross-multiplication) $\frac{1/2 \times 18.96}{2/3}$ hours or 14.22 hours is required for $\frac{1}{2}$ of Ne to diffuse

Hence the time taken for half the neon to diffuse is 14.22 hours.

Question 43

(a)(i) Dissociation and association

(ii) **Dissociation** makes the observed relative density of the compound to be lower than the expected from its molecular formula.

Examples:

- 1) Dissociation of $N_2O_4(g)$ into $NO_2(g)$.
- 2) Dissociation of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$.

Association makes the measured (observed) relative density of the compound to be greater than the expected from its molecular formula

Examples:

- 1) Association of two molecules of $AlCl_3$ to form a dimer which corresponds to the molecular formula of Al_2Cl_6 .
- 2) Association of two molecules of ethanoic acid to form a dimer which corresponds to the molecular formula of $C_4H_8O_4$.

- (b) Substituting $n = \frac{m}{M_r}$ in $PV = nRT$ gives $PV = \frac{mRT}{M_r}$

From which $M_r = \frac{mRT}{PV}$

If M_m is the average molar mass of the mixture and m_m is the mass of the mixture.

It follows that: $M_m = \frac{m_m RT}{PV}$

But $\frac{m_m}{V} = \rho_m$ where ρ_m is the density of the mixture

Then $M_m = \frac{\rho_m RT}{P} = \frac{3.45 \times 0.082 \times 298}{1.6} \text{ g/mol} = 52.69 \text{ g/mol}$

If:

X_u is the mole fraction of unknown gas

M_u is the molecular mass of unknown gas

X_k is the mole fraction of known gas and

M_k is the molecular mass of known gas.

It follows that: $M_m = X_u M_u + X_k M_k$

Where $X_u = 0.35$: $X_k = 1 - X_u = 1 - 0.35 = 0.65$ and $M_k = 64 \text{ g/mol}$

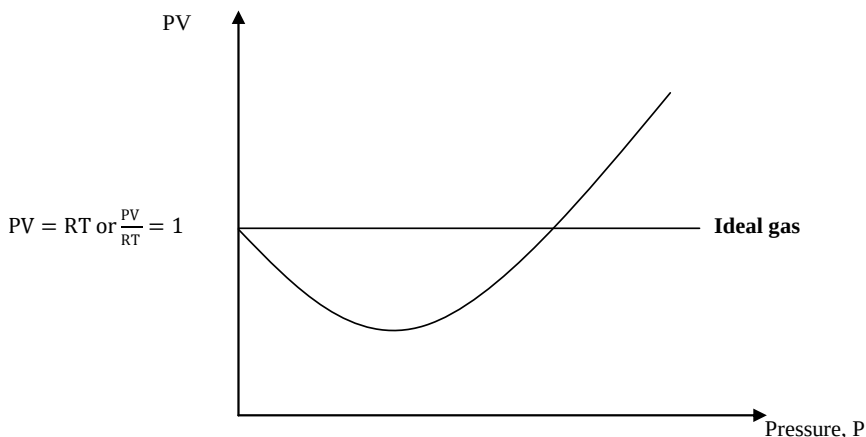
Substituting $52.69 = 0.35M_u + 0.65 \times 64$

From which $M_u = 31.69\text{g/mol}$

Hence molecular mass of the other component is 31.69g/mol

Question 44

(a) Amagat's curve to show deviation of CO_2 from ideal has behaviour is shown below:



(b) From $\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$

If: $P_1 = P_2 = P$ and $V_2 = V$ (P and V are constant)

$$\frac{PV}{n_1 T_1} = \frac{PV}{n_2 T_2} \quad \text{or} \quad n_1 T_1 = n_2 T_2$$

Substituting $n_1 \times 300 = n_2 \times 360$

$$\frac{n_1}{n_2} = \frac{360}{300} = 6/5$$

Thus $n_1 : n_2 = 6 : 5$ where n_1 is the number of moles of air before heating and n_2 is the number of moles of air after heating.

Then number of moles of air decreased (expelled) = $(6 - 5)\text{mol} = 1\text{mol}$

And percentage of air expelled = $\frac{\text{number of moles expelled}}{\text{original number of moles before heating}} \times 100\% = \frac{1}{6} \times 100\% = 16.67\%$

Hence the percentage of air expelled is 16.67%

Question 45

(a) An increase in temperature will increase the pressure inside the aerosol can in accordance with Gay-Lussac's law. So when the pressure inside the can goes beyond the pressure limit, will result into an explosion.

(b) Final volume, $V_{\text{final}} = V + 2V + V = 4V = V_2$

Since temperature is kept constant, Boyle's law is applicable

$$\text{That is } P_1 V_1 = P_2 V_2 \quad \text{or} \quad P_2 = \frac{P_1 V_1}{V_2}$$

For container 1: $P_1 = P$, $V_1 = V$

$$\text{Then } P_2 = \frac{P \times V}{4V} = \frac{1}{4} P \text{ atm}$$

For container 2: $P_1 = 2 P \text{ atm}$, $V_1 = 2V$

$$\text{Then } P_2 = \frac{2P \times 2V}{4V} = 1 P \text{ atm}$$

For container 3: $P_1 = 3 P \text{ atm}$, $V_1 = V$

$$\text{Then } P_2 = \frac{3P \times V}{4V} = \frac{3}{4} P \text{ atm}$$

By Dalton's law of partial pressure: $P_{\text{final}} = \left(\frac{P}{4} + P + \frac{3P}{4}\right) \text{ atm} = 2P \text{ atm}$

Hence the total final pressure is $2P \text{ atm}$

Question 46

(a) Boyle's law is applicable when amount of air is constant. When we fill air in the tyre, the amount of air is progressively increased in the tyre and therefore Boyle's law is inapplicable. At initial stages of filling air in the tyre, volume of the tyre increases and pressure remains almost constant in accordance with Avogadro's law and thereafter, volume of the tyre remains almost constant; but since amount of the gas in the tyre is still increasing, collision frequency between air molecules and the tyre's walls will increase making the pressure to increase too ($P \propto n$ at constant V and T). Eventually, both volume and pressure appear to increase.

(b) By Dalton's law of partial pressure: $P_T = P_{H_2O} + P_{CO}$

From which $P_{CO} = P_T - P_{H_2O} = (752 - 19.8)\text{mmHg} = 732.2\text{mmHg}$

From ideal gas equation $PV = nRT$, $n = \frac{PV}{RT}$

Thus $n_{CO} = \frac{732.2 \times 0.242}{760 \times 0.082 \times 295} \text{mol} = 0.00964\text{mol}$

But from the equation for the reaction, mole ratio of CO to $HCOONa$ is 1:1

Thus $n_{CO} = n_{HCOONa} = 0.00964\text{mol}$

Using $m = nM$; $M_{HCOONa} = 0.00964\text{mol} \times 68\text{g/mol} = 0.65552\text{g}$

Then $\%HCOONa = \frac{M_{HCOONa}}{M_T} \times 100\% = \frac{0.65552}{0.964} \times 100\% = 68\%$

Question 47

(a) Equation for the reaction: $2H_2 + O_2 \rightarrow H_2O$

From which mole ratio of H_2 to O_2 is 2:1; that is for each one mole of O_2 two moles of H_2 is required?

But it is given that $n_{H_2} = n_{O_2}$ and whence O_2 present in excess.

Thus the reactant remaining is **oxygen gas**

Calculation of the amount remaining:

By Dalton's law of partial pressure; total pressure exerted by gases before the sparking (reaction) is given by:

$$P_T = P_{O_2} + P_{H_2} + P_{H_2O}$$

Substituting $1146 = P_{O_2} + P_{H_2} + 24$ From which $P_{O_2} + P_{H_2} = 1122\text{mmHg}$

Because $n_{O_2} = n_{H_2}$; $P_{O_2} = P_{H_2}$

Thus $P_{O_2} + P_{O_2} = 2P_{O_2} = 1122\text{mmHg}$ or $P_{O_2} = 561\text{mmHg}$

But from the equation of the reaction: number of moles of O_2 reacted = $\frac{1}{2}n_{H_2}$

Thus number of moles of O_2 remained = $n_{O_2} - \frac{1}{2}n_{H_2}$

But $n_{O_2} = n_{H_2}$

Then number of moles of O_2 remained = $n_{O_2} - \frac{1}{2}n_{O_2} = \frac{1}{2}n_{O_2}$

And because pressure varies directly proportional to the number of moles, pressure exerted by the remained oxygen gas

$$= \frac{P_{O_2}}{2} = \frac{561\text{mmHg}}{2} = 280.5\text{mmHg}$$

Using $n = \frac{PV}{RT}$

Number of moles of O_2 gas remained = $\frac{280.5 \times 0.5}{760 \times 0.082 \times 298} \text{mol} = 0.00755\text{mol}$

Hence the number of reactant remaining is 0.00755mol of O_2

(b) From pressure law: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ From which $P_2 = \left(\frac{T_2}{T_1}\right)P_1$

Partial of O_2 at $90^\circ\text{C} = \frac{363}{298} \times 280.5$ or 341.68mmHg

And by Dalton's law of partial pressure:

$P_T = P_{H_2O} + P_{O_2} = (526 + 341.68)\text{mmHg} = 867.68\text{mmHg}$

Hence the total pressure at 90°C is 867.68mmHg

(c) $n_{H_2O} = \frac{P_{H_2O}V}{RT} = \frac{526 \times 0.5}{760 \times 0.082 \times 363} \text{mol} = 0.0116\text{mol}$

Hence number of moles of H_2O at 90°C is 0.0116mol

Question 48

(a) From Dalton's law of partial pressure: $P_T = P_{H_2} + P_{H_2O}$

From which $P_{H_2} = P_T - P_{H_2O} = (745 - 23.8)\text{mmHg} = 721.2\text{mmHg}$

Then $n_{H_2} = \frac{P_{H_2}V}{RT} = \frac{721 \times 0.09}{760 \times 0.082 \times 298} \text{mol} = 0.00349\text{mol}$

Hence number of moles of hydrogen gas collected is 0.00349mol

$$(b) \text{ Using } n_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}V}{RT} = \frac{23.8 \times 0.09}{760 \times 0.082 \times 298} \text{ mol} = 0.00012 \text{ mol}$$

Then number of molecules, $N = nN_A = 0.00012 \times 6.02 \times 10^{23} \text{ molecule} = 7.2 \times 10^{19} \text{ Molecule}$

Hence the number of molecules of water is $7.2 \times 10^{19} \text{ Molecule}$

$$(c) \text{ Using: } C = \sqrt{\frac{3RT}{M_r}}$$

$$C_{\text{H}_2} = \sqrt{\frac{3RT}{M_{\text{H}_2}}}; \quad C_{\text{H}_2\text{O}} = \sqrt{\frac{3RT}{M_{\text{H}_2\text{O}}}}$$

$$\text{Then } \frac{C_{\text{H}_2}}{C_{\text{H}_2\text{O}}} = \sqrt{\frac{M_{\text{H}_2\text{O}}}{M_{\text{H}_2}}} = \sqrt{\frac{18}{2}} = 3$$

Thus the ratio of speed of H_2 to H_2O vapour is 3

(d) H_2O deviate more from ideal behaviour

Explanation

H_2O molecules exhibit stronger intermolecular forces of attraction due to its greater molecular weight and therefore stronger Van der Waals dispersion forces. It also has hydrogen bonds which are very strong intermolecular forces of attraction. H_2O molecule has greater volume because it has greater size. Thus H_2O molecule occupies greater space and its volume cannot be neglected compared to the whole volume of the water vapour (gas).

Question 49

- CO_2 : according to Avogadro's law, they all contain the same number of particles, therefore, the heaviest molecule, CO_2 with molar mass of 44g/mol will have the greatest mass.
- All the same according to kinetic theory of gases: at the same temperature all gases have the same kinetic energy.
- CO_2 : Since it (CO_2) has greater molecular weight, it has strongest Van der Waals dispersion forces and therefore strongest intermolecular forces of attraction. Furthermore, having greatest molecular weight and therefore largest molecular size its molecules occupy greater space (volume).
- He: it has the smallest molar mass and therefore greatest rate of effusion

Question 50

(a)

- Airbags
- Refrigerator
- Air conditioner
- Airplanes

$$(b) \text{ Actual molar volume of sodium atoms} = \frac{68.52}{100} \times 23.68 \text{ cm}^3 = 16.2255 \text{ cm}^3/\text{mol}$$

$$\text{Volume of one sodium atom} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times 3.14 \times (1.86 \times 10^{-8} \text{ cm})^3 = 2.6941 \times 10^{-23} \text{ cm}^3/\text{atom}$$

Then actual molar volume = Volume of one atom $\times$ Avogadro's constant, N_A

From which;

$$N_A = \frac{\text{Actual molar volume}}{\text{Volume of one atom}} = \frac{16.2255 \text{ cm}^3/\text{mol}}{2.6941 \times 10^{-23} \text{ cm}^3/\text{atom}} = 6.02 \times 10^{23} \text{ atom/mol}$$

Hence the Avogadro's constant is 6.02×10^{23} .

Question 51

- At constant pressure, decrease in temperature (**cold** surface) leads to decrease in volume in accordance to Charles's law and hence the ball shrinks.
- Using Gay-Lussac's law to calculate the expected pressure of CO_2 at 1401K.

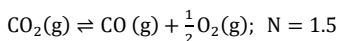
$$\text{That is } \frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{or} \quad P_2 = \left(\frac{T_2}{T_1}\right) P_1$$

Where $P_1 = 10 \text{ atm}$, $T_1 = 701 \text{ K}$, $T_2 = 1401 \text{ K}$

$$\text{Then } P_2 = \frac{1401 \times 10}{701} \text{ atm} = 19.9857 \text{ atm}$$

$$\text{Using } i = \frac{\text{Observed pressure}}{\text{Expected pressure}} = \frac{22.5 \text{ atm}}{19.9857 \text{ atm}} = 1.1258$$

CO_2 decompose according to the following equation:



$$\text{Then using } \alpha = \frac{i-1}{N-1} = \frac{1.1258-1}{1.5-1} = 0.2516 \text{ or } 25.16\%$$

Hence the percent of CO_2 that decomposes was 25.16%.

Question 52

(i) From ideal gas equation; $PV = nRT$; where $n = \frac{m}{M_r}$

$$PV = \frac{m}{M_r} RT; \text{ From which } m = \frac{PVM_r}{RT}$$

$$m = \frac{207000 \text{ Nm}^{-2} \times 8.98 \times 10^{-3} \text{ m}^3 \times 28 \text{ gmol}^{-1}}{8.31 \text{ Nm mol}^{-1} \text{ K}^{-1} \times 293 \text{ K}} \quad (1 \text{ Pa} = 1 \text{ Nm}^{-2}, 1 \text{ J} = 1 \text{ Nm and } 1 \text{ dm}^3 = 10^{-3} \text{ m}^3)$$

$$= 21.4 \text{ g}$$

Mass of nitrogen gas is 21.4g

(ii) From ideal gas equation; $PV = nRT$; $P = \frac{nRT}{V}$; $P \propto T$ (When V and n are constant)

Thus the increase in temperature will result in an increase in pressure of the tyres.

(iii) Nitrogen having fewer number of protons while shielding (screening) effect is the same for both; (both N and O have the same number of shells) experiences weaker effective nuclear attractive force.

Question 53

(a) A known mass of volatile substance is heated in Victor Meyer's tube. As a result, the liquid changes into vapour, the vapour, in turn, displaces an equal volume of air which is collected over water. The volume of air collected is measured at the pressure and temperature of the laboratory. This volume is converted to STP volume and using gram molar volume concept, molecular mass is calculated.

(b) From Graham's law: $\frac{R_{Ne}}{R_{He}} = \sqrt{\frac{M_{He}}{M_{Ne}}}$

$$\text{But } R_{Ne} = \frac{V_{Ne} \text{ diffused}}{t_{Ne}} = \frac{\frac{1}{2} V_{Ne}}{t_{Ne}} \quad (\text{Volume of Ne diffused is half of its original volume})$$

$$\text{And } R_{He} = \frac{V_{He} \text{ diffused}}{t_{He}} = \frac{\frac{2}{3} V_{He}}{t_{He}} \quad (\text{Volume of He shrunk to } \frac{1}{3} \text{ of original volume meaning } \frac{2}{3} \text{ of the original volume effused}).$$

$$\text{Then } \frac{\frac{\frac{1}{2} V_{Ne}}{t_{Ne}}}{\frac{\frac{2}{3} V_{He}}{t_{He}}} = \sqrt{\frac{M_{He}}{M_{Ne}}}$$

But $V_{Ne} = V_{He}$ (balloon was the same)

$$\text{Substituting: } \frac{3 \times t_{He}}{4 \times 22 \text{ hr}} = \sqrt{\frac{4}{20}}; t_{He} = 13.12 \text{ hours}$$

Hence the time is 13.12 hours.

PART TWO

Question 1

(a) No.

Explanation

For mixture to be separated into pure components by fractional distillation, vapour composition should change compared to liquid composition upon boiling. Azeotropes boil at constant temperature making the vapour composition the same as liquid composition and hence they cannot be separated by fractional distillation.

(b) Using Raoult's law; $P_{\text{soln}} = X_{\text{CP}}^L P_{\text{CP}}^0 + X_{\text{CH}}^L P_{\text{CH}}^0$ (Mixture of cyclopentane and cyclohexane is ideal solution).

$$\text{Where } X_{\text{CP}}^L = \frac{1}{1+3} = 0.25$$

$$\text{And } X_{\text{CH}}^L = 1 - X_{\text{CP}}^L = 1 - 0.25 = 0.75$$

$$\text{Substituting: } P_{\text{soln}} = 0.25 \times 331 \text{ mmHg} + 0.75 \times 113 \text{ mmHg} = 167.5 \text{ mmHg}$$

$$\text{Then } X_{\text{CP}}^V = \frac{X_{\text{CP}}^L P_{\text{CP}}^0}{P_{\text{soln}}} = \frac{0.25 \times 331 \text{ mmHg}}{167.5 \text{ mmHg}} = 0.494$$

The mole fraction of cyclopentane in the vapour above the solution is 0.494.

Question 2

(a)

(i) False

Reason:

Unlike compounds azeotropes consist of different molecules of different substances. Furthermore, components of azeotropic mixture can be separated by physical methods like azeotropic distillation. Also components of azeotropic mixture react independently; for example, only water in alcohol-water azeotrope reacts with CaO leaving alcohol unreacted.

(ii) True

Reason:

For a solution to obey Raoult's law in liquid phase, the intermolecular forces in pure liquids must be equal to intermolecular forces in the solution such that $P_A = X_A P_A^0$ and $P_B = X_B P_B^0$. Also the vapour phase of the solution must behave exactly as ideal gas such that it obeys Dalton's law of partial pressure, that is $P_{\text{soln}} = X_A P_A^0 + X_B P_B^0$

(b)

(i) Ideal solution

Explanation:

Like water, methanol possesses intermolecular hydrogen bonding accounted by presence of OH group. It is also bonded to very small non-polar (CH_3) group and thus making its polarity and strength of intermolecular forces very similar to those of water and hence even after mixing the two compounds in the solution, strength of intermolecular forces between methanol and water in the solution will remain the same making the solution ideal.

(ii) The mole fraction of 0.2 means that number of moles of methanol in 1 mol of the solution is 0.2mol.

And number of moles of water = $(1 - 0.2)\text{mol} = 0.8\text{mol}$

Using $m = n \times M_r = 0.8\text{mol} \times 32\text{g mol}^{-1} = 25.6\text{g} = 0.0256\text{kg}$

The molality = $\frac{n_{\text{su}}}{m_{\text{sv}} \text{ in kg}} = \frac{0.2\text{mol}}{0.0256\text{ kg}} = 7.8125\text{mol/kg}$

Molality of the solution is 7.8125mol/kg.

Question 3

(a) When an ideal solution is boiled at given temperature, the vapour phase is always richer in the more volatile component as compared to the liquid solution phase.

(b) Since X and Y formed ideal solution, then Raoult's law is applicable.

Thus $P_{\text{soln}} = X_X^L P_X^0 + X_Y^L P_Y^0$

For the first case;

$$550\text{mmHg} = \left(\frac{3\text{mol}}{3\text{mol} + 1\text{mol}}\right) P_X^0 + \left(\frac{1\text{mol}}{3\text{mol} + 1\text{mol}}\right) P_Y^0$$

From which;

$$\frac{3}{4} P_X^0 + \frac{1}{4} P_Y^0 = 550 \dots \dots \dots \text{(i)}$$

For the second case;

$$560\text{mmHg} = \left(\frac{4\text{mol}}{4\text{mol} + 1\text{mol}}\right) P_X^0 + \left(\frac{1\text{mol}}{4\text{mol} + 1\text{mol}}\right) P_Y^0$$

From which;

$$\frac{4}{5} P_X^0 + \frac{1}{5} P_Y^0 = 560 \dots \dots \dots \text{(ii)}$$

Solving the two equations above gives;

$P_X^0 = 600\text{mmHg}$ and $P_Y^0 = 400\text{mmHg}$

Question 4

(a) Due to the formation of azeotropic mixture, any attempt to separate alcohol from alcohol-water mixture by fractional distillation, will end up with distillate of the azeotrope containing about 96% alcohol and pure water as residue. So absolute alcohol cannot be prepared by fractional distillation unless suitable dehydrating agent like CaO is introduced to the distillate to eliminate water.

(b) Since the solution of hexane and pentane is ideal solution, Raoult's law is applicable.

Thus $P_{\text{soln}} = X_P^L P_P^0 + X_H^L P_H^0$

But $X_H^L = 1 - X_P^L$

It follows that; $P_{\text{soln}} = X_P^L P_P^0 + (1 - X_P^L) P_H^0$

Substituting $252 = 425X_P^L + (1 - X_P^L)151$

From which $X_P^L = 0.3686$

Mole fraction of pentane is 0.3686

Question 5

(a) Zeotrope is the liquid mixture whose vapour composition is not the same as the liquid composition at given temperature. Is the mixture like benzene-toluene mixture with liquid components that have different boiling points and therefore can be separated by fractional distillation.

(b) Using; $n = \frac{m}{M_r}$

$$n_A = \frac{100\text{g}}{140\text{g mol}^{-1}} = 0.7143\text{mol}$$

$$n_B = \frac{1000\text{g}}{180\text{g mol}^{-1}} = 5.5556\text{mol}$$

Using; Mole fraction, $X = \frac{n}{n_T}$

$$X_A = \frac{0.7143\text{mol}}{(0.7143 + 5.5556)\text{mol}} = 0.114$$

$$\text{And } X_B = 1 - X_A = 1 - 0.114 = 0.886$$

Assuming the solution obeys Raoult's law;

$$P_{\text{soln}} = X_A P_A^0 + X_B P_B^0$$

$$\text{Then } 475 = 0.114 P_A^0 + 0.886 \times 500$$

$$\text{From which } P_A^0 = 281\text{torr}$$

$$\text{And } P_A = X_A P_A^0 = 0.114 \times 281\text{torr} = 32\text{torr}$$

The vapour pressure of pure liquid A is 281torr

The vapour pressure of A in the solution 32torr

Question 6

(a) Positive deviation.

Reason:

With hydrogen bonds, ethanol is more polar than acetone which has no hydrogen bonds. Thus when acetone is mixed to ethanol, it tends to weaken the hydrogen bonds in ethanol and hence the intermolecular forces of attraction in the ethanol-water solution become smaller than intermolecular forces of attraction in ethanol leading to the positive deviation from Raoult's law.

(b) Assuming the mixture of A and B obeys Raoult's law;

$$P_{\text{soln}} = X_A P_A^0 + X_B P_B^0$$

$$\text{But } X_B = 1 - X_A$$

$$\text{Then } P_{\text{soln}} = X_A P_A^0 + (1 - X_A) P_B^0$$

$$\text{Substituting } 600 = 450 X_A + (1 - X_A) \times 700$$

$$\text{From which } X_A = 0.4 \text{ or } 40\% \text{ and } X_B = 1 - 0.4 = 0.6 \text{ or } 60\%$$

Hence liquid composition by mole is 40%A and 60%B

$$X_A^V = \frac{X_A P_A^0}{P_{\text{soln}}} = \frac{0.4 \times 450\text{mmHg}}{600\text{mmHg}} = 0.3 \text{ or } 30\%$$

$$\text{And } X_B^V = 1 - X_A^V = 1 - 0.3 = 0.7 \text{ or } 70\%$$

Hence vapour composition by mole is 30%A and 70%B

Question 7

(a) NaCl is non-volatile solute; introducing it in water, lowers the vapour pressure of water and hence the boiling point is increased.

On another hand, methanol is less polar liquid than water; introducing it in water weakens intermolecular forces between water molecules, increasing its vapour pressure and hence boiling point is decreased.

(b) Mixture of benzene and toluene is ideal solution, so it obeys Raoult's law.

$$\text{Thus } P_{\text{soln}} = X_B P_B^0 + X_T P_T^0; \text{ where } X_T = 1 - X_B$$

$$\text{Substituting } 0.83 = 1.1 X_B + (1 - X_B) \times 0.7$$

$$\text{From which } X_B = 0.325$$

Mole fraction of benzene in the liquid phase is 0.325

Then mole fraction of benzene in the vapour phase, X_B^V

$$= \frac{X_B P_B^0}{P_{\text{soln}}} = \frac{0.375 \times 1.1\text{atm}}{0.83\text{atm}} = 0.497 \text{ and } X_B^V = 1 - 0.497 = 0.503$$

Thus for every 1mol of vapour mixture, there is 0.497mol of benzene and 0.503mol of toluene.

Using $m = nM_r$;

$$\text{Mass of benzene} = 0.497\text{mol} \times 78\text{g mol}^{-1} = 38.766\text{g}$$

$$\text{Mass of toluene} = 0.503\text{mol} \times 92\text{g mol}^{-1} = 46.276\text{g}$$

$$\% \text{benzene by mass} = \frac{m_b}{m_{\text{total}}} = \frac{38.766\text{g}}{(38.766 + 46.276)\text{g}} = \frac{38.766\text{g}}{85.042\text{g}} \times 100\% = 45.58\%$$

Hence the percentage by mass of benzene in vapour is 45.58%

Question 8

(a)

(i) Azeotrope (or azeotropic mixture)

(ii) Two; namely:

1. Minimum boiling azeotrope/positive azeotrope, example ethanol-water mixture containing 95.6% $\left(\frac{m}{m}\right)$ ethanol.
2. Maximum boiling azeotrope/negative azeotrope, example nitric acid-water mixture containing 68% $\left(\frac{m}{m}\right)$ nitric acid.

(b) Using $m = \rho V$ Mass of pentane = 25mL $\times$ 0.63g/mL = 15.75gMass of hexane = 45mL $\times$ 0.66g/mL = 29.7gThen using; $n = \frac{m}{M_r}$

$$\text{Number of moles of pentane, } n_p = \frac{15.75\text{g}}{72\text{gmol}^{-1}} = 0.21875\text{mol}$$

$$\text{Number of moles of hexane, } n_H = \frac{29.7\text{g}}{86\text{gmol}^{-1}} = 0.34535\text{mol}$$

Using; Mole fraction, $X = \frac{n}{n_T}$

$$X_p = \frac{0.21875\text{mol}}{(0.21875 + 0.34535)\text{mol}} = 0.3878$$

$$\text{And } X_H = 1 - X_p = 1 - 0.3878 = 0.6122$$

Since the solution of pentane and hexane is ideal, it obeys Raoult's law;

$$\text{Thus } P_{\text{soln}} = X_p P_p^0 + X_H P_H^0$$

$$\text{Substituting; } P_{\text{soln}} = 0.3878 \times 511\text{mmHg} + 0.6122 \times 150\text{mmHg} = 289.9958\text{mmHg}$$

$$X_p^V = \frac{X_p P_p^0}{P_{\text{soln}}} = \frac{0.3878 \times 511\text{mmHg}}{289.9958\text{mmHg}} = 0.68$$

$$\text{And } X_H^V = 1 - X_p^V = 1 - 0.68 = 0.32$$

Hence vapour composition by mole fraction is 0.68 and 0.32 for pentane and heptane respectively.

Question 9

(a)

1. Must be immiscible in water.
2. Must not decompose at the temperature of steam.
3. Must have fairly high vapour pressure at 100°C
4. Its impurities must be non-volatile.
5. It must be non-reactive to water.

(b) Using $\frac{m_Q}{m_w} = \frac{P_Q M_Q}{P_w M_w}$

$$\text{Where } P_Q = 100900\text{Pa} - P_w = (100900 - 94300)\text{Pa} = 6600\text{Pa}$$

$$\text{Substituting } \frac{m_Q}{m_w} = \frac{6600\text{Pa} \times 120\text{gmol}^{-1}}{94300\text{Pa} \times 18\text{gmol}^{-1}} = 0.4666$$

$$\text{From which percentage of Q} = \left(\frac{0.4666}{0.4666+1} \right) \times 100\% = 31.8\%$$

$$\text{And percentage of water is } (100 - 31.8)\% = 68.2\%$$

Hence the composition of distillate is 31.8% and 68.2% for Q and water respectively.

Question 10

(a) Zeotropic mixture is the liquid mixture whose vapour composition is not the same as the liquid composition at given temperature while azeotropic mixture is the liquid mixture whose vapour composition is the same as liquid composition at given temperature. Thus zeotropic is the mixture with liquid components that have different boiling points and therefore can be separated by fractional distillation while azeotropic mixture boils at constant temperature and cannot be separated by fractional distillation.

(b) Assuming the methanol-propanol solution is ideal, Raoult's law becomes applicable.

$$\text{Thus } P_{\text{soln}} = X_M^L P_M^0 + X_P^L P_P^0$$

$$\text{But } X_M^L = 1 - X_P^L$$

$$\text{It follows that; } P_{\text{soln}} = X_P^L P_P^0 + (1 - X_P^L) P_M^0$$

$$\text{Substituting } 174 = 44.6 X_P^L + (1 - X_P^L) 303$$

$$\text{From which } X_P^L = 0.499 \text{ or } 49.9\%$$

$$\text{And } X_M^L = 1 - 0.499 = 0.501 \text{ or } 50.1\%$$

Hence the composition of the solution by mole is 49.9% and 50.1% for propanol and methanol respectively.

Question 11

- (a) In very dilute solution there are much more solvent-solvent forces of attraction than solvent-solute forces of attractions (as number of solvent molecules is too large compared to number of solute molecular) and hence intermolecular forces of attraction in the solution become almost equal to intermolecular forces of attraction in pure liquids.

- (b) Mole fraction of liquid A, $X_A = \frac{80}{100} = 0.8$

And mole fraction of liquid B, $X_B = 1 - X_A = 1 - 0.8 = 0.2$

Since the given solution is ideal, it obeys Raoult's law;

Thus $P_{\text{soln}} = X_A P_A^0 + X_B P_B^0$

Substituting: $P_{\text{soln}} = 0.8x + 0.2y$

$$X_A^V = \frac{X_A P_A^0}{P_{\text{soln}}} = \frac{0.8x}{0.8x+0.2y} \text{ and } X_B^V = \frac{X_B P_B^0}{P_{\text{soln}}} = \frac{0.2y}{0.8x+0.2y}$$

Hence the mole fraction of the vapour is $\frac{0.8x}{0.8x+0.2y}$ and $\frac{0.2y}{0.8x+0.2y}$ for A and B respectively.

Question 12

- (a)
(i) It represents the solution which obeys Raoult's law exactly over the entire range of concentration.
(ii) Ideal solutions are formed by mixing the two components which are identical in molecular size, in structure and have almost identical intermolecular forces. In these solutions, the intermolecular forces between the components in the solution are of same magnitude as the intermolecular forces in pure components.
- (b) Mole fraction of toluene in vapour phase, $X_T^V = 1 - X_B^V = 1 - 0.65 = 0.35$

$$\text{Using } X_T^V = \frac{X_T^L P_T^0}{P_{\text{soln}}}$$

$$\text{From which } 0.35 = \frac{0.7X_T^L}{P_{\text{soln}}} \dots\dots\dots(i)$$

But the mixture of benzene and toluene forms ideal solution and therefore it obeys Raoult's law.

Thus $P_{\text{soln}} = X_T^L P_T^0 + X_B^L P_B^0$; where $X_B^L = 1 - X_T^L$

It follows that: $P_{\text{soln}} = X_T^L P_T^0 + (1 - X_T^L) P_B^0 \dots\dots\dots(ii)$

Substituting (ii) to (i);

$$0.35 = \frac{0.7X_T^L}{X_T^L P_T^0 + (1 - X_T^L) P_B^0}$$

From which;

$$0.35 = \frac{0.7X_T^L}{0.7X_T^L + 1.1(1 - X_T^L)}$$

Solving above equation gives $X_T^L = 0.4583$

Hence the mole fraction of toluene in the liquid phase is approximately 0.46

Question 13

- (a) It represents the constant boiling point liquid mixture whose composition does not change on distillation.

Type: Minimum boiling azeotrope.

Example: A mixture of ethanol and water containing 95.6% ethanol forms minimum boiling azeotrope.

- (b) Since the given solution is ideal, Raoult's law is applicable.

Thus $P_{\text{soln}} = X_A^L P_A^0 + X_M^L P_M^0$

But $X_M^L = 1 - X_A^L$

It follows that; $P_{\text{soln}} = X_A^L P_A^0 + (1 - X_A^L) P_M^0$

But at the boiling point, vapour pressure of the solution is equal to the external pressure.

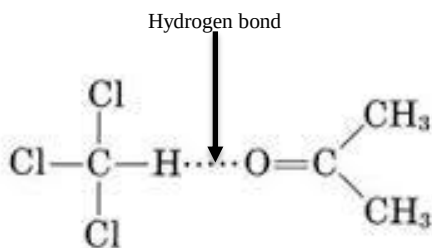
Thus $0.248\text{atm} = 0.342X_A^L + 0.188(1 - X_A^L)$

From which $X_A^L = 39$

Mole fraction of acetone in the solution is 0.39.

Question 14

- (a) The solution of chloroform and acetone has lower vapour pressure than ideal solution because of intermolecular hydrogen bonds between chloroform and acetone molecules in the solution which are stronger intermolecular forces than dipole-dipole forces in pure chloroform and acetone. As a result, total vapour pressure becomes less than the corresponding ideal solution of same composition (i.e. negative deviations). Therefore, the boiling points of solutions are increased and form maximum boiling azeotropes.



(b) Partial vapour pressure of methyl alcohol, $P'_M = X'_M P_M^0$

Substituting $P'_M = 0.305 \times 96 \text{ torr} = 29.28 \text{ torr}$

Hence vapour pressure of methyl alcohol is 29.28 torr

Question 15

(a)

(i) There are three types.

(ii)

1. Gaseous solution

This is the solution in which the solvent is a gas.

In these solutions; the solute may be liquid, solid or gas. For example, a mixture of oxygen and nitrogen gas is a gaseous solution.

2. Liquid solution

This is the solution in which the solvent is a liquid.

In these solutions, the solute may be gas, liquid or solid. For example, a solution of sodium chloride in water is a liquid solution

3. Solid solution

This is the solution in which the solvent is a solid.

The solute in this solution may be gas, liquid or solid. For example, a solution of copper in zinc is a solid solution.

(iii) Hydrogen in palladium (in which hydrogen gas is a solute and the solid is solvent)

(b) Using; Mole fraction, $X = \frac{n}{n_T}$

$$\text{Mole fraction of dichloroethane, } X_{DC} = \frac{0.03 \text{ mol}}{(0.03 + 0.05) \text{ mol}} = 0.375$$

$$\text{And mole fraction of dibromoethane, } X_{DB} = 1 - X_{DC} = 1 - 0.375 = 0.625$$

Since the given solution is ideal, it obeys Raoult's law;

$$\text{Thus } P_{\text{soln}} = X_{DC} P_{DC}^0 + X_{DB} P_{DB}^0$$

Substituting;

$$P_{\text{soln}} = 0.375 \times 133 \text{ torr} + 0.625 \times 11.4 \text{ torr} = 57 \text{ torr}$$

$$X_{DC}^V = \frac{X_{DC} P_{DC}^0}{P_{\text{soln}}} = \frac{0.375 \times 133 \text{ torr}}{57 \text{ torr}} = 0.875$$

$$\text{And } X_{DB}^V = 1 - X_{DC}^V = 1 - 0.875 = 0.125$$

Hence vapour composition by mole fraction is 0.875 and 0.125 for dichloroethane and dibromoethane respectively.

Question 16

(a) In immiscible solution each liquid exerts pressure independently thus making the vapour pressure of the solution greater than either of the two components and hence boiling point will be less than either of the two.

(b)

(i) More volatile.

Reason:

Addition of B in the solution increased the vapour pressure of the solution (from $2 \times 10^5 \text{ Pa}$ to $2.1 \times 10^5 \text{ Pa}$)

(ii) Since the solution is ideal; $P_{\text{soln}} = X_A P_A^0 + X_B P_B^0$

Initially:

$$X_A = \frac{n_A}{n_A + n_B} = \frac{1 \text{ mol}}{(1+2) \text{ mol}} = \frac{1}{3} \text{ and } X_B = 1 - \frac{1}{3} = \frac{2}{3}$$

$$\text{Then } 2 \times 10^5 = \frac{1}{3} P_A^0 + \frac{2}{3} P_B^0 \dots \dots \dots (i)$$

After addition of one mole of B:

$$n_B = (1 + 2) \text{ mol} = 3 \text{ mol}$$

$$X_A = \frac{n_A}{n_A + n_B} = \frac{1 \text{ mol}}{(1+3) \text{ mol}} = \frac{1}{4} \text{ and } X_B = 1 - \frac{1}{4} = \frac{3}{4}$$

Then $2.1 \times 10^5 = \frac{1}{4} P_A^0 + \frac{3}{4} P_B^0 \dots\dots\dots(ii)$

Solving (i) and (ii) simultaneously gives:

$$P_A^0 = 1.2 \times 10^5 \text{ Pa and } P_B^0 = 2.4 \times 10^5 \text{ Pa}$$

Question 17

(a) Raoult's law relates the partial vapour pressure of a particular component in ideal solution to its mole fraction.

(b) Using; $n = \frac{m}{M_r}$

$$\text{Number of moles of heptane, } n_H = \frac{5.32\text{g}}{86\text{g mol}^{-1}} = 0.06186\text{mol}$$

$$\text{Number of moles of octane, } n_O = \frac{8.8\text{g}}{114\text{g mol}^{-1}} = 0.07719\text{mol}$$

Using; Mole fraction, $X = \frac{n}{n_T}$

$$X_H = \frac{0.06186\text{mol}}{(0.06186 + 0.07719)\text{mol}} = 0.4449$$

$$\text{And } X_O = 1 - X_H = 1 - 0.4449 = 0.5551$$

Since the solution is ideal, it obeys Raoult's law;

$$\text{Thus } P_{\text{soln}} = X_H P_H^0 + X_O P_O^0$$

$$\text{Substituting; } P_{\text{soln}} = 0.4449 \times 0.522\text{atm} + 0.5551 \times 0.238\text{atm} = 0.36435\text{atm}$$

$$X_O^V = \frac{X_O P_O^0}{P_{\text{soln}}} = \frac{0.5551 \times 0.238\text{atm}}{0.36435\text{atm}} = 0.36$$

Hence the mole fraction of octane in the vapour is 0.36

Question 18

(a)

1. The liquid should have large molecular mass compared to that of water.
2. The liquid should have a fairly high vapour pressure at temperature close to 100°C.

(b) Using $\frac{m_o}{m_w} = \frac{P_o \times M_o}{P_w \times M_w}$

$$\text{But } \frac{m_o}{m_w} = 0.48, P_o = 5.3\text{kPa}, P_w = 95\text{kPa and } M_w = 18\text{g/mol}$$

$$\text{Then } 0.48 = \frac{5.3\text{kPa} \times M_o}{95\text{kPa} \times 18\text{g/mol}}$$

$$\text{From which } M_o = 155\text{g/mol}$$

Molar mass of the organic acid is 155g/mol

Question 19

(a)

- (i) The law instructs that partial vapour pressure of a particular constituent (component) in a solution which contains two or more volatile miscible liquids is the product of its mole fraction and its vapour pressure of the pure liquid at given temperature.
 - (ii) Real vapour pressure of non-ideal solution with negative deviation is smaller than that predicted by Raoult's law.
- (b) Since the solution is very dilute (mole fraction of benzene is 0.09), the given solution is ideal and hence Raoult's law is applicable.

$$\text{Partial vapour pressure of benzene, } P_B = X_B P_B^0 = 0.09 \times 75.2\text{mmHg} = 6.768\text{mmHg}$$

$$\text{Partial vapour pressure of ethanol, } P_E = X_E P_E^0$$

$$\text{But } X_E = 1 - X_B = 1 - 0.09 = 0.91$$

$$\text{It follows that, } P_E = 0.91 \times 43.6\text{mmHg} = 39.676\text{mmHg}$$

$$\text{Using } P_{\text{soln}} = P_B + P_E \quad (\text{Dalton's law of partial pressure})$$

$$P_{\text{soln}} = (6.768 + 39.676)\text{mmHg} = 46.444\text{mmHg}$$

(i) Hence total vapour pressure of the mixture is 46.444mmHg

$$(ii) X_B = \frac{P_B}{P_{\text{soln}}} = \frac{6.768}{46.444} = 0.146$$

Hence the mole fraction of benzene in the vapour phase is 0.146

Question 20

- (a) Increase in temperature **increases concentration** and **speed** of vapour particles leading to **more frequent collisions** between vapour particles and walls of the container and hence greater vapour pressure.
- (b) Using $\frac{M_N}{M_W} = \frac{P_N M_N}{P_W M_W}$

Where N and W stand for nitrobenzene and water respectively

By Dalton's law of partial pressure;

$$P_N + P_W = \text{atmospheric pressure} = 1.013 \times 10^5 \text{ Pa}$$

$$\text{Then } P_N = 1.013 \times 10^5 \text{ Pa} - P_W = (1.013 \times 10^5 - 9.749 \times 10^4) \text{ Pa} = 3810 \text{ Pa}$$

$$\text{Also } M_W = 18 \text{ g mol}^{-1} \text{ and } M_N = 127 \text{ g mol}^{-1}$$

$$\text{Then } \frac{M_N}{M_W} = \frac{3810 \text{ Pa} \times 127 \text{ g mol}^{-1}}{9.749 \times 10^4 \text{ Pa} \times 18 \text{ g mol}^{-1}} = 0.2757$$

$$\% \left(\frac{m}{m} \right) \text{ Nitrobenzene} = \left(\frac{0.2757}{1 + 0.2757} \right) \times 100\% = 21.6\%$$

The percentage of nitrobenzene is 21.6%

Question 21

- (a) Solvent extraction is the method of removing (extracting) a solute from a certain solvent by introducing the second solvent (**extractive solvent**) which is immiscible to the first one and then allowing the solute to distribute itself in the two solvents. The layer of extractive solvent is then removed with significant amount of the solute and on successive extractions which are done by introducing fresh extractive solvent again and again, the solute is finally completely removed from the first solvent (or very small amount remain in the first solvent).
- (b) Using: $W_r = W_o \left(\frac{V_b}{V_b + K_d V_a} \right)^n$

Where:

W_r is the mass of solute which remain in residue solution after n extractions.

W_o is the original mass of the solute before extraction

V_b is the volume of residue solution

V_a is the volume of an extraction solvent used in each extraction (experiment)

n is the number extractions.

K_d is the partition coefficient

First case:

$$W_o = 50 \text{ g}, V_b = 1000 \text{ cm}^3, V_a = 1000 \text{ cm}^3, K_d = 3 \text{ and } n = 1$$

$$\text{Then } W_r = 50 \left(\frac{1000}{1000 + (1000 \times 3)} \right)^1 = 12.5 \text{ g}$$

The mass remained by using single extraction is 12.5g

Second case:

$$W_o = 50 \text{ g}, V_b = 1000 \text{ cm}^3, V_a = 500 \text{ cm}^3, K_d = 3 \text{ and } n = 2$$

$$\text{Then } W_r = 50 \left(\frac{1000}{1000 + (500 \times 3)} \right)^2 = 8 \text{ g}$$

The mass remained by using two extraction is 8g

Comparison:

Smaller amount of acid is left by using two extractions than one extraction.

Recommendation:

To get best result of extracting the acid from water, the volume of ether should be divided in smaller portions as possible rather than using the whole volume at once.

- (ii) The acid dissociates in water and thus the molecular state of acid (solute) is not strictly the same in the two solvents. So in this case, the partition law used to derive the given partition coefficient is not strictly valid.

Question 22

- (a) **Similarity:** They both separate components of the mixture based on the boiling point.

Difference: Steam distillation separates thermally unstable component of the mixture which is immiscible to water while fractional distillation separates thermally stable components of miscible liquid mixture. Steam distillation is therefore takes place at temperature below the boiling point of components while fractional distillation takes place at boiling point of components.

(b) (i) Using $\frac{n_c}{n_w} = \frac{P_c}{P_w}$ (For immiscible liquids)

Where n_c and n_w is the number of moles of Chlorobenzene and water respectively in the distillate.

P_c and P_w is the vapour pressure of Chlorobenzene and water respectively at 91°C

$$\frac{n_c}{n_w} = \frac{760-540}{540} = \frac{11}{27} \quad \text{or } n_c : n_w = 11 : 27$$

$$\%n_c = \left(\frac{11}{11+27} \right) \times 100\% = 28.9\%$$

$$\%n_w = (100 - 28.9)\% = 71.1\%$$

Hence the mole composition of distillate is 28.9% chlorobenzene and 71.1% water

(ii) Using $\frac{m_c}{m_w} = \frac{P_c M_c}{P_w M_w}$

Where M_c and M_w are molar masses of Chlorobenzene and water respectively

m_c and m_w are masses of Chlorobenzene and water respectively in the distillate.

$$\text{Then } \frac{m_c}{m_w} = \frac{(760-540) \times 112.5}{540 \times 18} = \frac{275}{108}$$

$$m_c : m_w = 275 : 108$$

$$\% m_c = \left(\frac{275}{275+108} \right) \times 100\% = 71.8\%$$

$$\% m_w = (100 - 71.8)\% = 28.2\%$$

Hence the mass composition of the distillate is 71.8% Chlorobenzene and 28.2% water.

(iii) If 90% of chlorobenzene has been steam distilled:

$$\text{Mass of chlorobenzene in the distillate} = \frac{90}{100} \times 20\text{g} = 18\text{g}$$

If m_T is the total mass of the distillate

$$\text{It follows that } \frac{71.8 m_T}{100} = 18\text{g} \quad \text{or } m_T = \frac{100 \times 18\text{g}}{71.8} = 25\text{g}$$

$$\text{Using } V = \frac{m}{\rho}$$

$$\text{Total volume of distillate} = \frac{25}{1.1} \text{cm}^3 = 22.72 \text{cm}^3$$

Hence total volume of distillate obtained is 22.72cm^3

Note: In this calculation it has been assumed that the density of the mixture of two immiscible liquids is equal to the density of chlorobenzene (1.1g/cm^3) because density of pure water is 1g/cm^3 so the density of the mixture must lie between 1 and 1.1g/cm^3 ; chlorobenzene having greater proportional by mass, the density of the mixture must be very close to 1.1g/cm^3 .

Question 23

(a)

- (i) Negative deviation.
- (ii) Ion-ion interactions.

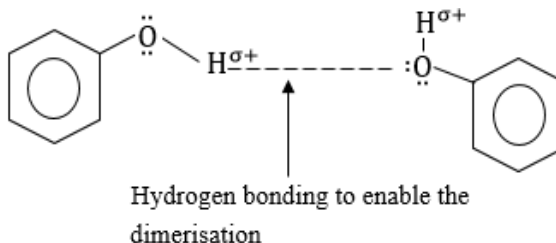
(b)

- (i) Let C_1 and C_2 be concentration of phenol in water and chloroform respectively.

C_1	8.836	15.322	23.876
C_2	23.876	71.534	173.900
$\frac{C_1}{C_2}$	0.370	0.214	0.137
$\frac{C_1}{\sqrt{C_2}}$	1.808	1.812	1.811

Since $\frac{C_1}{C_2}$ is not constant while $\frac{C_1}{\sqrt{C_2}}$ is constant of approximated value of 1.8, phenol dimerises in chloroform

- (ii) Dimerisation of phenol is possible due to very strong hydrogen bonding existing between its molecules when the phenol is in chloroform.



Question 24

(a) Let:

C_1 be $[x]$ in solvent A

C_2 be $[x]$ in solvent B

α be degree of dissociation of x

n be number of molecules of x associated

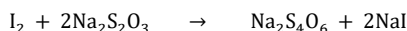
Then:

$$(i) \quad K = \frac{n\sqrt[n]{C_1}}{C_2}$$

$$(ii) \quad K = \frac{C_1(1-\alpha)}{\sqrt[n]{C_2}}$$

$$(iii) \quad K = \frac{C_1}{C_2(1-\alpha)}$$

(b) Iodine and sodium thiosulphate reacts together according to the following equation:



From which mole ratio of I_2 to $Na_2S_2O_3$ is 1:2

But number of moles, $n = []V$

Thus the product of molar concentration of each solution and its respective volume must satisfy the mole ratio.

$$\text{That is: } \frac{[I_2] \times \text{Volume of iodine solution}}{[Na_2S_2O_3] \times \text{Volume of thiosulphate solution}} = \frac{1}{2}$$

For Experiment I

$$\text{For } CCl_4 \text{ layer: } \frac{[I_2] \times 25}{0.1 \times 27.7} = \frac{1}{2} \text{ or } [I_2] = 0.0554M$$

$$\text{For water layer: } \frac{[I_2] \times 25}{0.01 \times 3.15} = \frac{1}{2} \text{ or } [I_2] = 0.00063M$$

$$\text{Then } K_1 = \frac{[I_2] \text{ in } CCl_4 \text{ layer}}{[I_2] \text{ in water layer}} = \frac{0.0554}{0.00063} = 87.94$$

For Experiment II

$$\text{For } CCl_4 \text{ layer: } \frac{[I_2] \times 25}{0.1 \times 21.2} = \frac{1}{2} \text{ or } [I_2] = 0.0424M$$

$$\text{For water layer: } \frac{[I_2] \times 25}{0.01 \times 2.4} = \frac{1}{2} \text{ or } [I_2] = 0.00048M$$

$$\text{Then } K_2 = \frac{[I_2] \text{ in } CCl_4 \text{ layer}}{[I_2] \text{ in water layer}} = \frac{0.0424}{0.00048} = 88.33$$

For experiment III

$$\text{For } CCl_4 \text{ layer: } \frac{[I_2] \times 25}{0.1 \times 14} = \frac{1}{2} \text{ or } [I_2] = 0.028M$$

$$\text{For water layer: } \frac{[I_2] \times 25}{0.01 \times 1.6} = \frac{1}{2} \text{ or } [I_2] = 0.00032M$$

$$\text{Then } K_3 = \frac{[I_2] \text{ in } CCl_4 \text{ layer}}{[I_2] \text{ in water layer}} = \frac{0.028}{0.00032} = 87.5$$

$$K_d = \frac{K_1 + K_2 + K_3}{3} = \frac{87.94 + 88.33 + 87.5}{3} = 87.9$$

The mean distribution constant of iodine between CCl_4 and water is 87.9

Let mass of iodine which will dissolve in water be x

Then mass of iodine in CCl_4 will be $5 - x$

$$\text{It follows that: } 87.9 = \frac{5 - x}{x/2} = \frac{2(5 - x)}{x}; \quad x = 0.1112g$$

Hence 0.1112g of iodine will dissolve in water

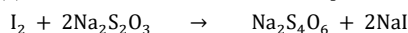
Question 25

- (a) Intermolecular forces in A and B should be equal in such a way that intermolecular forces in the solution is equal to intermolecular forces in pure A and pure B.

$$A \dots \dots \dots A = B \dots \dots \dots B = A \dots \dots \dots B$$

Where; $\dots \dots \dots$ represents intermolecular forces.

- (b) Iodine reacts with sodium thiosulphate according to the following equation:



From which mole ratio of I_2 to $Na_2S_2O_3$ is 1:2

$$\text{Thus } \frac{[I_2] \times \text{Volume of iodine solution}}{[Na_2S_2O_3] \times \text{Volume of thiosulphate solution}} = \frac{1}{2}$$

$$\text{For aqueous layer: } \frac{[I_2] \times 25}{0.01 \times 4.5} = \frac{1}{2} \text{ or } [I_2] = 0.0009M$$

$$\text{Number of moles of } I_2 \text{ in } 50\text{cm}^3 \text{ of aqueous solution} = \frac{50}{1000} \times 0.0009 \text{ moles} = 4.5 \times 10^{-5} \text{ moles} \quad (n=MV)$$

$$\text{Mass of } I_2 \text{ in } 50\text{cm}^3 \text{ of aqueous solution} = 4.5 \times 10^{-5} \times 254g = 0.01143g \quad (m = nM_r)$$

$$\text{Mass of } I_2 \text{ in } 50\text{cm}^3 \text{ in tetrachloromethane}(CCl_4) = (1 - 0.01143) = 0.98857g$$

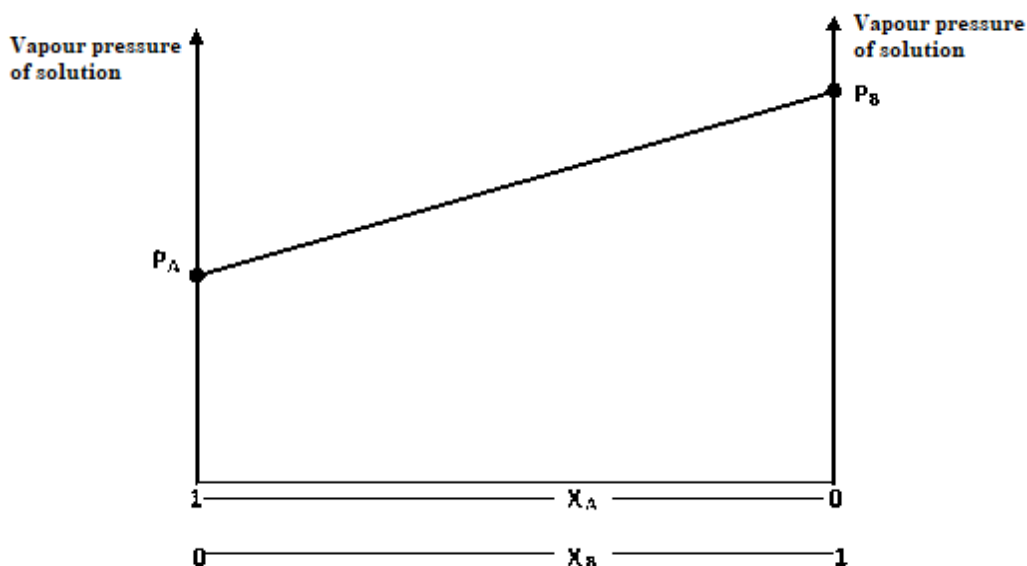
$$K_d = \frac{\text{Concentration of } I_2 \text{ in } CCl_4 \text{ layer}}{\text{Concentration of } I_2 \text{ in aqueous layer}} = \frac{0.98857}{0.01143}$$

$$(\text{Mass in equal volume of } 50\text{ cm}^3 \text{ of each layer}) = 86.5$$

Hence the distribution constant of iodine between tetrachloromethane and water is 86.5.

Question 26

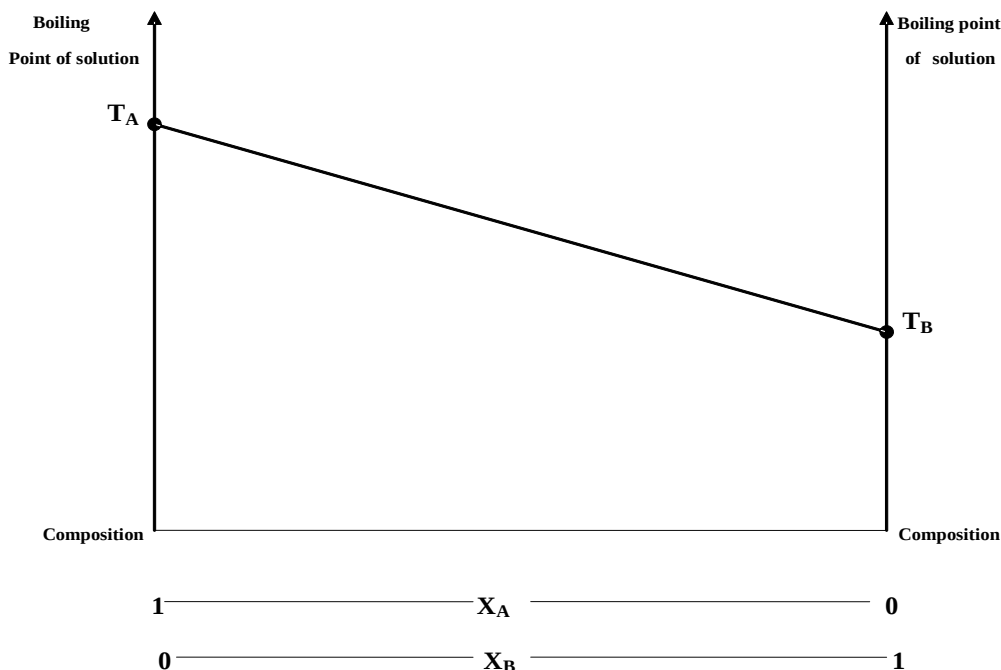
- (a)



Where P_A is the vapour pressure of pure A

P_B is the vapour pressure of pure B

(b)



Where T_A is the boiling point of pure **A**

T_B is the boiling point of pure **B**

(c) The solution will boil in such a way that the vapour formed is richer in **B** (more volatile component). So on successive distillation and condensation the pure **B** is obtained as distillate in collector and pure **A** remain in the distillation flask as residue.

Question 27

(a) Not ideal solution.

Explanation

An ideal solution would have a vapour pressure at any mole fraction of H_2O between that of pure propanol and pure water (between 74 torr and 71.9 torr). The vapor pressures of the solution are not between these limits so it is not an ideal solution.

(b) From the data, the vapour pressures of the various solutions are greater than in the ideal solution (positive deviation from Raoult's law). This occurs when the intermolecular forces in solution are weaker than the intermolecular forces in pure solvent and pure solute. This will cause the solution making process endothermic (positive) and hence the enthalpy of solution (ΔH_{soln}) will be positive.

(c) Weaker.

Explanation

The interactions between propanol and water molecules are weaker than between the pure substances since the solution exhibits a positive deviation from Raoult's law.

(d) When $X_{H_2O} = 0.54$ the vapour pressure is highest as compared to the other solutions. Since a solution boils when the vapour pressure of the solution equals the external pressure, then the solution with $X_{H_2O} = 0.54$ should have the lowest normal boiling point; this solution will have a vapour pressure equal to 1 atm at a lower temperature as compared to the other solutions.

Special name: Azeotropic mixture (minimum boiling azeotrope).

Question 28

$$n_{\text{Acetone}} = \frac{50\text{g}}{58\text{g mol}^{-1}} = 0.862\text{mol}$$

$$n_{\text{Methanol}} = \frac{50\text{g}}{32\text{g mol}^{-1}} = 1.5625\text{mol}$$

$$n_{\text{T}} = n_{\text{Acetone}} + n_{\text{Methanol}} = 2.4245\text{mol}$$

$$X_{\text{Acetone}} = \frac{n_{\text{Acetone}}}{n_{\text{T}}} = \frac{0.862\text{mol}}{2.4245\text{mol}} = 0.36$$

$$X_{\text{Methanol}} = \frac{n_{\text{Methanol}}}{n_{\text{T}}} = \frac{1.5625\text{mol}}{2.4245\text{mol}} = 0.64$$

From Raoult's law;

$$P_{\text{soln}} = X_{\text{Acetone}}P_{\text{Acetone}}^{\circ} + X_{\text{Methanol}}P_{\text{Methanol}}^{\circ} = 0.36 \times 271\text{torr} + 0.64 \times 143\text{torr} = 189.08\text{torr}$$

The vapour pressure of the solution is approximately 189torr

$$X_{\text{Acetone}}^{\text{V}} = \frac{X_{\text{Acetone}}P_{\text{Acetone}}^{\circ}}{P_{\text{soln}}} = \frac{0.36 \times 271\text{torr}}{189\text{torr}} = 0.52$$

$$\text{And } X_{\text{Methanol}}^{\text{V}} = 1 - X_{\text{Acetone}}^{\text{V}} = 1 - 0.52 = 0.48$$

The vapour composition for acetone and methanol in terms of mole fractions are 0.52 and 0.48 respectively.

Explanation on the discrepancies:

The observed vapour pressure is smaller than the calculated vapour pressure from Raoult's law suggesting that the solution shows negative deviation from Raoult's law.

Question 29

(a)

- (i) If the volume of the container is suddenly increased, then the vapour pressure would decrease initially. This is because the amount of vapour remains the same, but the volume increases suddenly. As a result, the same amount of vapour is distributed in a larger volume.
- (ii) Since the temperature is constant, the rate of evaporation also remains constant. When the volume of the container is increased, the density of the vapour phase decreases. As a result, the rate of collisions of the vapour particles also decreases. Hence, the rate of condensation decreases initially.
- (iii) When equilibrium is restored finally, the rate of evaporation becomes equal to the rate of condensation. In this case, only the volume changes while the temperature remains constant. The vapour pressure depends on temperature and not on volume. Hence, the final vapour pressure will be equal to the original vapour pressure of the system.

(b)

- (i) From Raoult's law;

$$P_{\text{soln}} = X_{\text{A}}^{\text{L}}P_{\text{A}}^{\circ} + X_{\text{B}}^{\text{L}}P_{\text{B}}^{\circ}$$

$$\text{Where } X_{\text{B}}^{\text{L}} = 1 - X_{\text{A}}^{\text{L}}$$

$$\text{Substituting; } 600 = 450X_{\text{A}}^{\text{L}} + (1 - X_{\text{A}}^{\text{L}})700$$

$$\text{From which } X_{\text{A}}^{\text{L}} = 0.4$$

$$\text{And } X_{\text{B}}^{\text{L}} = 1 - 0.4 = 0.6$$

Hence the composition by mole fraction is as follows;

Mole fraction of A is 0.4

Mole fraction of B is 0.6

- (ii) In the vapour phase;

$$X_{\text{A}}^{\text{V}} = \frac{X_{\text{A}}^{\text{L}}P_{\text{A}}^{\circ}}{P_{\text{soln}}} = \frac{0.4 \times 450}{600} = 0.3$$

$$X_{\text{B}}^{\text{V}} = 1 - X_{\text{A}}^{\text{V}} = 1 - 0.3 = 0.7$$

Hence the vapour composition of the vapour phase by mole fraction is as follows;

Mole fraction of A is 0.3

Mole fraction of B is 0.7

Question 30

- (a)
- Partial vapour pressure of a particular constituent (component) in a solution which contains two or more volatile miscible liquids is the product of its mole fraction and its vapour pressure of the pure liquid at given temperature.
 - Propanol-ethanol solution
 - Toluene-benzene solution
 - Heptane-hexane solution
 - Intermolecular forces between the components in the solution is the same as those intermolecular forces in pure components.
 - The gaseous phase of the solution act as an ideal gas where the use ideal gas law is applicable.
- (b) Let number of moles of uranium in the organic layer be n_o and number of moles of uranium in the water layer be n_w

$$\text{Then from; } K_d = \frac{[\text{Uranium}]_{\text{in organic layer}}}{[\text{Uranium}]_{\text{in water layer}}}$$

$$\text{Substituting; } 50 = \frac{\frac{n_o}{200}}{\frac{n_w}{500}} = \frac{500n_o}{200n_w}$$

$$\text{From which; } \frac{n_o}{n_w} = \frac{50 \times 200}{500} = 20$$

Hence the ratio of number of moles of uranium in organic solvent layer to water layer is 20:1

Question 31

(a) An alcohol-water solution has a higher vapour pressure than that of pure water because alcohol is a volatile solute and therefore contributes significantly to the vapour of the solution. This high vapour pressure accounts for the lower boiling point in alcohol-water solution.

On another hand, a salt-water solution has a lower vapour pressure than that of pure water because salt is a non-volatile solute and solute-solvent interaction decrease the vapour of the solution. This low vapour pressure accounts for the higher boiling point in salt-water solution.

(b) (i) Partition coefficient

$$\text{(ii) Given that: } \frac{\text{Concentration of phenylamine in water}}{\text{Concentration of phenylamine in ethoxyethane}} = 0.2$$

Let mass of phenylamine extracted in ethoxyethane layer be x

$$\text{Then } \frac{20-x}{x/100} = 0.2, \quad \frac{20-x}{x} = 0.2 \text{ or } x = 16.67 \text{ g per dm}^3$$

But exact volume used was 100 cm^3

$$\text{So exact mass extracted was } \frac{100}{1000} \times 16.67 \text{ g} = 1.667 \text{ g}$$

Hence 1.667g of phenyl amine was extracted in phenylamine layer

(iii) By dividing the total volume of the extractive solvent (ethoxyethane) into as many smaller portions as possible rather than using the whole volume at once.

Question 32

- (a)
- Polar liquid may form partially miscible mixture which are normally behaving as non-ideal solution with positive deviation. For example, ethanol and water are both polar liquid but the ethanol-water mixture is non-ideal solution with positive deviation. Also some polar liquids like sulphuric acid ionises in the polar solvent, water, resulting to ion-ion interactions in the solution and hence the solution becomes non-ideal with negative deviation.
 - The given statement does not hold for any solution. Non-ideal solution with positive deviation has the boiling point which lower than either of the pure component while non-ideal solution with negative deviation has boiling point which is higher than either of the pure component.
 - Simple fractional distillation cannot be used to get pure water and pure ethanol from the mixture due to the formation of azeotropic mixture as the ethanol-water mixture is non-ideal solution.

$$\text{(b) Using; } K_d = \frac{\text{Mass concentration of G in pentan-1-ol (in gdm}^{-3}\text{)}}{\text{Mass concentration of G in aqueous solution (in gdm}^{-3}\text{)}}$$

$$\text{Where; Mass concentration of G in pentan-1-ol} = \frac{\text{mass of G}}{V_{\text{Soln in dm}^3}}$$

$$\text{But } V_{\text{Soln}} = 100 \text{ cm}^3 = \frac{100}{1000} \text{ dm}^3 = 0.1 \text{ dm}^3$$

$$\text{The mass concentration of G in pentan-1-ol} = \frac{1.5 \text{ g}}{0.1 \text{ dm}^3} = 15 \text{ gdm}^{-3}$$

Original mass of G in 500cm^3 of aqueous solution = $\frac{500}{1000} \times 4\text{g} = 2\text{g}$

Then mass of G in 500cm^3 of aqueous solution after extraction = $(2 - 1.5)\text{g} = 0.5\text{g}$

Mass concentration of G in aqueous solution = $\frac{0.5\text{g}}{0.5\text{dm}^3} = 1\text{gdm}^{-3}$

Substituting: $K_d = \frac{15\text{gdm}^{-3}}{1\text{gdm}^{-3}} = 15$

The partition coefficient of the solute G between pentan-1-ol and water is 15.

Let mass (in grams) of G remained in the aqueous solution be x

Then mass of G which will be extracted in the propan-1-ol will be $0.5 - x$

$$\text{Then } K_d = 15 = \frac{\frac{(0.5 - x)\text{g}}{0.1\text{dm}^3}}{\frac{x\text{g}}{0.5\text{dm}^3}} = \frac{5(0.5 - x)}{x}$$

From which; $20x = 2.5$; $x = 0.125\text{g}$

The mass of G remained in aqueous layer after further extraction is 0.125g.

Question 33

(a)

(i) $(0.2 + 12.25)\text{kPa} = 12.45\text{kPa}$

(ii) It would make no difference. The total vapour pressure will still be 12.45kPa because the vapour pressure of immiscible mixture is independent of the proportions of components.

(b) A liquid boils when its vapour pressure becomes equal to the atmospheric pressure. At 99°C , the total pressure is 100.1kPa ($2.34\text{kPa} + 97.76\text{kPa}$) which is slightly less than the atmospheric pressure. That means that it is close to, but below its boiling point.

Pure water must have a vapour pressure of 101.325kPa at 100°C (normal boiling point of water).

The combined water and ethyl benzoate vapour pressure reach 101.325kPa at temperature less than 100°C (boiling point of immiscible liquid mixture is less than either of the two components) and hence the mixture must boil somewhere between 99°C and 100°C .

Question 34

(a)

(i) Benzene-toluene and methanol-ethanol solution.

(ii) Hydrochloric acid solution (HCl-water solution) and acetone-chloroform solution.

(iii) Ethanol-water solution and benzene-phenol solution.

(iv) Hydrogen-platinum solution and copper-zinc solution (brass alloy).

(b) $n_{\text{benzene}} = \frac{m_{\text{benzene}}}{M_{\text{benzene}}} = \frac{3.88}{78} \text{ moles} = 0.04974\text{mol}$

$$n_{\text{toluene}} = \frac{m_{\text{toluene}}}{M_{\text{toluene}}} = \frac{2.45}{92} \text{ moles} = 0.02663\text{mol}$$

$$X_{\text{benzene}} = \frac{n_{\text{benzene}}}{n_{\text{benzene}} + n_{\text{toluene}}} = \frac{0.04974}{0.04974 + 0.02663} = 0.65$$

$$X_{\text{toluene}} = 1 - X_{\text{benzene}} = 1 - 0.65 = 0.35$$

The solution of benzene and toluene is ideal; therefore, it obeys Raoult's law.

$$\text{Then } P_{\text{soln}} = X_{\text{benzene}} P_{\text{benzene}}^0 + X_{\text{toluene}} P_{\text{toluene}}^0$$

$$P_{\text{soln}} = (0.65 \times 75)\text{mmHg} + (0.35 \times 22)\text{mmHg} = 56.45\text{mmHg}$$

$$\text{Then } X_{\text{benzene}}^V = \frac{P_{\text{benzene}}}{P_{\text{soln}}}$$

$$\text{But } P_{\text{toluene}} = X_{\text{benzene}} P_{\text{benzene}}^0 = (0.65 \times 75) = 48.75\text{mmHg}$$

$$\text{So } X_{\text{benzene}}^V = \frac{48.75\text{mmHg}}{56.45\text{mmHg}} = 0.86$$

Hence the mole fraction of benzene in the vapour is 0.86.

Question 35

- (a)
1. It avoids thermal decomposition
 2. Its equipment is relatively inexpensive
 3. It generates products which are free from organic solvents
 4. It does not involve subsequent separation steps
 5. It requires less fuel for extraction of oil

$$(b) X_A = \frac{n_A}{n_A + n_B} = \frac{0.65 \text{ mol}}{(0.25 + 0.65) \text{ mol}} = 0.72$$

$$X_B = 1 - X_A = 1 - 0.72 = 0.28$$

Since the solution obeys Raoult's law; $P_{\text{soln}} = X_A P_A^0 + X_B P_B^0$

$$\text{From which; } P_B^0 = \frac{P_{\text{soln}} - X_A P_A^0}{X_B}$$

But at normal boiling point of the solution; $P_{\text{soln}} = 1 \text{ atm}$

$$\text{Then substituting } P_B^0 = \frac{(1 - (0.72 \times 0.7)) \text{ atm}}{0.28} = 1.771 \text{ atm}$$

The vapour pressure of pure B is 1.771 atm

Question 36

- (a)
- (i) Decrease in concentration makes the solution more ideal while increase in concentration makes the solution to deviate more from ideal behaviour.
 - (ii) If the intermolecular forces in the solution are similar to intermolecular forces in pure components the solution will be more ideal while different intermolecular forces in the solution compared to those present in the pure components makes the solution to show greater deviation from ideal behaviour.

$$(b) P_x \text{ at } 95^\circ\text{C} = 760 \text{ mmHg} - P_w = (760 - 635) \text{ mmHg} = 125 \text{ mmHg}$$

$$\text{Using } \frac{m_x}{m_w} = \frac{P_x M_x}{P_w M_w}$$

$$\text{Substituting given values: } \frac{m_x}{m_w} = \frac{125 \times 160}{635 \times 18} = \frac{2000}{1143} \text{ or } m_x : m_w = 2000 : 1143$$

$$\text{If } m_x = 40 \text{ g; then } \frac{40 \text{ g}}{m_w} = \frac{2000}{1143}$$

$$m_w = \frac{1143 \times 40}{2000} \text{ g} = 22.86 \text{ g}$$

So mass of water in the distillate is 22.86 g

And mass of X in the distillate is 40 g (Given)

Hence the mass of the distillate is $(40 + 22) \text{ g} = 62 \text{ g}$

Question 37

- (a)
- (i) For the solution to be ideal it must obey Raoult's law over the **entire range of concentration (at any concentration)**. Even non-ideal solution may obey Raoult's if the solution is very dilute.
 - (ii) Formation of non-ideal solution with positive deviation is endothermic process and thus the solution becomes cold to touch. If the solution is warm to touch it must be non-ideal solution with negative deviation whose formation is exothermic process.

$$(b) \text{ Using } \frac{m_c}{m_w} = \frac{P_c M_c}{P_w M_w}$$

$$M_c = \text{molar mass of Chlorobenzene (C}_6\text{H}_5\text{Cl)} = 112.5 \text{ g/mol}$$

$$M_w = \text{molar mass of water} = 18 \text{ g/mol}$$

$$\text{Then } \frac{23.7}{10} = \frac{112.5 P_c}{18 P_w} \text{ or } \frac{P_c}{P_w} = 0.3792$$

$$\text{Thus } P_c - 0.3792 P_w = 0 \dots \dots \dots (i)$$

$$\text{But } P_c + P_w = 101300 \dots \dots \dots (ii)$$

Solving the two equations simultaneously gives:

$$P_c = 27852 \text{ Pa and } P_w = 73448 \text{ Pa}$$

The vapour pressure of water is 73448 Pa and the vapour pressure of chlorobenzene is 27852 Pa.

Question 38

- (a)
- Vapour pressure becomes smaller as intermolecular forces becomes stronger.
 - Vapour pressure is temperature dependent whereby it increases as temperature increases and hence it becomes necessary to state temperature at which vapour pressure has been measured.
 - High vapour pressure of a substance implies that smaller temperature raise is needed to increase the vapour pressure to atmospheric pressure and thus lower boiling point and hence high volatility of the substance.
- (b) Since the solution obeys Raoult's law: $P_{\text{soln}} = X_C P_C^0 + X_M P_M^0$ (where C stands for chloroform and M stands for methanol).

But $X_C + X_M = 1$

Or $X_M = 1 - X_C$

So $P_{\text{soln}} = X_C P_C^0 + (1 - X_C) P_M^0$

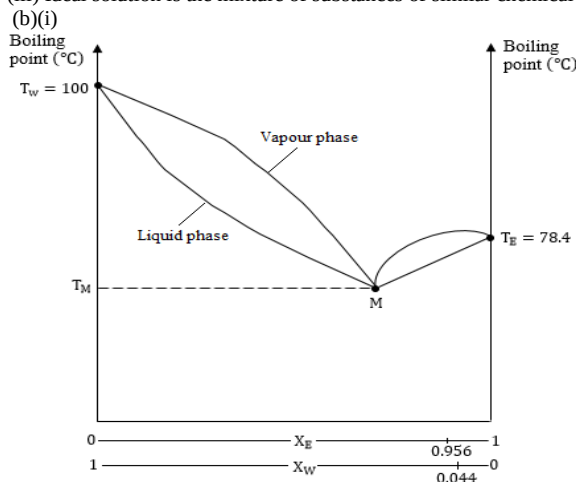
$P_{\text{soln}} = X_C (P_C^0 - P_M^0) + P_M^0$

Or $X_C = \frac{P_{\text{soln}} - P_M^0}{P_C^0 - P_M^0} = \frac{(0.255 - 0.192) \text{ atm}}{(0.311 - 0.192) \text{ atm}} = 0.53$

The mole fraction of chloroform in the solution is 0.53.

Question 39

- Is the saturated vapour pressure is the vapour pressure of the liquid in equilibrium with excess liquid at **given temperature**.
- Azeotropic point is the boiling point of the azeotropic mixture.
- Ideal solution is the mixture of substances of similar chemical structures and polarities.



Where: T_w is the boiling point of pure water

T_E is the boiling point of pure ethanol

T_M is the boiling point of azeotropic mixture (azeotropic point)

M is the azeotropic mixture

X_E is the mole fraction of ethanol

X_W is the mole fraction of water

(ii) The solution will boil in such a way that the vapour formed is richer in ethanol until its percentage in the collector rises to 95.6%. Finally on successive distillation and condensation the filtrate in the collector will be azeotropic mixture with 95.6% ethanol and the residue in the distillation flask will be pure water.

(iii) By introducing suitable dehydrating agent like calcium oxide (CaO) so as to remove water which is only 4.4%.

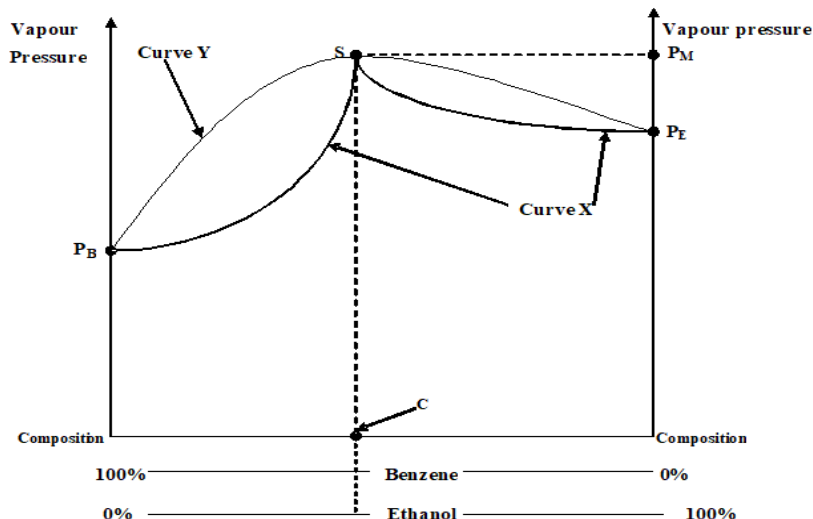
Question 40

- (a) Curve x represent vapour phase of the solution

Curve y represent liquid phase of the solution

- (b) **Q** is the vapour formed after distillation (boiling) of liquid **P** at given temperature and **R** is the liquid formed after condensation of vapour **Q**.

(c) A sketched graph to illustrate the vapour pressure – composition relationship for benzene ethanol system



Question 41

- (a) Non-volatile solute lowers vapour pressure of the solution. The lowering in vapour pressure means that the liquid solution will need higher temperature to raise its vapour pressure so that it equalises to atmospheric pressure and hence its boiling point elevates. Also the lowering in vapour pressure means that the solid phase of the solution will need lower temperature to raise its vapour pressure so that it equalises to the vapour pressure of liquid solution and hence lowering in freezing point.
- (b) Freezing point depression, $\Delta T = 0^\circ\text{C} - (-0.415^\circ\text{C}) = 0.415^\circ\text{C}$

$$\text{Using } \Delta T = iK_f m \text{ or } i = \frac{\Delta T}{K_f m} = \frac{0.415^\circ\text{C}}{1.86^\circ\text{C kg mol}^{-1} \times 0.118 m} = 1.89$$

$$\text{From } \pi V = nRT \text{ or } \pi = \frac{nRT}{V} = iCRT$$

$$\text{Substituting } \pi = iCRT = 1.89 \times 0.118 \times 0.082 \times 283 = 5.18 \text{ atm.}$$

Assumption: The solution is dilute (density of solution is equal to density of water) and thus the numerical value of molality (0.118m) is equal to the numerical value of molarity (0.118M).

Question 42

(a) Reason

Water flows into carrot by osmosis.

Explanation

Fresh water is hypotonic with respect to the carrot. So when limped carrot is placed in fresh water, the carrot absorbs water by osmosis and hence it regains its firmness.

$$(b) \text{ Using } \Delta T = K_b m = K_b \times \frac{m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$$

$$\text{Substituting } \Delta T = 0.52 \text{ K kg mol}^{-1} \times \frac{18 \text{ g}}{180 \text{ g/mol} \times 1 \text{ kg}} = 0.052 \text{ K}$$

But boiling point of pure water is 373K

Hence boiling point of solution = $(373 + 0.052) \text{ K} = 373.052 \text{ K}$

Question 43

- (a) "When a non-volatile solute is dissolved in the solvent at given temperature, the lowering of the vapour pressures of the solvent in the solution varies directly proportional to the mole fraction of the solute."

Derivation:

Consider a non-volatile solute is dissolved in a liquid solvent to form very dilute solution:

$$\text{By Raoult's law: } P_{sv} = X_{sv} P_{sv}^0$$

$$\text{and } P_{su} = X_{su} P_{su}^0$$

Where:

P_{sv} and P_{su} are partial vapour pressures exerted in solution by solvent and non-volatile solute respectively.

P_{sv}^o and P_{su}^o are vapour pressures of pure solvent and pure non-volatile solute respectively.

X_{sv} and X_{su} are mole fractions in the solution for solvent and non-volatile solute respectively.

By combining Raoult's law and Dalton's law of partial pressures: $P_{soln} = X_{sv} P_{sv}^o + X_{su} P_{su}^o$

But for non-volatile solute, $P_{su}^o = 0$

Then $P_{soln} = X_{sv} P_{sv}^o$

But $X_{sv} = 1 - X_{su}$ ($X_{sv} + X_{su} = 1$)

The $P_{soln} = (1 - X_{su}) P_{sv}^o$ or $P_{soln} = P_{sv}^o - X_{su} P_{sv}^o$ Or $X_{su} P_{sv}^o = P_{sv}^o - P_{soln}$

But $P_{sv}^o - P_{soln}$ = Lowering in the vapour pressure of the solvent, ΔP

It follows that: $\Delta P = X_{su} P_{sv}^o$

But P_{sv}^o is constant at given temperature

Hence $\Delta P \propto X_{su}$ (Raoult's law for lowering of vapour pressure)

(b) Because KI completely dissociates to give two ions per formula unit, $i = 2$.

Then using $\Delta T = iK_f m$

$$\text{Or } m = \frac{\Delta T}{iK_f} = \frac{(0 - (-1.95))^{\circ}\text{C}}{2 \times 1.86^{\circ}\text{C kg mol}^{-1}} = 0.5242 \text{ mol/kg}$$

Using $m = nM_r$;

Mass of the solute (KI) in 1kg (1000g) of the solvent = $0.5242 \text{ mol} \times 166 \text{ g/mol} = 87 \text{ g}$

Mass of the solution = $m_{su} + m_{sv} = (1000 + 87) \text{ g} = 1087 \text{ g}$

Thus mass of solution containing 87g of solute is 1087g

Also using $\pi V = nRT$ or $\pi = \frac{nRT}{V} = iCRT$

From which $C = \frac{\pi}{iRT} = \frac{25}{2 \times 0.082 \times 298} \text{ mol/L} = 0.51154 \text{ mol/L}$

Using mass concentration = molarity $\times$ molar mass

Mass concentration of the solute (KI) in the solution = $0.51154 \text{ mol/L} \times 166 \text{ g/mol} = 85 \text{ g/L}$

Using volume of solution = $\frac{\text{mass of solute}}{\text{volume of solution}}$

Volume of solution containing 87g of solute = $\frac{87 \text{ g}}{85 \text{ g/L}} = 1.0235 \text{ L} = 1023.5 \text{ mL}$

Thus mass of solution containing 87g of solute is 1023.5mL

Hence 1087g of the solution corresponds to 1023.5mL of the solution.

Using density of solution, $\rho = \frac{\text{mass of solution}}{\text{volume of solution}}$

Thus $\rho = \frac{1087 \text{ g}}{1023.5 \text{ mL}} = 1.062 \text{ g/mL}$

Density of the solution is 1.062g/mL

Question 44

(a)

(i) Osmosis is the spontaneous flow of solvent through semi-permeable membrane from a solution of low solute concentration to one of higher solute concentration whereas osmotic pressure is the external pressure required to be applied in the solution side to prevent osmosis in the solvent-solution system.

(ii) Yes.

Explanation:

From experiment, it can be shown that:

$$\pi V = nRT \text{ or } \pi = CRT \text{ where } C = \frac{n}{V}$$

Where π is the osmotic pressure exerted by n moles of solute dissolved in the solution of volume, V at absolute temperature, T .

If T is constant, RT gives another constant and the above equation becomes; $\pi = C \times \text{constant}$ or $\pi \propto C$

Since the osmotic pressure varies directly proportional to molar concentration, C ; it is colligative property.

$$(b) \Delta T = K_b m = K_b \times \frac{m_{su}}{M_{su} \times m_{sv} \text{ in kg}} = \frac{0.52 m_{su}}{342 \times 0.5} = 0.00304 m_{su}$$

Thus boiling point of solution = $100 + 0.00304 m_{su}$

$$\text{Also } \Delta T = K_f m = K_f \times \frac{m_{su}}{M_{su} \times m_{sv} \text{ in kg}} = \frac{1.86 m_{su}}{342 \times 0.5} = 0.0109 m_{su}$$

Thus freezing point of solution = $0 - 0.0109 m_{su} = -0.0109 m_{su}$

But; boiling point of solution – freezing point of solution = 105

$$\text{Thus } 100 + 0.00304 m_{su} - (-0.0109 m_{su}) = 105$$

From which $m_{su} = 359g$

Hence the required mass of sucrose to be added is 359g

Question 45

(a)

- 1.2% sodium chloride solution is hypertonic with respect to 0.9% sodium chloride solution or blood cells. So when red blood cells are placed in this solution, water flows out of the cell and they shrink due to loss of water by osmosis.
- 0.4% sodium chloride solution is hypotonic with respect to 0.9% sodium chloride solution or blood cells. So when red blood cells are placed in this solution, water flows into the cells through osmosis and they swell.

(b)

Constituent element	C	H	N	O
Percentage composition by mass	42.9	2.4	16.6	38.1
Mass of each in 100g of the compound	42.9g	2.4g	16.6g	38.1g
Number of moles of each; $n = \frac{m}{M_r}$	$\frac{42.9g}{12g/mol} = 3.575mol$	$\frac{2.4g}{1g/mol} = 2.4mol$	$\frac{16.6g}{14g/mol} = 1.1857mol$	$\frac{38.1g}{16g/mol} = 2.38125mol$
Divide by smallest to get simplest ratio	$\frac{3.575mol}{1.1857mol} = 3$	$\frac{2.4mol}{1.1857mol} = 2$	$\frac{1.1857mol}{1.1857mol} = 1$	$\frac{2.38125mol}{1.1857mol} = 2$

$$m_{sv} = \rho V = 0.779 \text{ g/mL} \times 75.0 \text{ mL} = 58.425 \text{ g} = 0.058425 \text{ kg}$$

$$\Delta T = 6.5^\circ\text{C} - 0^\circ\text{C} = 6.5^\circ\text{C}$$

$$\text{Using } \Delta T = K_f m = K_f \times \frac{m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$$

$$\text{From which; } M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}} = \frac{20.2 \times 3.16}{6.5 \times 0.058425} \text{ g/mol} = 168 \text{ g/mol}$$

Let the molecular formula be $(C_3H_2NO_2)_n$

$$\text{Then } 36n + 2n + 14n + 32n = M_r = 168; 84n = 168; n = 2$$

Hence molecular formula of the compound is $C_6H_4N_2O_4$

Question 46

(a)

- Molarity measures concentration of solute in the solution as the ratio of number of moles of the solute to the volume of the solution whereas molality is measured as the ratio of number of moles of the solute to the mass of solvent. Thus the unit of molarity is mol/L while that of molality is mol/kg.
- It is easier to measure volume and hence molarity with greater accuracy than to measure mass and hence molality.
- Measuring freezing point depression and boiling point elevation involve varying temperature of the solution; so because volume and thus molarity changes as temperature changes molarity does not suit in their measurements unlike mass and thus molality whose value is not affected by temperature change.
However, since measurements of osmotic pressure are done at fixed temperature (usually room temperature) the easier and more accurate method which is molarity is preferred to molality.

(b) Mass of an electrolyte (solute) in 100g of the compound is 18.2g

Mass of water (solvent) is 100g – 18.2g or 81.8g

$$\text{Using } n = \frac{m}{M_r};$$

$$n_{\text{su}} = \frac{18.2\text{g}}{162\text{g/mol}} = 0.1123\text{mol} \text{ and } n_{\text{sv}} = \frac{81.8\text{g}}{18\text{g/mol}} = 4.5444\text{mol}$$

$$X_{\text{su}} = \frac{n_{\text{su}}}{n_{\text{su}} + n_{\text{sv}}} = \frac{0.1123\text{mol}}{0.1123\text{mol} + 4.5444\text{mol}} = 0.0241$$

$$\text{Using } \Delta P = iX_{\text{su}}P_{\text{sv}}^{\circ}$$

$$\text{From which } i = \frac{\Delta P}{X_{\text{su}}P_{\text{sv}}^{\circ}} = \frac{(26.02 - 23.51)\text{torr}}{0.0241 \times 26.02\text{torr}} = 4$$

Hence the electrolyte dissociates into 4 ions per formula unit.

Question 47

(a) Molarity is given by the following formula; molarity = $\frac{\text{number of moles of solute}}{\text{volume of solution in dm}^3}$

Whereas molality is given by the following formula; molality = $\frac{\text{number of moles of solute}}{\text{mass of solvent in kg}}$

But density of water is 1kg/dm³. That is 1kg of solvent is contained in 1dm³.

Thus numerical value of mass of solvent in kg = numerical value of volume of the solvent in dm³.

It follows that: numerical value of molality = $\frac{\text{number of moles of solute}}{\text{Volume of solvent in dm}^3}$

Whereas, numerical value of molarity = $\frac{\text{number of moles of solute}}{\text{volume of solution in dm}^3}$

Where; volume of solution = volume of solvent + volume of solute

But for very dilute solution, volume of solute is negligible compared to the volume of the solvent and therefore;

$$\text{volume of solution} = \text{volume of solvent}$$

Therefore; numerical value of molarity = $\frac{\text{number of moles of solute}}{\text{volume of solvent in dm}^3}$

And hence numerical values of molality = numerical value of molarity if the solution is very dilute.

(b) Using $\pi_{\text{ob}}V = n_{\text{ob}}RT$

$$\text{Thus observed number of solute particles in the solution, } n_{\text{ob}} = \frac{\pi_{\text{ob}}V}{RT} = \frac{0.399 \times 1}{0.082 \times 298} \text{mol} = 0.01633\text{mol}$$

Assuming complete ionisation of each given salt:

MgCl₂ gives three ions per formula unit,

NaCl gives two ions per formula unit.

$$\text{It follows that if } x \text{ is the mass of MgCl}_2 \text{ in the mixture, then: } \pi_{\text{ob}} \text{ for MgCl}_2 = 3 \times \frac{x\text{g}}{95\text{g/mol}} = \frac{3x}{95} \text{mol}$$

$$\text{And } \pi_{\text{ob}} \text{ for NaCl} = 2 \times \frac{(0.5-x)\text{g}}{58.5\text{g/mol}} = \frac{1-2x}{58.5} \text{mol}$$

$$\text{Thus } \frac{3x}{95} + \frac{1-2x}{58.5} = 0.01633; 95 - 14.5x = 90.75$$

$$\text{From which; } x = 0.2931\text{g}$$

$$\%\text{MgCl}_2 = \frac{0.2931}{0.5} \times 100\% = 58.62\%$$

Hence the mass percent of MgCl₂ is approximately 59%.

Question 48

- (a) 4% starch solution

Reason:

4% starch solution having smaller solute concentration it is hypotonic solution compared to 6% starch solution and thus during osmosis solvent molecules will move from 4% starch solution to 6% starch solution. Consequently, the volume of 4% starch solution will decrease as osmosis occurs.

- (b) Using
- $m = \rho V$
- ;

Mass of the solution in 1L (1000mL) = $1.8\text{g/mL} \times 1000\text{mL} = 1800\text{g}$

Using $m = nM_r$;

Mass of the solute (KBr) in 1L of the solution = $2.7\text{mol} \times 119\text{g/mol} = 321.3\text{g}$

Thus mass of solvent (water) in 1L of the solution = $(1800 - 321.3)\text{g} = 1478.7\text{g} = 1.4787\text{kg}$

Then molality of the solution = $\frac{2.7\text{mol}}{1.4787\text{kg}} = 1.826\text{mol/kg}$

It follows that; $\Delta T = iK_b m$ (Where by assuming complete ionisation, $i = 2$)

$$= 2 \times 0.52^\circ\text{Ckgmol}^{-1} \times 1.4787\text{mol/kg} = 1.54^\circ\text{C}$$

But boiling point of pure water is 100°C

Hence the normal boiling point of the solution = $100^\circ\text{C} + 1.54^\circ\text{C} = 101.54^\circ\text{C}$

Question 49

- (a)

- (i)
- Name:**
- reverse osmosis.

Definition: Is the forced flow of solvent through semi-permeable membrane from the solution side to the solvent side by applying external pressure which is greater than osmotic pressure to the solution side.

(i) To fresh water container.

(ii) Semi-permeable membrane.

(iii) Film of cellulose acetate

(iv) **Desalination of water** in the purification of drinking water process (in potable water production).

- (b) Using
- $\pi V = nRT = \frac{m}{M_r} RT$
- or
- $\pi = \frac{mRT}{VM_r}$

Then for urea: $\pi_u = \frac{m_u RT}{VM_u} = \frac{8\text{g} \times RT}{1\text{L} \times 60\text{g/mol}}$

And for another solute: $\pi_{su} = \frac{m_{su} RT}{VM_{su}}$

Where mass of the solute in 100g of the solution is 5g.

But 5% solution is so dilute that $\rho_{\text{solution}} = \rho_{\text{water}} = 1\text{g/mL}$

Thus 100g of the solution is equivalent to 100mL (0.1L) of the solution.

Then $\pi_{su} = \frac{5\text{g} \times RT}{0.1\text{L} \times M_{su}}$

But $\pi_u = \pi_{su}$ (isotonic solutions)

$$\frac{8.6\text{g} \times RT}{1\text{L} \times 60\text{g/mol}} = \frac{5\text{g} \times RT}{0.1\text{L} \times M_{su}}$$

From which $M_{su} = \frac{5 \times 60\text{g/mol}}{0.1 \times 8.6} = 349\text{g/mol}$

Hence the molar mass is 349g/mol.

Question 50

- (a) In the solution,
- BaCl_2
- ionises to give three ions per formula unit while
- NaCl
- gives two ions per formula unit. As result,
- 0.1mBaCl_2
- has higher solute concentration leading to larger boiling point elevation and hence higher boiling point of the solution.

- (b)
- $P_{\text{soln}} = \frac{80}{100} \times P_{\text{sv}}^\circ = 0.8P_{\text{sv}}^\circ$

Then $\Delta P = P_{\text{sv}}^\circ - P_{\text{soln}} = 0.2P_{\text{sv}}^\circ$

Using $M_{su} = \frac{m_{su} \times M_{sv} \times P_{\text{sv}}^\circ}{m_{sv} \times \Delta P}$

$$\text{From which } m_{\text{su}} = \frac{m_{\text{sv}} \times \Delta P \times M_{\text{su}}}{M_{\text{sv}} \times P_{\text{sv}}^0} = \frac{114 \text{ g} \times 0.2 P_{\text{sv}}^0 \times 40 \text{ g/mol}}{114 \text{ g/mol} \times P_{\text{sv}}^0} = 8 \text{ g}$$

Hence the mass of the solute is 8g.

Question 51

(a) 0.12M in CaCl_2

Reason:

CaCl_2 being an electrolyte dissociates in the solution to give greater number of solute particles than the non-electrolyte, sucrose which does not dissociate in the solution. So 0.12M CaCl_2 has greater number of solute particles in the solution leading to more lowering in vapour pressure and hence lower vapour pressure of the solution.

(b) Using $n = \frac{m}{M_r}$;

$$n_{\text{su}} = \frac{50 \text{ g}}{342 \text{ g/mol}} = 0.1462 \text{ mol}$$

$$n_{\text{sv}} = \frac{500 \text{ g}}{18 \text{ g/mol}} = 27.7778 \text{ mol}$$

$$X_{\text{su}} = \frac{n_{\text{su}}}{n_{\text{su}} + n_{\text{sv}}} = \frac{0.1462 \text{ mol}}{0.1462 \text{ mol} + 27.7778 \text{ mol}} = 0.0052$$

$$\text{Using } \Delta P = X_{\text{su}} P_{\text{sv}}^0 = 0.0052 \times 23.8 \text{ mmHg} = 0.124 \text{ mmHg}$$

Hence the vapour pressure lowering is 0.124 mmHg

Question 52

(a)

(i) Theoretical value of Van't Hoff's factor is total number of ions formed per formula unit under assumption that the compound is completely dissociated in the solution. Hence the theoretical value of Van't Hoff's factor is 3.

(ii) Like any other ionic compound, MgCl_2 possess some degree of polarization and therefore some covalent characters with tendency of existing as molecule. So even after dissociation, **ion pairing** between some Mg^{2+} and Cl^- will occur leading to the formation of undissociated MgCl_2 and thus the number of solute particles in the solution is decreased. Hence the practical value of Van't Hoff's factor is less than 3.

(iii) By diluting the solution to infinite whereby the compound becomes almost completely dissociated and there so much water that hinder interaction between ions (which are very far apart due to dominance of water amount in the solution) and hence ion pairing becomes almost impossible.

$$(b) \Delta P = \frac{5}{100} \times P_{\text{sv}}^0 = 0.05 P_{\text{sv}}^0$$

$$\text{Using } M_{\text{su}} = \frac{m_{\text{su}} \times M_{\text{sv}} \times P_{\text{sv}}^0}{m_{\text{sv}} \times \Delta P}$$

$$\text{From which } m_{\text{su}} = \frac{m_{\text{sv}} \times \Delta P \times M_{\text{su}}}{M_{\text{sv}} \times P_{\text{sv}}^0} = \frac{100 \text{ g} \times 0.05 P_{\text{sv}}^0 \times 60 \text{ g/mol}}{18 \text{ g/mol} \times P_{\text{sv}}^0} = 16.67 \text{ g}$$

Hence the mass of the solute is approximately 17g

$$\text{Using molality} = \frac{n_{\text{su}}}{m_{\text{sv}} \text{ in kg}} = \frac{m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}} = \frac{17 \text{ g}}{60 \text{ g/mol} \times 0.1 \text{ kg}} = 2.8 \text{ mol/kg}$$

The molality of the solution is 2.8m

Question 53

(a) Sugar being non-volatile will lead to lowering of the vapour pressure of water in the solution as the solute reduce the chance of water vapour to escape into the air and it is also lowers the concentration of water.

(b) **First case:** Calculating molar mass of monobasic acid **B** by using the osmotic pressure

$$\text{From } M_r = \frac{mRT}{\pi V} = \frac{0.2 \times 0.082 \times 288 \times 760}{94.6 \times 1} \text{ g/mol} = 37.9 \text{ g/mol}$$

Thus molar mass of **B** in water is 37.9 g/mol

Second case: Calculating molar mass of monobasic acid **B** using freezing point depression:

$$\Delta T = K_f m = \frac{K_f m_B}{M_B \times m_{\text{benzene}} \text{ in kg}}$$

$$\text{From which: } M_B = \frac{K_f \times m_B}{\Delta T \times m_{\text{benzene}} \text{ in kg}}$$

$$\text{But } K_f = K_{1000} = \frac{K_{100}}{10} = \frac{49}{10} = 4.9 \text{ per } 1000 \text{ g}$$

$$\text{Substituting given values: } M_B = \frac{4.9 \times 4}{2.13 \times 0.1} \text{ g/mol}$$

Thus molar mass of **B** in benzene is 92 g/mol

Third Case: calculating molar mass of monobasic acid **B** by using volume of neutralisation of the acid.



From which mole ratio of HA to NaOH is 1: 1

Number of mole of NaOH = $\frac{10.9 \times 1}{1000}$ moles = 0.0109 moles

Thus number of moles of HA was also 0.0109 moles

From $n = \frac{m}{M_r}$, $M_r = \frac{m}{n}$

Molar mass of B in water = $\frac{0.5}{0.0109}$ g/mol = 46 g/mol

Thus formula mass of B (if there would be neither dissociation nor association of B) is 46 g/mol

CONCLUSION

Molar mass of B in benzene is twice the formula mass of B while in water is less than the formula mass. This suggests that, in water, B undergoes dissociation while in benzene, two molecules of B undergo association to form a dimer which corresponds with molecular formula of H_2A_2

Question 54

(a) $MgCl_2$ is better option.

Reason:

$MgCl_2$ is more effective because it gives greater number of ions per formula unit ($MgCl_2$ gives 3 ions while NaCl gives 2 ions) and therefore it exhibits greater freezing point depression per given amount.

(b) $M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}}$

But; $\Delta T = 0^\circ C - (-0.435)^\circ C = 0.435^\circ C$ (Pure water freezes at $0^\circ C$)

$M_{su} = \frac{1.86 \times 15}{0.435 \times 1} \text{ g/mol} = 64 \text{ g/mol}$

Observed molar mass of calcium nitrate ($Ca(NO_3)_2$) is 64 g/mol

But expected molar mass of $Ca(NO_3)_2 = 40 + (62 \times 2) = 164 \text{ g/mol}$

$i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{164}{64} = 2.5625$

Calcium nitrate dissociate according to the following equation.

$Ca(NO_3)_2 \rightleftharpoons Ca^{2+} + 2NO_3^{2-}$; $N = 3$

$\alpha = \frac{i - 1}{N - 1} = \frac{2.5625 - 1}{3 - 1} = 0.78125$ or 78.125%

Hence degree of dissociation of the salt is 78.125%

Question 55

(a) $0.08m CaCl_2 < 0.1m NaCl < 0.04m Na_2CO_3 < 0.1m$ sugar

(b) When naphthalene is dissolved in benzene:

Freezing point depression, $\Delta T = (5.481 - 4.91)^\circ C = 0.571^\circ C$

Using $\Delta T = \frac{K_f \times m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$

$0.571 = \frac{K_f \times 0.321}{128 \times 0.025}$ From which $K_f = 5.7^\circ C \text{ kg/mol}^{-1}$

So the molar freezing point depression constant for 1000g of benzene, K_f is $5.7^\circ C \text{ kg/mol}^{-1}$

When benzoic is dissolved in benzene:

Using $M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}} = \frac{5.7 \times 0.305}{(5.481 - 5.226)} \text{ g/mol} = 273 \text{ g/mol}$

Hence the relative molecular mass of benzoic acid in the benzene solution is 273.

Question 56

Using $M_{su} = \frac{K_b \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}}$

But $m_{sv} = m_{\text{water}} = \rho_{\text{water}} = 25 \text{ mL} \times \frac{0.997 \text{ g}}{\text{mL}} = 24.925 \text{ g}$

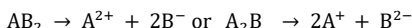
Boiling point of pure water is $100^\circ C$

So boiling elevation, $\Delta T = (100.45 - 100)^\circ C = 0.45^\circ C$

Then $M_{su} = \frac{0.52 \times 1.5}{0.45 \times 0.024925} \text{ g/mol} = 69.5 \text{ g/mol}$

(a) The molar mass of the compound if it is non-electrolyte is 69.5 g/mol

(b) Ideally, the ionic compound exists as ions i.e. it tends to ionise completely according to the following equations:



Either of the two equations gives the following results:

Expected number of particles = 1

Observed number of particles = 3

Since number of particles varies inversely proportional to the molar mass of the compound.

$$\frac{\text{Observed number of particles}}{\text{Expected number of particles}} = \frac{\text{Expected molar mass}}{\text{Observed molar mass}}$$

But expected molar mass = molar mass of the compounds obtained before ionisation (dissociation) and it is actual molar mass as suggested by its normal molecular formula

And observed (experimental) molar mass is the molar mass obtained after dissociation (chemical reaction) of the compound = Molar mass obtained in boiling elevation experiment = 69.5g/mol

It follows that:
$$\frac{3}{1} = \frac{\text{Expected molar mass}}{69.5}$$

Expected molar mass = $69.5 \times 3 = 208.5\text{g/mol}$

Hence the actual molar mass of the compound is 208.5g/mol

(c) The formula from boiling elevation is after ionisation of the compound which gives unexpectedly greater number of solute particles (ions) thus leading to unexpectedly higher boiling point elevation and hence the formula from experiment gives smaller molar mass than the actual molar mass calculated from the actual formula of the compound (AB_2 or A_2B)

$$i = \frac{\text{Observed number of particles}}{\text{Expected number of particles}} = \frac{3}{1} = 3$$

Van't Hoff's factor, i , is 3

Question 57

(a)

(i) Van't Hoff's factor is greater than 1.

Reason:

CH_3COOH being an electrolyte undergoes dissociation in water.

(ii) Van't Hoff's factor is smaller than 1.

Reason:

In a solvent which has no hydrogen bonds, CH_3COOH undergoes association (dimerization) to form dimer.

(iii) Van't Hoff's factor is equal to 1.

Reason:

$\text{CO}(\text{NH}_2)_2$ being non-electrolyte undergoes neither dissociation nor association in water.

(b) Using $\Delta P = \frac{m_{\text{urea}} \times M_{\text{water}} \times P_{\text{water}}}{M_{\text{urea}} \times m_{\text{water}}}$

Substituting given values: $2.5 = \frac{m_{\text{urea}} \times 18 \times 31.8}{60 \times 450}$

$m_{\text{urea}} = 117.9\text{g}$

Mass of urea is 117.9g

Question 58

(a) The elevation in boiling point is a colligative property and depends upon the number of moles of solute added. Higher the concentration of solute added, higher will be the elevation in boiling point. Thus, 2M glucose solution has higher boiling point than 1 M glucose solution.

(b) When the external pressure applied becomes more than the osmotic pressure of the solution, then the solvent molecules from the solution pass through the semipermeable membrane to the solvent side. This process is called reverse osmosis.

(c) $\Delta P = P - P_{\text{soln}} = (0.196 - 0.194)\text{atm} = 0.002\text{atm}$

Using: $M_{\text{su}} = \frac{m_{\text{su}} \times M_{\text{sv}} \times P}{\Delta P \times m_{\text{sv}}}$

Substituting given values: $M_{\text{su}} = \frac{2 \times 18 \times 0.196}{0.002 \times 90.1} = 39\text{g/mol}$

Hence the approximate molecular mass of the solute is 39g/mol

Question 59

(a) The osmotic pressure method has the advantage over elevation in boiling point or depression in freezing point for determining molar masses of macromolecules because:

1. Osmotic pressure is measured at the room temperature and the molarity of solution is used instead of molality.
2. Compared to other colligative properties, its magnitude is large and therefore measurable even for very dilute solutions.

(b) $\Delta T = \frac{K_b \times m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}} = \frac{2.53 \times 2.4}{154 \times 0.075} ^\circ\text{C} = 0.53^\circ\text{C}$

Boiling point of solution = $T_o + \Delta T = (80.1 + 0.53)^\circ\text{C} = 80.63^\circ\text{C}$

Question 60

- (a) When a non-volatile solute is dissolved in a solvent, the vapour pressure decreases. As a result, the solvent freezes at a lower temperature.
 (b) Using $M_r = \frac{mRT}{\pi V}$;

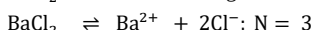
$$\text{Substituting given values: } M_r = \frac{10 \times 0.082 \times 288}{3.2 \times 1} = 73.8 \text{ g/mol}$$

Thus the observed molar mass of BaCl_2 is 73.8 g/mol

But the expected molar mass of $\text{BaCl}_2 = 137 + (2 \times 35.5) = 208 \text{ g/mol}$

$$i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{208}{73.8} = 2.818$$

BaCl_2 dissociate according to the following equation:



$$\alpha = \frac{i - 1}{N - 1} = \frac{2.818 - 1}{3 - 1} = 0.909 \text{ or } 90.9\%$$

Hence the apparent degree of dissociation of BaCl_2 is 90.9%

Question 61

- (a) Hypertonic solution is C: 0.1M aqueous ammonium phosphate.

Explanation:

With formula $(\text{NH}_4)_3\text{PO}_4$, ammonium phosphate undergoes dissociation in aqueous solution to give four ions per molecule and therefore giving greatest concentration of solute in the solution and hence highest osmotic pressure.

- (b) Using;

$$\Delta T = \frac{K_f m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}};$$

$$m_{\text{sv}} = m_{\text{water}} = \rho V = 6000 \text{ cm}^3 \times \frac{1 \text{ g}}{\text{cm}^3} = 6000 \text{ g} = 6 \text{ kg}$$

$$\text{Then } 13 = \frac{1.86 \times m_{\text{su}}}{62 \times 6}; m_{\text{su}} = 2600 \text{ g or } 2.6 \text{ kg}$$

Mass of ethylene glycol required is 2.6 kg

Question 62

- (a) Adding the salt which is non-volatile causes freezing point depression and therefore makes melting point of the resulting solution to be below ice temperature and hence the ice will melt upon addition of the salt.

$$(b) \text{ From } \pi V = \frac{mRT}{M_r}, \quad \frac{m}{v} = \frac{\pi M_r}{RT}$$

$$\text{So } C = \frac{\pi M_r}{RT} = \frac{2.32 \times 180}{0.082 \times 285} = 17.9 \text{ g/dm}^3$$

Hence concentration of glucose is 17.9 g/dm³

Question 63

- (a) Isotonic solutions have the same osmotic pressure which means equal concentration and hence osmosis will not occur.

$$(b) \text{ Using } \Delta P = \frac{m_{\text{su}} \times M_{\text{sv}} \times P_{\text{sv}}}{M_{\text{su}} \times m_{\text{sv}}} = \frac{4.1 \times 78 \times 10000}{128 \times 60} \text{ Nm}^{-2} = 416.4 \text{ Nm}^{-2}$$

Thus the lowering in vapour pressure of benzene is 416.4 Nm⁻²

New vapour pressure of benzene in the solution = (10000 - 416.4) Nm⁻² = 9583.6 Nm⁻²

Hence the vapour pressure of benzene in the solution will be decreased to 9583.6 Nm⁻² after dissolving the given amount of naphthalene

Question 64

- (a) The Van't Hoff's factor is large when the degree of dissociation (or ionisation) is large too. When the solution is more concentrated, the degree of dissociation is lowered and therefore the Van't Hoff's factor becomes smaller.

$$(b) \text{ Using } \Delta P = \frac{m_{\text{su}} \times M_{\text{sv}} \times P_{\text{sv}}}{M_{\text{su}} \times m_{\text{sv}}}$$

$$\text{Where: } \Delta P = P_{\text{sv}} - P_{\text{soln}} = (2333 - 2311) \text{ Nm}^{-2} = 22 \text{ Nm}^{-2}$$

$$M_{\text{su}} = 342 \text{ g/mol}$$

$$M_{\text{sv}} = 18 \text{ g/mol}$$

$$P_{\text{sv}} = 2333 \text{ Nm}^{-2}$$

$$\text{Then } 22 = \left(\frac{m_{\text{su}}}{m_{\text{sv}}} \right) \times \frac{18 \times 2333}{342}, \quad \frac{m_{\text{su}}}{m_{\text{sv}}} = \frac{342 \times 22}{18 \times 2333} = 0.1792$$

Neglecting volume of sucrose, so that $V_{\text{soln}} = V_{\text{water}}$

$$\text{Then } m_{\text{sv}} = \rho_{\text{water}} \times V_{\text{soln}}$$

But $\rho_{\text{water}} = 1\text{gcm}^{-3} = 1000\text{g/dm}^3$

$$\text{So } \frac{m_{\text{su}}}{V_{\text{soln}} \times 1000\text{gdm}^{-3}} = 0.1792, \quad \frac{m_{\text{su}}}{V_{\text{soln}}} = 0.1792 \times 1000\text{gdm}^{-3} = 179.2\text{gdm}^{-3}$$

But $\frac{m_{\text{su}}}{V_{\text{soln}}} = \text{mass concentration of solute(sucrose)}$

Hence the concentration of sucrose is 179.2g/dm^3

Question 65

- (a) Whether is through formation of precipitate of lead (II) chloride whereby two moles of chloride ions form one mole of lead (II) chloride precipitate or through formation of complex whereby four moles of chloride ions form one mole of complex $[\text{PbCl}_4]^{2-}$, the introduction of lead (II) ions decreases number of solute particles which means less lowering in vapour pressure and hence increase in vapour pressure.
- (b) Mass of the compound in 100g of solution is 2g

Then mass of water in 100g of solution is $(100-2)\text{g} = 98\text{g}$

$$\text{Using } M_{\text{su}} = \frac{K_b \times m_{\text{su}}}{\Delta T \times m_{\text{sv}} \text{ in kg}} = \frac{0.52 \times 2}{(99.877 - 99.7) \times 0.098} = 60\text{g/mol}$$

The relative molecular mass of the compound is 60

Question 66

- (a)
- In determining molar mass of non-volatile solute.
 - In estimating degree of dissociation of solute in a solvent.
 - In making anti-freeze (mixture of ethylene glycol and water) to prevent freezing of radiator in automobiles.
 - In salting roads so as to prevent formation of ice over the road in cold regions.

(b) Using $M_{\text{su}} = \frac{K_b \times m_{\text{su}}}{\Delta T \times m_{\text{sv}} \text{ in kg}}$

Where boiling point of pure ethanol is 78.1°C

$$K_b = 1.07^\circ\text{C mol}^{-1}\text{kg} \text{ and } m_{\text{sv}} = 16.15\text{g} = 0.01615\text{kg}$$

Boiling point/ $^\circ\text{C}$	Mass benzoic acid dissolved/ g	Relative molecular mass
78.230	0.2400	122.315
78.360	0.4727	120.455
78.505	0.7470	122.202

$$\text{Then finding average of relative molecular masses, } \frac{122.315 + 120.455 + 122.202}{3} = 121.657$$

Hence the relative molecular mass of benzoic acid is 121.657

Question 67

- (a) 0.1MBaCl_2

Explanation:

Van't Hoff's factor is high when degree of ionisation (dissociation) is high. BaCl_2 being more ionic as result of its lower degree of polarization resulted from weaker polarizing power of larger sized Ba^{2+} than Ca^{2+} in CaCl_2 has greater degree of ionisation in aqueous solution.

(b) Using $M_{\text{su}} = \frac{K_b \times m_{\text{su}}}{\Delta T \times m_{\text{sv}} \text{ in kg}}$

$$\text{Thus molecular mass of sulphur} = \frac{2.35 \times 0.36}{0.14 \times 0.024} = 252\text{g/mol}$$

Let the molecular formula of sulphur be S_n

$$\text{Then } 32n = M_r = 252 \text{ or } n = 8$$

Hence the molecular formula of sulphur in carbon disulphide is S_8

Question 68

- (a) As a solution freezes, the solvent molecules are removed from the solution which causes an increase in the concentration. This causes further freezing temperature depression.
- (b) Mass of solution in a car radiator = $\rho V = 4\text{dm}^{-3} \times 1\text{kgdm}^{-3} = 4\text{kg} = 4000\text{g}$

Let the least mass of glycerol be yg

The mass of water (solvent) = $(4000 - y)\text{g}$.

$$\text{Using } \Delta T = \frac{K_f \times m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}$$

It follows that: $6 = \frac{1.86y \times 1000}{92 \times (4000 - y)}$ or $y = 923\text{g}$

Hence the least mass of glycerol is 923g

Question 69

(a)

(i) Van't Hoff theory of dilute solutions

(ii) **First law:**

For dilute solution of a given solute, at constant temperature, the osmotic pressure of the solution is directly proportional to its mass concentration.

Second law:

The osmotic pressure of given concentration of solution is directly proportional to its absolute temperature.

Third law:

Osmotic pressure and temperature being the same, equal volumes of solution contains equal number of moles (or molecules) of the solute.

$$(b) \text{ Using } \frac{\pi_2}{T_2} = \frac{\pi_1}{T_1}, \quad \pi_2 = \frac{T_2}{T_1} \times \pi_1$$

Where $T_1 = 15^\circ\text{C} = 288\text{K}$, $T_2 = 0^\circ\text{C} = 273\text{K}$, $\pi_1 = 100000\text{Nm}^{-2}$

Then $\pi_2 = \frac{273}{288} \times 100000\text{Nm}^{-2} = 94792\text{Nm}^{-2}$

Hence the osmotic pressure at 0°C is 94792Nm^{-2}

Question 70

(a) For dissociation the Van't Hoff's factor is greater than one and its value is large when the degree of dissociation (or ionisation) is large too. When the solution is more concentrated, the degree of dissociation is lowered and therefore the Van't Hoff's factor becomes smaller. In some cases, high concentration may lead to association between solute particles making the factor much smaller where it becomes less than one.

$$(b) \quad C_1 = \frac{7\text{g}}{100\text{cm}^3} = 0.07\text{g/cm}^{-3}$$

$\pi_1 = 9.3\text{atm}$, $T_1 = 18^\circ\text{C} = 291\text{K}$, $\pi_2 = 10\text{atm}$, $T_2 = 10^\circ\text{C} = 283\text{K}$

$$\text{Using } \frac{\pi_1}{C_1 T_1} = \frac{\pi_2}{C_2 T_2}$$

$$\text{From which } C_2 = \left(\frac{\pi_2}{\pi_1}\right) \left(\frac{T_1}{T_2}\right) C_1 = \frac{10 \times 291 \times 0.07}{9.3 \times 283} \text{gcm}^{-3} = 0.0774\text{gcm}^{-3}$$

But the volume of second solution is 250 cm^3

Using $m = CV$

Then required mass of the compound is $0.0774 \times 250\text{g} = 19.35\text{g}$

Hence the required mass of the compound is 19.35g

Question 71

(a) The Van't Hoff's factor approaches the ideal value when the salt undergoes complete ionisation. FeCl_3 having higher degree of polarisation as result of greater polarising power of smaller sized and higher charged Fe^{3+} than Na^+ in NaCl , is more covalent in character and hence it has lower degree of ionisation than NaCl .

$$(b) \text{ Using } M_r = \frac{mRT}{\pi V}$$

Then M_r for the acid = $\frac{1 \times 0.082 \times 285 \times 760}{288 \times 1} \text{gmol}^{-1} = 61.67 \text{gmol}^{-1}$

Hence the relative molecular mass of the acid is 61.67

$$\Delta T = \frac{K_f \times m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}} = \frac{1.86 \times 1}{61.67 \times 1} = 0.03^\circ\text{C}$$

(Assuming density of solution = density of water = 1kg/dm^3)

Freezing point depression = 0.03°C

Freezing point = $0^\circ\text{C} - 0.03^\circ\text{C} = -0.03^\circ\text{C}$

Hence the freezing point of the solution is -0.03°C

Question 72

(a)

(i) A solute in a solution behaves exactly like a gas and the osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature occupying the same volume.

(ii) The depression of the freezing point of dilute solutions is proportional to the amount of the dissolved substance.

$$(b) \text{ For urea solution: } \pi V = \frac{mRT}{M_r} \text{ or } \pi = \frac{mRT}{M_r}$$

but $\frac{m}{V} = \text{Mass concentration, } C$

$$\text{Thus } \pi = \frac{CRT}{M_r} = \frac{1.754RT}{60} \dots \dots \dots (i)$$

$$\text{For sugar solution: } \pi = \frac{CRT}{M_r} = \frac{10RT}{M_r} \dots \dots \dots (ii)$$

Since the two solutions are isotonic (have the same osmotic pressure)

$$\text{Then (i) = (ii) or } \frac{10RT}{M_r} = \frac{1.754RT}{60} \text{ or } M_r = \frac{60 \times 10}{1.754} \text{ g mol}^{-1} = 342 \text{ g mol}^{-1}$$

Hence the relative molecular mass of the sugar is 342

Question 73

(a)

(i)

1. Lowering in vapour pressure
2. Freezing point depression
3. Boiling point elevation

(ii)

1. Beckmann's method
2. Landsberger's method

(iii) Diluted solution

Explanation

Better result of determination of molar mass by colligative properties are obtained when the solution is almost ideal and the solution containing non-volatile solution becomes almost ideal when it is dilute.

(iv) Reason to oppose:

It is difficult to measure osmotic pressure as it requires a more advanced apparatus and hence the experiment cannot be carried out as an ordinary laboratory process.

Reason to support:

1. The osmotic pressure measurements are taken around room temperature.
2. The molarity of the solution is used in measuring osmotic pressure instead of molality. It is easier to measure molarity than molality.
3. It is useful for determination of molar mass of biomolecules (polymers) as they are generally not stable at higher temperatures.
4. It is useful for determination of molar mass of substances with large molar mass as the osmotic pressure is measurable for those substances unlike boiling point elevation and freezing point depression.

(b) Using $\pi = \frac{CRT}{M_r}$

For solution A: $\pi_A = \frac{C_A \times R \times 273}{M_{\text{glucose}}}$

For solution B: $\pi_B = \frac{C_B \times R \times 293}{M_{\text{glucose}}}$ but $\pi_A = \pi_B$

It follows that: $\frac{C_B \times R \times 293}{M_{\text{glucose}}} = \frac{C_A \times R \times 273}{M_{\text{glucose}}} = 324100$

For $\frac{C_B \times 0.082 \times 293}{180} = \frac{324100}{103100}$; $C_B = 23.55 \text{ g/dm}^3$

For $\frac{C_A \times 0.082 \times 273}{180} = \frac{324100}{103100}$; $C_A = 25.28 \text{ g/dm}^3$

$C_A - C_B = (25.28 - 23.55) \text{ g/dm}^3 = 1.73 \text{ g/dm}^3$

Hence there is 1.73g more grams of glucose per dm³ of solution A than of solution B.

Question 74

(a)

- (i) Non-volatile ions and compounds present in the water in the beef lower the freezing point of the beef below -1 °C.
- (ii) Unlike glycerine which is non-electrolyte (covalent), NaCl being strong ionic (electrolyte) ionises almost completely to give twice as much as its number of moles.

(b)

Concentration in g/dm ³ , C	Osmotic pressure in mmHg	Osmotic pressure in atm, π	R in atmdm ³ K ⁻¹ Using: $R = \frac{\pi M_r}{CT}$
10	535	0.70	0.083
20	1016	1.34	0.080
40	2082	2.74	0.081
60	3075	4.05	0.080

Finding the average of $R = \frac{R_1 + R_2 + R_3 + R_4}{4} = \frac{0.083 + 0.080 + 0.081 + 0.080}{4} = 0.081 \text{ atm dm}^3 \text{ K}^{-1} \approx R$ in gases

Hence there is the analogy between gases and dilute solution as both have similar value of molar gas constant.

Question 75

(a) $0.01 \text{M Ba}_3(\text{PO}_4)_2 < 0.01 \text{M Li}_3\text{PO}_4 < 0.01 \text{M Na}_2\text{SO}_4 < 0.01 \text{M KCl} < 0.01 \text{M C}_2\text{H}_5\text{OH}$

Reason:

Freezing points of given solutions are lower than that of pure water and the depression varies directly proportional to the number of particle (concentration) of solute formed after ionisation. The number decreases in order of $\text{Ba}_3(\text{PO}_4)_2$, Li_3PO_4 , Na_2SO_4 , KCl and finally $\text{C}_2\text{H}_5\text{OH}$ which does not ionise at all and hence the freezing points of solutions follow the reverse order.

(b) Molarity of monobasic acid, $\text{HA} = 1 \text{ mol/dm}^3$ (A molar solution)

But for very dilute solution

Volume of solution = Volume of water (solvent) = 1 dm^3

And density of solution = Density of water = 1 kg/dm^3

So mass of water (solvent) $1 \text{ kg/dm}^3 \times 1 \text{ dm}^3 = 1 \text{ kg}$

Therefore molality of monobasic acid = 1 mol/kg

(Generally if the solvent is water and the solution is very dilute then the numerical value of molarity = numerical value of molality)

Expected freezing point depression, $\Delta T = K_f m = 1.86 \times 1^\circ\text{C} = 1.86^\circ\text{C}$

But observed freezing point depression = $0^\circ\text{C} - (-1.93^\circ\text{C}) = 1.93^\circ\text{C}$

Vant hoff's factor, $i = \frac{\text{Observed colligative property}}{\text{Expected colligative property}} = \frac{\text{Observed freezing point depression}}{\text{Expected freezing point depression}} = \frac{1.93}{1.86} = 1.0376$

The acid (HA) ionises according to the following equation:



Then $\alpha = \frac{i - 1}{N - 1} = \frac{1.0376 - 1}{2 - 1} = 0.0376$ or 3.76%

The degree of ionisation of the acid is 3.76% $\pi = \frac{i n R T}{V}$

But $\frac{n}{V} = [\] = 1 \text{ M}$

Thus $\pi = i [\] R T = 1.0376 \times 1 \times 0.082 \times 285 \text{ atm} = 24.25 \text{ atm}$

Hence the osmotic pressure of the solution is 24.25 atm

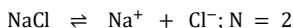
Question 76

(a)

- Is the process of measuring freezing point depression so as to determine molar mass of non – volatile solute.
- Is the process of measuring boiling point elevation so as to determine molar mass of the non-volatile solute.
- If the two solutions have the same freezing point, then the freezing point depression, ΔT of their solution are also equal.

For NaCl solution

NaCl ionises according to the following equation:



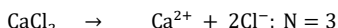
So if the compound ionises completely (entirely dissociated), $i = N = 2$.

And $\Delta T = \frac{i K_f m_{\text{NaCl}}}{M_{\text{NaCl}} \times m_{\text{sv}} \text{ in kg}} = \frac{2 \times 3 K_f}{58.5 \times 1} = \frac{4 K_f}{39}$

So $\Delta T = \frac{4 K_f}{39} \dots \dots \dots$ (i)

For CaCl_2 solution

CaCl_2 ionises according to the following equation:



So if the compound ionises completely, $i = 3$.

If the required mass of CaCl_2 is m

Then $\Delta T = \frac{3 K_f \times m}{111 \times 0.1} = \frac{10 m K_f}{37} \dots \dots \dots$ (ii)

Since freezing point depression is the same for the two solutions. It follows that by equating (i) and (ii) gives: $\frac{4 K_f}{39} = \frac{10 m K_f}{37}$

or $m = \frac{4 \times 37}{39 \times 10} \text{ g} = 0.379 \text{ g}$

The mass of anhydrous calcium chloride per 100 g of water is 0.379 g

Question 77

- (a)
- Are properties of solution which depend on the relative amount of solute and solvent but not on the nature of the solute. Are properties of solution which are boiling point elevation, boiling point elevation, lowering in vapour pressure and osmotic pressure.
 - Is the temperature at which vapour pressure exerted by liquid phase of a substance is equal to that exerted by its solid phase. Is the temperature at which liquid phase and solid phase of the substance co-exist at equilibrium.
 - Is the component of the solution which does not produce vapour at the boiling point of solution. Non-volatile solutes are substances with low vapour pressure and high boiling point.
 - Is the temperature at which vapour pressure of a substance is equal to atmospheric pressure (external pressure). Is the temperature at which liquid phase and gas phase of the substance are at equilibrium.
- (b) **For NaCl:** Using $\alpha = \frac{i-1}{N-1}$ Where $\alpha = 0.97$ and $N = 2$

$$\text{Then } 0.97 = \frac{i-1}{2-1} \text{ or } i = 1.97 ;$$

$$\text{It follows that } \Delta T = iK_f m = \frac{iK_f m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$$

1dm³ of water = 1kg of water;

$$\text{Then } \Delta T = \frac{1.97 \times 20K_f}{58.5} = \frac{394K_f}{585} \dots \dots \dots (i)$$

For glycerol (covalent solute which neither associate nor dissociate in the solution)

$$\Delta T = \frac{m_g K_f}{62 \times 1} \dots \dots \dots (ii)$$

Equating (i) and (ii) (The two solutions have the same anti-freezing effect)

$$\frac{394K_f}{585} = \frac{m_g K_f}{62}, \quad m_g = \frac{62 \times 394}{585} g = 41.76g$$

Mass of glycerol which is required is 41.76g

Question 78

- (a) Not satisfactory

Explanation:

Osmotic pressure as one of colligative properties is only applicable when the solution is ideal which demands the solution to be dilute and not concentrated.

- (b) **For non- electrolyte solute:**

$$K_f = \frac{\Delta T \times M_{su} \times m_{sv} \text{ in kg}}{m_{su}} = \frac{0.167 \times 58 \times 0.09}{0.47} = 1.85^\circ \text{Ckgmol}^{-1}$$

For zinc chloride solution

$$\text{Using } M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}} = \frac{1.85 \times 2.9}{0.111 \times 1} \text{g mol}^{-1} = 48.33 \text{g/mol}$$

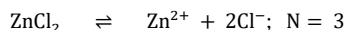
Observed molar mass of zinc chloride = 48.33g/mol

But expected molar mass of zinc chloride (ZnCl₂)

$$= 65 + (2 \times 35.5) = 136 \text{g/mol}$$

$$\text{Using } i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{136}{48.33} = 2.814$$

ZnCl₂ Ionises (dissociates) according to the following equation:



$$\alpha = \frac{i-1}{N-1} = \frac{2.814-1}{3-1} = 0.907 \text{ or } 90.7\%$$

Apparent degree of dissociation of zinc chloride is 90.7%

Question 79

- (a) (i) Colligative properties are properties of solution which depend on the relative amount of solute and solvent and not on the nature of the solute.

These are: lowering of vapour pressure, boiling point elevation, freezing point depression and osmotic pressure.

$$(b) \text{ Using } M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}} = \frac{5 \times 0.75}{0.255 \times 0.125} = 118 \text{g/mol}$$

Since the observed molar mass is almost twice the expected molar mass of ethanoic acid (the expected molar mass of ethanoic acid as its molecular formula, CH₃COOH suggests is 60g/mol), the acid exists as a **dimer** in benzene solution

Question 80

(a) (i) Boiling point of a liquid is the temperature at which vapour pressure of the liquid is equal to the atmospheric (external) pressure.

(ii) Increase in external pressure increases boiling point and vice versa.

(b) KI ionises according to the following equation: $\text{KI} \rightarrow \text{K}^+ + \text{I}^-$; $N = 2$

So since the salt ionises (dissociates) completely, $i = 2$

$$\text{Using } \Delta T = \frac{iK_f m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}} = \frac{2 \times 1.8 \times 1.66}{166 \times 0.1} ^\circ\text{C} = 0.36^\circ\text{C}$$

$$\text{Freezing point of solution} = T_o - \Delta T$$

Where T_o is the freezing point of pure water 0°C

$$\text{Freezing point of the solution} = 0^\circ\text{C} - 0.36^\circ\text{C} = -0.36^\circ\text{C}$$

The solution will freeze at -0.36°C

Question 81

(a)

(i) Are properties of the solution which depend on relative amount of solute and solvent and not on the nature of the solute.

(ii) Is the boiling point elevation of the solvent in the solution which is obtained when one mole of non-volatile solute is dissolved in 1kg of solvent.

(iii) Is the pressure required to be applied to the side of higher solute concentration so as to prevent movement of solvent molecules by osmosis.

(b) Using $\Delta T = iK_b \times \text{Molality}$

Where; $\Delta T = (104.4 - 100)^\circ\text{C} = 4.4^\circ\text{C}$ (100°C is the boiling point of pure water).

And $K_b = 0.512^\circ\text{C kg mol}^{-1}$ (Given)

Substituting $4.4^\circ\text{C} = 1.8 \times 0.512^\circ\text{C kg mol}^{-1} \times \text{Molality}$

$$\text{Molality} = 4.7743 \text{ mol/kg}$$

Thus the required molality for the NaCl solution to boil at 104.4°C is 4.7743 mol/kg

$$\text{But } \% \left(\frac{m}{m} \right) \text{ of NaCl} = \left(\frac{\text{mass of NaCl}}{\text{mass of solution}} \right) \times 100\%$$

$$\text{And mass of NaCl} = n_{\text{NaCl}} \times M_{\text{NaCl}} = 4.7743 \text{ mol} \times 58.5 \text{ g/mol} = 279.29655 \text{ g}$$

$$\text{The mass of solution mass of NaCl (solute) + mass of H}_2\text{O (solvent)} = (279.29655 \text{ g}) + (1000 \text{ g}) = 1279.29655 \text{ g}$$

$$\text{Thence } \% \left(\frac{m}{m} \right) \text{ of NaCl} = \left(\frac{279.29655 \text{ g}}{1279.29655 \text{ g}} \right) \times 100\% = 21.8 \%$$

Whence in terms of mass percentage, 21.8% NaCl boils at 104.4°C .

But the given mass percentage is 13.5% which is smaller than the required 21.8%; hence **the solute would be added** to increase the percentage and make the boiling point of solution 104.4° .

$$\text{Using mass} = \text{Density} \times \text{Volume}$$

$$\text{Mass of the given solution} = 1.12 \text{ g/mL} \times 100 \text{ mL} = 112 \text{ g}$$

$$\text{Out of which; mass of NaCl} = \frac{13.5}{100} \times 112 \text{ g} = 15.12 \text{ g. Then let mass of NaCl added be } x \text{ in grams.}$$

$$\text{It follows that } 21.8 = \left(\frac{15.12+x}{112+x} \right) \times 100; \text{ From which } x = 11.9$$

Hence the mass of NaCl added is 11.9 g

Question 82

(a)

(i) Molarity

Explanation:

Molarity depends on the volume which is temperature dependent unlike molality which depends on mass and the mass is not affected by temperature.

(ii) Measurement of freezing point depression or boiling point elevation involves changing the temperature of the solution, the action which would change the molarity of the solution. Since molality is temperature independent, it becomes more appropriate to be used in their respective mathematical equations than molarity.

(b) From Raoult's law of relative lowering in the vapour pressure:

$$X_{\text{su}} = \frac{\Delta P}{P_o^{\text{sv}}}; \text{ but } X_{\text{su}} = \frac{n_{\text{su}}}{n_{\text{su}} + n_{\text{sv}}}$$

And for very dilute solution; $n_{\text{su}} + n_{\text{sv}} \approx n_{\text{sv}}$

$$\text{Thence } \frac{n_{\text{su}}}{n_{\text{sv}}} = \frac{\Delta P}{P_o^{\text{sv}}}$$

$$\text{But } n_{\text{su}} = \frac{m_{\text{su}}}{M_{\text{su}}} \text{ and } n_{\text{sv}} = \frac{m_{\text{sv}}}{M_{\text{sv}}}$$

$$\text{Then } \frac{m_{\text{su}} \times M_{\text{sv}}}{M_{\text{su}} \times m_{\text{sv}}} = \frac{\Delta P}{P_{\text{sv}}^0}$$

$$\text{From which } M_{\text{su}} = \frac{m_{\text{su}} \times M_{\text{sv}} \times P_{\text{sv}}^0}{m_{\text{sv}} \times \Delta P}$$

Where:

$$M_{\text{sv}} = \text{molar mass of water (solvent)} = 18 \text{ g/mol}$$

$$P_{\text{sv}}^0 = \text{vapour pressure of pure water} = 1.992 \times 10^4 \text{ Nm}^{-2}$$

$$\Delta P = \text{Lowering in vapour pressure} = P_{\text{sv}}^0 - P_{\text{soln}} = (1.992 - 1.891) \times 10^4 \text{ Nm}^{-2} = 1.01 \times 10^4 \text{ Nm}^{-2}$$

$$m_{\text{su}} = \text{mass of solute} = 10.6 \text{ g}$$

$$m_{\text{sv}} = \text{mass of solvent (water)} = 90 \text{ g}$$

$$\text{Substituting } M_{\text{su}} = \frac{10.6 \text{ g} \times 18 \text{ g/mol} \times 1.992 \times 10^4 \text{ Nm}^{-2}}{90 \text{ g} \times 1.01 \times 10^4 \text{ Nm}^{-2}} = 41.8 \text{ g/mol}$$

Hence the molecular mass is 41.8 g/mol

Question 83

(a)

- (i) Due to **dissociation** of the electrolyte, the observed number of solute particles becomes larger than the expected one leading to the greater freezing point depression and hence the observed freezing point becomes lower.
- (ii) Diluted solution.

Explanation:

In accordance to Ostwald's dilution law, the degree of dissociation (ionisation) is greater in the more diluted solution and therefore the discrepancy becomes greater. Furthermore, ion interaction and hence ion pairing is less in the diluted solution.

$$(b) \text{ Using } \Delta T = K_f m = \frac{K_f \times m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}$$

$$\text{Where } \Delta T = (25.5 - 24.59)^\circ\text{C} = 0.91^\circ\text{C}$$

$$M_{\text{su}} = 18 \text{ g mol}^{-1}$$

$$m_{\text{sv}} = 10 \text{ g} = 0.01 \text{ kg}$$

$$\text{Substituting } 0.91 = \frac{0.1 \times m_{\text{su}}}{18 \times 0.01}$$

$$\text{From which; } m_{\text{su}} = 0.018 \text{ g}$$

The mass of water in the sample is 0.018 g

Question 84

- (a) Osmotic pressure is the pressure required to be applied to the side of higher solute concentration so as to prevent movement of solvent molecules by osmosis.

Reverse osmosis is the non-spontaneous flow of solvent through semi-permeable membrane from a solution of higher solute concentration to one of lower solute concentration.

$$(b) 1 \text{ mole of particles} = 6.02 \times 10^{23} \text{ particles}$$

$$\text{But mass of 1 particle} = 10^{-9} \text{ g}$$

$$\text{Thus molar mass of particles} = 10^{-9} \text{ g/particle} \times 6.02 \times 10^{23} \text{ particles/mol} = 6.02 \times 10^{14} \text{ g/mol}$$

$$\text{Then using; molarity} = \frac{\text{Mass concentration in g/L}}{\text{Molar mass}}$$

$$\text{Molarity of solid particles} = \frac{60 \text{ g/L}}{6.02 \times 10^{23} \text{ g/mol}} = 9.9668 \times 10^{-14} \text{ mol/L}$$

$$\text{Then from; } \pi v = nRT; \pi = \left(\frac{n}{v}\right) RT \text{ or } \pi = [\] RT$$

$$\text{Substituting; } \pi = 9.9668 \times 10^{-14} \text{ mol/L} \times 0.082 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} = 2.44 \times 10^{-12} \text{ atm}$$

Hence the osmotic pressure of the suspension is $2.44 \times 10^{-12} \text{ atm}$

Question 85

(a)

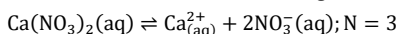
- (i) The addition of table salt which is non-volatile solute decreases the vapour pressure of water and hence boiling point of water is raised.
- (ii) The non-volatile solute decreases the vapour pressure of the solvent, making the solid phase to need lower temperature for its vapour pressure to be equal to the vapour pressure of liquid phase and hence the freezing point is lowered.

$$(b) \text{ Using } \Delta T = i K_f m$$

$$\text{From which } i = \frac{\Delta T}{K_f m}$$

$$\text{Substituting } i = \frac{0.265}{1.86 \times 0.05} = 2.85$$

Calcium nitrate dissociates according to the following equation:



$$\text{Using } \alpha = \frac{i - 1}{N - 1}$$

$$\text{Substituting } \alpha = \frac{2.85 - 1}{3 - 1} = 0.925$$

Hence the degree of dissociation is 0.925 or 92.5%

Question 86

(a) Using freezing point depression, $\Delta T = K_f m$

$$\text{Where } m = \frac{n_{\text{su}}}{m_{\text{sv}} \text{ in kg}} = \frac{m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}$$

$$\text{Then } \Delta T = \frac{K_f \times m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}$$

Where:

m_{su} = mass of solute = 22.5g

M_{su} = molar mass of solute = 342g/mol

m_{sv} = mass of solvent = 450g = 0.45kg

$$\text{Substituting } \Delta T = \frac{1.86 \times 22.5}{342 \times 0.45}^{\circ}\text{C} = 0.27^{\circ}\text{C}$$

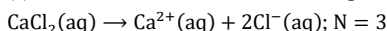
Then the freezing point, $T_f = 0^{\circ}\text{C} - \Delta T = (0 - 0.27)^{\circ}\text{C} = -0.27^{\circ}\text{C}$

Then freezing point of solution is -0.27°C

(b) The potassium chloride solution has **larger** freezing point than cane sugar solution and hence the ice **will first separate in the potassium chloride solution**.

Question 87

(a) Calcium chloride ionises according to the following equation:



Thus assuming complete ionisation, Van't Hoff's factor, $i = N = 3$

$$\text{Using } \Delta T = iK_b m = 3 \times 1.22^{\circ}\text{C kg/mol} \times 3.725 \text{ mol/kg} = 13.6^{\circ}\text{C}$$

Boiling point of the solution, $T_b = (78.5 + 13.6)^{\circ}\text{C} = 92.1^{\circ}\text{C}$

$$\text{Also } \Delta T = iK_f m = 3 \times 1.99^{\circ}\text{C kg/mol} \times 3.725 \text{ mol/kg} = 22.2^{\circ}\text{C}$$

Freezing point of the solution, $T_f = (-117.3 - 22.2)^{\circ}\text{C} = -139.5^{\circ}\text{C}$

(b) Practical boiling point will be smaller while practical freezing point will be greater than their respective calculated values.

Explanation

Practically calcium chloride has some covalent character; so it will not ionise completely making number of dissociated solute particles smaller. Fewer solute particles

as result of that pairing between ions (Ca^{2+} and Cl^{-}) means smaller of both boiling point elevation and freezing point depression which in turn means lower boiling point and higher freezing point.

Question 88

$$\rho_{\text{soln}} = 1.071 \text{ g cm}^{-3} = 1071 \text{ g dm}^{-3}$$

Thus; Mass of solution in 1 dm^3 of the solution is 1071g

$$\text{Then mass of the solute (NaCl) in } 1 \text{ dm}^3 = \frac{1}{100} \times 1071 \text{ g} = 10.71 \text{ g}$$

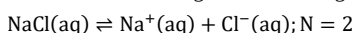
Using $\pi V = nRT$;

$$\text{From which } \pi = \frac{nRT}{V} = \frac{mRT}{VM_r}$$

$$\text{Expected osmotic pressure, } \pi_{\text{ex}} = \frac{1071 \text{ g} \times 0.082 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{1 \text{ dm}^3 \times 58.5 \text{ g mol}^{-1}} = 4.47 \text{ atm}$$

$$\text{Then Van't Hoff's factor, } i = \frac{\pi_{\text{ob}}}{\pi_{\text{ex}}} = \frac{7.83 \text{ atm}}{4.47 \text{ atm}} = 1.75$$

NaCl ionises according to the following equation;



$$\text{Then using; } \alpha = \frac{i - 1}{N - 1}$$

$$\text{Substituting } \alpha = \frac{1.75 - 1}{2 - 1} = 0.75$$

The fraction of NaCl which exists as ion pair is 0.75 or 75%

Mass of NaCl in 100g of solution is 1g

Thus;

Mass of solute (NaCl)=1g

Mass of solvent (Water) = (100 – 1)g = 99g

Freezing point depression, $\Delta T = iK_f m = \frac{i \times K_f m_{su}}{m_{su} \times m_{sv} \text{ in kg}}$

$$\Delta T = \frac{1.75 \times 1.86^\circ\text{C kg mol}^{-1} \times 1\text{g}}{58.5\text{g mol}^{-1} \times 0.099\text{kg}} = 0.562^\circ\text{C}$$

Freezing point of the solution, $T_f = 0^\circ\text{C} - \Delta T = 0^\circ\text{C} - 0.562^\circ\text{C} = -0.562^\circ\text{C}$

The freezing point of the solution – 0.562°C

Question 89

Constituent elements	C	O	N	H
%age of each	19.93	26.7	46.7	6.67
Mass of each in 100g of the compound	19.93g	26.7g	46.7g	6.67g
Number of moles of each, $n = \frac{m}{M_r}$	$\frac{19.93}{12\text{g mol}^{-1}} = 1.66\text{mol}$	$\frac{26.7}{16\text{g mol}^{-1}} = 1.67\text{mol}$	$\frac{46.7}{14\text{g mol}^{-1}} = 3.336\text{mol}$	$\frac{6.67}{1\text{g mol}^{-1}} = 6.67\text{mol}$
Dividing by smallest to get simpler ratio	$\frac{1.66\text{mol}}{1.66\text{mol}} = 1$	$\frac{1.67\text{mol}}{1.66\text{mol}} = 1=1$	$\frac{3.336\text{mol}}{1.66\text{mol}} = 2$	$\frac{6.67\text{mol}}{1.66\text{mol}} = 4$

The empirical formula is CON_2H_4

Using $\Delta T = K_b m = \frac{K_b \times m_{su}}{m_{su} \times m_{sv} \text{ in kg}}$

From which: $M_{su} = \frac{K_b \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}}$

Where:

$$\Delta T = (82.3 - 80.2)^\circ\text{C} = 2.1^\circ\text{C}$$

$$m_{su} = 5\text{g}$$

$$m_{sv} = 100\text{g} = 0.1\text{kg}$$

$$\text{Substituting: } m_{su} = \frac{2.53 \times 5}{2.1 \times 0.1} \text{g mol}^{-1} = 60\text{g mol}^{-1}$$

Let the molecular formula be $(\text{CON}_2\text{H}_4)_n$

$$\text{Then } 12n + 16n + 28n + 4n = M_r = 60$$

$$60n = 60; n = 1$$

The molecular formula is CON_2H_4

Question 90

(a)

(i) Is the solution which does not produce vapour at the boiling point of the solution. It is the solute with low vapour pressure and high boiling point; for example, table salt.

(ii) Solute with large molar mass like protein, exerts very small colligative properties. While very small osmotic pressure is measurable, very small boiling point elevation and freezing point depression are not measurable and hence the osmotic becomes more reliable for the determination. Furthermore, these large molecules are thermally unstable so they would decompose if the boiling point elevation is used unlike osmotic pressure which is measured at room temperature.

(b) From $n = \frac{m}{M_r}$;

$$n_{\text{glucose}} = \frac{50\text{g}}{180\text{g mol}^{-1}} = 0.2778\text{mol}$$

$$n_{\text{water}} = \frac{60\text{g}}{18\text{g mol}^{-1}} = 3.3333\text{mol}$$

$$X_{\text{water}} = \frac{n_{\text{water}}}{n_{\text{total}}} = \frac{3.3333\text{mol}}{0.2778\text{mol}} = 0.9917$$

From Raoult's law and Dalton's law of partial pressure;

$$P_{\text{soln}} = X_{\text{water}} P_{\text{water}}^0 + X_{\text{glucose}} P_{\text{glucose}}^0$$

Since glucose is non-volatile solute; $P_{\text{glucose}}^0 = 0$

$$\text{Thus } P_{\text{soln}} = X_{\text{water}} P_{\text{water}}^0 = 0.9917 \times 23.8\text{torr} = 23.6\text{torr}$$

The vapour pressure of the solution is 23.6torr.

Question 91

(a)

Solution	Van't Hoff factor, i	Effective molality of solute, m
0.010mNa ₃ PO ₄	4	0.04m
0.020mCaBr ₂	3	0.06m
0.020mKCl	2	0.04m
0.020mHF	$1 < i < 2$ or slightly greater than 1	$0.02m < m < 0.04m$ or slightly greater than 0.02m.

- (b) 0.010mNa₃PO₄ and 0.020mKCl (Both have effective molality of 0.04m).
 (c) 0.020mCaBr₂ (It has largest effective molality and therefore largest freezing point depression).
 (d) 0.020mHF (It has smallest effective molality and therefore smallest lowering in vapour pressure).
 (e) 0.020mHF (It has effective molality which is closer to 0.02m).

Question 92

- (a) Cucumber will lose water by osmosis and eventually will shrivel.

Explanation:

In the concentrated salt solution there is higher solute concentration than that present inside the cucumber. Thus the salt is hypertonic with respect to cucumber and therefore water will flow from the cucumber to the solution by osmosis and consequently it will shrivel.

- (b) $\Delta T = (0 - (-2.24))^\circ\text{C} = 2.24^\circ\text{C}$

Using $\Delta T = K_f m$

But $m = \frac{n_{\text{su}}}{m_{\text{sv}} \text{ in kg}}$

It follows that: $\Delta T = \frac{K_f \times n_{\text{su}}}{m_{\text{sv}} \text{ in kg}}$

From which $n_{\text{su}} = \frac{\Delta T \times m_{\text{sv}} \text{ in kg}}{K_f} = \frac{2.24 \times 0.15}{1.86} = 0.18$

Let mass of sugar be s

Then mass of salt will be $10.4 - s$

Then using $n = \frac{m}{M_r}$

Number of moles of sugar = $\frac{s}{342}$

Number of moles of table salt (NaCl) = $\frac{10.4 - s}{58.5}$

Assuming complete ionisation of NaCl in water whereby one mole of the salt ionises to give two moles of ions.

Number of moles of solute due table salt = $\frac{2 \times (10.4 - s)}{58.5} = \frac{20.8 - 2s}{58.5}$

Then total number of moles of solute in the solution = $\frac{s}{342} + \frac{20.8 - 2s}{58.5} = 0.18$; $58.5s + 7113.6 - 684s = 3601.26$; $s = 5.6\text{g}$

Percent by mass of sugar = $\frac{5.6\text{g}}{10.4\text{g}} \times 100\% = 53.8\%$

Question 93

- (a) Yes, I would keep.

Reason:

The antifreeze does not only depress freezing point but also elevates the boiling point. The elevation of boiling point enables the radiator to work even at summer (when temperature is high) without the boiling overs.

- (b) Using $\Delta T = K_f m$

But $m = \frac{n_{\text{su}}}{m_{\text{sv}} \text{ in kg}}$ and $n_{\text{su}} = \frac{m_{\text{su}}}{M_{\text{su}}}$

It follows that: $\Delta T = \frac{K_f \times m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}} = \frac{1.86 \times 651}{62 \times 2.505} = 7.8^\circ\text{C}$

Freezing point = $0^\circ\text{C} - 7.8^\circ\text{C} = -7.8^\circ\text{C}$

The freezing point of the solution is -7.8°C

Question 94

(a) Seawater and distilled water are **not** boiling at the same temperature.

Explanation:

Sea water contain dissolved salts like sodium chloride and magnesium chloride which are non-volatile. These salts cause boiling point elevation making the seawater to boil at higher temperature than distilled water which is pure water.

(b) 1molal solution means one mole of solute is dissolved in 1kg of the solvent (water).

Then using $n = \frac{m}{M_r}$

Number of moles of water in 1kg of it = $\frac{1000g}{18g/mol} = 55.56mol$

$$X_{su} = \frac{n_{su}}{n_{su} + n_{sv}} = \frac{1}{1 + 55.56} = 0.01768$$

$$\Delta P = X_{su} P_{sv}^o = 0.01768 \times 12.3kPa = 0.22kPa$$

$$P_{soln} = P_{sv}^o - \Delta P = 12.3kPa - 0.22kPa = 12.08kPa$$

The vapour pressure of the solution is 12.08kPa.

Question 95

Constituent elements	C	H	Cl
%age of each	49.02	2.743	48.23
Mass of each in 100g of the compound	49.02g	2.743g	48.23g
Number of moles of each, $n = \frac{m}{M_r}$	$\frac{49.02g}{12g/mol^{-1}}$ $= 4.085mol$	$\frac{2.743g}{1g/mol^{-1}}$ $= 2.743mol/mol$	$\frac{48.23g}{35.5g/mol^{-1}}$ $= 1.378mol$
Dividing by smallest to get simpler ratio	$\frac{4.085mol}{1.378mol} = 3$	$\frac{2.743mol}{1.378mol} = 2$	$\frac{1.378mol}{1.378mol} = 1$

The empirical formula is C₃H₂Cl

$$\text{Using } \Delta T = K_f m = \frac{K_f \times m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$$

From which:

$$M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}}$$

$$\text{Where: } \Delta T = (5.5 - 1.12)^\circ C = 4.38^\circ C, \quad m_{su} = 3.15g, \quad m_{sv} = 25g = 0.025kg$$

$$\text{Substituting: } m_{su} = \frac{5.12 \times 3.15}{4.38 \times 0.025} g/mol^{-1} = 147g/mol^{-1}$$

Let the molecular formula be (C₃H₂Cl)_n

$$\text{Then } 36n + 2n + 35.5n = M_r = 147$$

$$73.5n = 147; n = 2$$

The molecular formula is C₆H₄Cl₂

Mass of water (solvent) is 100g – 18.2g or 81.8g

Using $n = \frac{m}{M_r}$;

$$n_{su} = \frac{3.15g}{147g/mol} = 0.0214mol \text{ and } n_{sv} = \frac{25g}{78g/mol} = 0.32mol$$

$$X_{benzene} = X_{sv} = \frac{n_{sv}}{n_{su} + n_{sv}} = \frac{0.32mol}{0.0214mol + 0.32mol} = 0.937$$

$$\text{Using } P_{soln} = X_{sv} P_{sv}^o = 0.937 \times 150mmHg = 140.55mmHg$$

Vapour pressure of benzene above the solution is 140.55mmHg.

Question 96

(a) No.

Reason:

It boils at a much lower boiling point than water (For substance to be regarded as non-volatile, its boiling point must be above that of water, 100°C).

$$(b) \text{ Using } \pi V = nRT = \frac{m}{M_r} RT \text{ or } \pi = \frac{mRT}{VM_r}$$

Where mass of the solute in 100g of the solution is 5g and 1g for sugar and substance X respectively.

But if the solution is so dilute, then $\rho_{\text{solution}} = \rho_{\text{water}} = 1\text{g/mL}$

Thus 100g of the solution is equivalent to 100mL (0.1L) of the solution.

Then for cane sugar:

$$\pi_c = \frac{m_c RT}{VM_u} = \frac{5\text{g} \times RT}{0.1\text{L} \times 342\text{g/mol}}$$

And for another solute, X:

$$\pi_x = \frac{m_x RT}{VM_x} = \frac{1\text{g} \times RT}{0.1\text{L} \times M_x}$$

But $\pi_u = \pi_x$ (isotonic solutions)

$$\frac{5\text{g} \times RT}{0.1\text{L} \times 342\text{g/mol}} = \frac{1\text{g} \times RT}{0.1\text{L} \times M_x}$$

$$\text{From which } M_x = \frac{342\text{g/mol}}{5} = 68.4\text{g/mol}$$

Hence the molar mass is 68.4g/mol.

Question 97

(a) Not directly proportional.

Reason:

Molarity is temperature dependent. So as the temperature changes during the boiling process, molarity will be continuously changing and hence the change of boiling point with respect to molarity will not be linear.

(b) Mass of CCl_4 (solvent) is $100\text{mL} \times 1.58\text{g/mL} = 158\text{g}$

Using $n = \frac{m}{M_r}$;

$$n_{\text{su}} = \frac{0.5\text{g}}{65\text{g/mol}} = 0.0076923\text{mol} \text{ and } n_{\text{sv}} = \frac{158\text{g}}{154\text{g/mol}} = 1.025974\text{mol}$$

$$X_{\text{sv}} = \frac{n_{\text{sv}}}{n_{\text{su}} + n_{\text{sv}}} = \frac{1.025974\text{mol}}{1.025974\text{mol} + 0.0076923\text{mol}} = 0.99256$$

Using $P_{\text{soln}} = X_{\text{sv}} P_{\text{sv}}^0 = 0.99256 \times 143\text{mmHg} = 141.94\text{mmHg}$

Vapour pressure of the solution is 141.94mmHg.

Question 98

(a)

(i)

- Colligative properties depend on concentration of solute in the solution and not on the nature of solute.
- Colligative properties are tied together in a manner that changing concentration of solute in the solution changes all colligative properties at the same time.
- Colligative properties are useful in determination of molar mass of non-volatile substances.

(ii) Non-colligative properties include the following:

- Viscosity
- Density
- Surface tension
- Solubility
- Electrolytic conductivity

(b) Using $\pi = i \times [\] RT$

Then for glucose ($i = 1$): $\pi_g = 0.01\text{M} \times RT$

And for sodium sulphate: $\pi_s = i \times 0.004\text{M} \times RT$

But $\pi_g = \pi_s$ (isotonic solutions); $0.01\text{M} \times RT = i \times 0.004\text{M} \times RT$

From which; $i = 2.5$

Na_2SO_4 ionises in water according to the following equation: $\text{Na}_2\text{SO}_4 \rightarrow 2\text{Na}^+ + \text{SO}_4^{2-}$; $N = 3$

$$\alpha = \frac{i - 1}{N - 1} = \frac{2.5 - 1}{3 - 1} = 0.75 \text{ or } 75\%$$

Hence the degree of dissociation is 75%.

Question 99

(a) Beaker B

Reason

Beaker B contain the solution (salt water), thus there is lowering in vapour pressure due to presence of salt(non-volatile solute) making the vapour pressure in beaker B lower than that of beaker A which contain pure water (solvent). Lower vapour pressure of liquid in beaker B means less evaporation.

(b) Mass of the solution containing 4g of NaCl is 100g

Then using $V = \frac{m}{\rho}$

The 100g corresponds to $V_{\text{soln}} = \frac{100\text{g}}{1.02\text{g/mL}} = 98\text{mL} = 0.098\text{L}$

Using $\pi = i \times \frac{nRT}{V} = i \times \frac{m_{\text{NaCl}}RT}{M_{\text{NaCl}}V}$

Assuming complete dissociation of NaCl, $i = 2$.

Then $\pi = 2 \times \frac{4 \times 0.082 \times 298}{58.5 \times 0.098} \text{ atm} = 34 \text{ atm}$

The osmotic pressure is 34atm

Since temperature is kept constant, $\pi \propto C$

And thus $\frac{\pi_1}{C_1} = \frac{\pi_2}{C_2}$

From which $C_2 = \frac{C_1 \times \pi_2}{\pi_1} = \frac{0.3 \times 34}{7.3} = 1.4\text{M}$

The concentration to be synthesized = $C_2 - C_1 = (1.4 - 0.3)\text{M} = 1.1\text{M}$

Hence the yeast cell must synthesize 1.1M of glycerol.

Question 100

(a) Water molecules will move toward the solution where the solute has been added from another solution (with less solute).

Reason:

The solution with more added solute has more solute concentration and therefore it becomes hypertonic. So to equalize concentration in the two solutions water molecules have to move by osmosis toward it.

(b) Using $\Delta T = K_f m$

But $m = \frac{n_{\text{su}}}{m_{\text{sv}} \text{ in kg}}$ and $n_{\text{su}} = \frac{m_{\text{su}}}{M_{\text{su}}}$

It follows that: $\Delta T = \frac{K_f \times m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}$

From which $K_f = \frac{\Delta T \times M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}{m_{\text{su}}}$

For biphenyl-naphthalene mixture:

Where $\Delta T = (69 - 68.5)^\circ\text{C} = 0.5^\circ\text{C}$

$m_{\text{sv}} \text{ in kg} = \frac{100}{1000} \text{ kg} = 0.1 \text{ kg}$ and $M_{\text{su}} = 128 \text{ g/mol}$

Substituting; $K_f = \frac{0.5 \times 128 \times 0.1}{2.67} = 2.4^\circ\text{C kg mol}^{-1}$

The freezing point depression constant is $2.4^\circ\text{C kg mol}^{-1}$

Using $\Delta T = \frac{K_f \times m_{\text{su}}}{M_{\text{su}} \times m_{\text{sv}} \text{ in kg}}$

From which; $M_{\text{su}} = \frac{K_f \times m_{\text{su}}}{\Delta T \times m_{\text{sv}} \text{ in kg}}$

Substituting (for biphenyl-unknown compound mixture): $M_{\text{su}} = \frac{2.4 \times 1}{(69 - 68.86) \times 0.1} = 171 \text{ g/mol}$

Molar mass of the unknown compound is 171 g/mol .

PART THREE

Question 1

(a) Because the chances that three particles colliding at the same time, with proper orientation and sufficient energy, are extremely small.

$$(b) R = k[A]^x[B]^y$$

$$R_1 = 5.02 \times 10^{-4} = k[0.1]^x[0.1]^y$$

$$R_2 = 2.51 \times 10^{-4} = k[0.1]^x[0.05]^y$$

$$R_3 = 1.251 \times 10^{-4} = k[0.05]^x[0.05]^y$$

$$\frac{R_1}{R_2} = \frac{5.02 \times 10^{-4}}{2.51 \times 10^{-4}} = \left(\frac{0.1}{0.05}\right)^y$$

$$2^1 = 2^y \text{ or } y = 1$$

$$\frac{R_2}{R_3} = \frac{5.02 \times 10^{-4}}{2.51 \times 10^{-4}} = \left(\frac{0.1}{0.05}\right)^2$$

$$2^1 = 2^x \text{ or } x = 1$$

(i) So the order of reaction with respect to A is 1 and the order of reaction with respect to B is 1

(ii) Substituting obtained values for x and y in R_1

$$5.02 \times 10^{-4} \text{ Ms}^{-1} = k \times 0.1 \text{ M} \times 0.1 \text{ M} \text{ from which } k = 0.0502 \text{ M}^{-1} \text{ s}^{-1}$$

(iii) From the simplified Arrhenius equation:

$$\log k_1 = -\frac{E_a}{2.303RT_1} + \log A \dots\dots\dots (i)$$

$$\text{And } \log k_2 = -\frac{E_a}{2.303RT_2} + \log A \dots\dots\dots (ii)$$

$$\text{Take (ii) - (i) give } \log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\text{Where } k_2 = 6.71 \text{ M}^{-1} \text{ sec}^{-1}, k_1 = 0.0502 \text{ M}^{-1} \text{ sec}^{-1}$$

$$T_2 = 342 \text{ K}, T_1 = 298 \text{ K and } R = 8.314$$

$$\text{Then } \log\left(\frac{6.71}{0.0502}\right) = \frac{E_a}{2.303 \times 8.314} \left(\frac{342 - 298}{342 \times 298}\right) \text{ or } E_a = 94289 \text{ J/mol or } 94.289 \text{ kJ/mol}$$

Hence the activation energy of the reaction is 94.289 kJ/mol

$$(iv) \text{ From } \log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\text{Then } \log\left(\frac{k_2}{0.0502}\right) = \frac{94289}{2.303 \times 8.314} \left(\frac{310 - 298}{310 \times 298}\right)$$

$$\text{From which } k_2 = 0.219 \text{ M}^{-1} \text{ Sec}^{-1}$$

Question 2

(a)

(i) **True:** Increase in temperature tends to increase frequency of collision between reacting particles and make the collision more energetic. It also increases the value of rate constant. These facts make increase number of reacting particles which attain activation energy and hence the rate of reaction is increased.

(ii) **False:** Most of the reactions are positively catalysed thus leading to increase the rate of reaction by lowering the activation energy. However, for negative catalysed reactions the rate of reaction is decreased by increasing activation energy thus making the statement true in few cases.

(iii) **False:** The rate of zero order chemical reaction is independent to concentration.

$$(b) \text{ Using: } \log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$$

$$\text{Where } k = 2.2 \times 10^{-5} \text{ sec}^{-1}$$

$$t = 1 \text{ hour} = 3600 \text{ sec}$$

$$\text{Then } \log\left(\frac{a}{a-x}\right) = \frac{2.2 \times 10^{-5} \times 3600}{2.303} = 0.034$$

$$\text{It follows that: } \frac{a}{a-x} = \log^{-1}(0.034) = 1.08$$

$$\text{Then } \frac{a-x}{a} = \frac{1}{1.08} = 0.92 = \text{Fraction of undecomposed sample}$$

$$\text{Thus undecomposed percentage of the sample is } 0.92 \times 100\% = 92\%$$

$$\text{Hence the percentage decomposition of the sample after 1 hour} = (100 - 92)\% = 8\%$$

Question 3

(a)

1. Unimolecular elementary reactions.
2. Bimolecular elementary reactions.
3. Termolecular elementary reactions.

$$(b) R = k[A]^x[B]^y$$

Then

$$R_1 = 5.02 \times 10^{-4} = k[0.1]^x[1]^y \dots\dots\dots (i)$$

$$R_2 = 1.004 \times 10^{-3} = k[0.2]^x[1]^y \dots\dots\dots (ii)$$

$$R_3 = 2.000 \times 10^{-3} = k[0.2]^x[2]^y \dots\dots\dots (iii)$$

$$\frac{R_2}{R_1} = \frac{1.004 \times 10^{-3}}{5.02 \times 10^{-4}} = \left(\frac{0.2}{0.1}\right)^x$$

$$2^1 = 2^x \text{ or } x = 1$$

$$\frac{R_3}{R_2} = \frac{2.008 \times 10^{-3}}{1.004 \times 10^{-3}} = \left(\frac{2}{1}\right)^y$$

$$2^1 = 2^y \text{ or } y = 1$$

$$\text{Overall order is } (x + y) = 1 + 1 = 2$$

Hence the reaction is of the second order

Question 4

- (a) Activation energy minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy.

That is; Activation energy = Threshold energy – Average energy

$$(b) R = k[HgI_2]^x[C_2O_4^{2-}]^y$$

$$R_1 = 0.502 \times 10^4 = k[0.0836]^x[10.202]^y \dots\dots\dots (i)$$

$$R_2 = 2.08 \times 10^4 = k[0.0836]^x[0.404]^y \dots\dots\dots (ii)$$

$$R_3 = 1.06 \times 10^4 = k[0.0418]^x[0.404]^y \dots\dots\dots (iii)$$

$$\frac{R_2}{R_1} = \frac{2.08 \times 10^4}{0.502 \times 10^4} = \left(\frac{0.404}{0.202}\right)^y$$

$$4 = 2^y$$

$$2^2 = 2^y \text{ or } y = 2$$

$$\frac{R_2}{R_3} = \frac{2.08 \times 10^4}{1.06 \times 10^4} = \left(\frac{0.0836}{0.0418}\right)^x ; 2^1 = 2^x \text{ or } x = 1$$

- The order of the reaction with respect to $C_2O_4^{2-}$ is 2 and the order of the reaction with respect to HgI_2 is 1.
- Rate law expression for the reaction is obtained by substituting obtained values of x and y in $R = k[HgI_2]^x[C_2O_4^{2-}]^y$
So the rate law expression for this reaction is $R = k[HgI_2][C_2O_4^{2-}]^2$
- Substituting values for x and y in R_1

$$0.52 \times 10^4 \text{ mol dm}^{-3} \text{ min}^{-1} = k (0.0836 \text{ mol dm}^{-3}) (0.202 \text{ mol dm}^{-3})^2$$

$$\text{From which } k = 1524384 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$$

$$\text{The value of rate constant is } 1524384 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$$

$$(iv) \text{ Overall order of the reaction} = x + y = 1 + 2 = 3$$

Thus the reaction is of the third order

Question 5

- It increases frequency of collision between reacting particles.
- Checking whether the reaction is of first order or not by calculation of rate constants:

$$\text{From the equation of first order chemical reaction: } \log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$$

$$\text{From which } k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$$

And initial concentration, a = 1.0023M

Time/Min	(a - x) or [C ₁₂ H ₁₂ O ₁₁]/M	$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$
30.00	0.9022	3.51×10^{-3}
60.00	0.8077	3.59×10^{-3}
90.00	0.7253	3.59×10^{-3}
130.00	0.6300	3.57×10^{-3}
160.00	0.5010	3.47×10^{-3}
200.00	0.5020	3.47×10^{-3}

- (i) From the above it has been shown that the rate constant at different time in the reaction course is the same. Thus the reaction obeys the first order equation and hence the reaction is of the first order.

$$k = \frac{k_1 + k_2 + k_3 + k_4 + k_5 + k_6}{6}$$

$$k = \frac{(3.51 + 3.59 + 3.57 + 3.47 + 3.59 + 3.47) \times 10^{-3}}{6} = 3.53 \times 10^{-3} \text{ min}^{-1}$$

Thus the rate constant, $k = 3.53 \times 10^{-3} \text{ min}^{-1}$

For first order chemical reaction, $t_{1/2} = \frac{0.693}{k}$

$$t_{1/2} = \frac{0.693}{3.53 \times 10^{-3}} = 196.3 \text{ minutes}$$

Hence the half-life for the reaction is 196.3 minutes

- (ii) Substituting $t = 4 \text{ hours} = 240 \text{ minutes}$ and $a = 1.0023 \text{ M}$ to $\log \left(\frac{a}{a-x} \right) = \frac{kt}{2.303}$

$$\log \left(\frac{1.0023}{a-x} \right) = \frac{3.53 \times 10^{-3} \times 240}{2.303}$$

From which $(a - x) = 0.43 \text{ M}$

So concentration of C₁₂ H₁₂ O₁₁ after 4 hours is 0.43 M

Question 6

- (a) The spark initiates combustion of coal by providing heat required for overcoming activation energy of the reaction. The reaction being exothermic, once initiated it produces more heat to enable more combustion of unreacted coal. Adding the fact that the coal is in the form of dust which has large surface area, the reaction is very fast, and as consequence of these facts, an explosion results.

- (b) Half-life for first order chemical reaction is given by: $t_{1/2} = \frac{0.693}{k}$ or $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1590 \text{ yr}} = 4.35849 \times 10^{-4} \text{ yr}^{-1}$

$$\text{Using } \log \left(\frac{a}{a-x} \right) = \frac{kt}{2.303}$$

From which $t = \frac{2.303}{k} \log \left(\frac{a}{a-x} \right)$ where $a = 100$ and $a - x = 25$

$$\text{Then } t = \frac{2.303}{4.3589 \times 10^{-4}} \log \left(\frac{100}{25} \right) = 3181.25$$

Hence it will take about 3180 years for given sample to decay to 25%

Question 7

- (a) Activation energy of combustion of coal is too high to be achieved at room temperature.

- (b) For first order chemical reaction: $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{300 \text{ sec}} = 2.31 \times 10^{-3} \text{ sec}^{-1}$

$$\text{Using first order equation: } t = \frac{2.303}{k} \log \left(\frac{a}{a-x} \right)$$

With $t = 1200 \text{ seconds}$, $a = 100$ (initially was 100% of the isotope)

$$\text{It follows that: } \log \left(\frac{100}{a-x} \right) = \frac{2.31 \times 10^{-3} \times 1200}{2.303}$$

From which $(a - x) = 6.25$

Thus 6.25% of the isotope will remain after 1200 seconds

Question 8

(a) This may occur if:

1. The collision has insufficient energy to overcome activation energy of the reaction.
2. Particles in the collision have improper orientation for the reaction to take place.

(b) Using $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$

Where $k_1 = 4.46 \times 10^{-5} /s$, $k_2 = 1.5 \times 10^{-3} /s$

$T_1 = 293K$, $T_2 = 328K$, $R = 8.314$

$$\log\left(\frac{1.5 \times 10^{-3}}{4.46 \times 10^{-5}}\right) = \frac{E_a}{2.303 \times 8.314} \left(\frac{328 - 293}{293 \times 328}\right)$$

From which $E_a = 80269J/mol$ or $80.269kJ/mol$

Activation for the reaction is $80.269kJ/mol$

Question 9

(a) No;

Explanation:

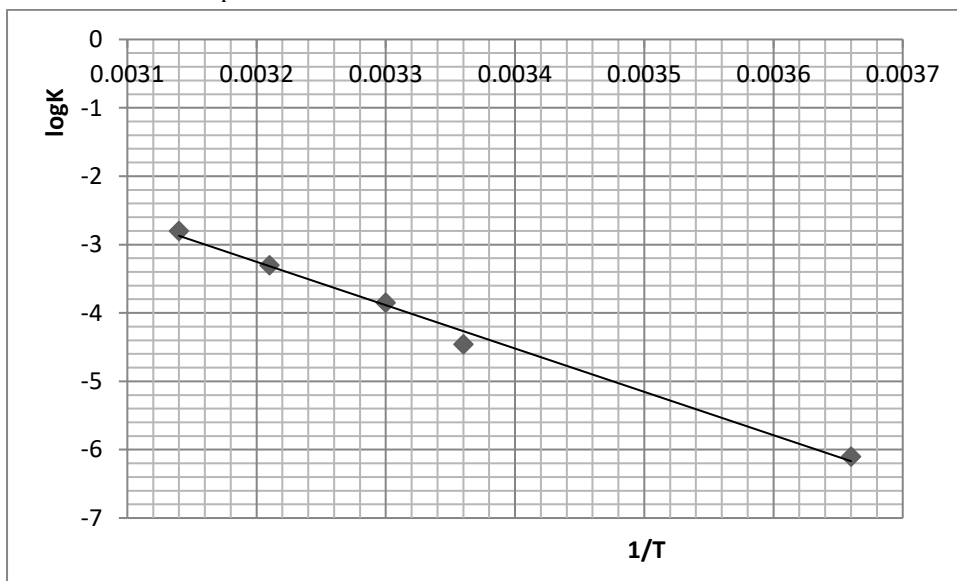
Reaction rates are compared in moles (not mass). Although the same mass of two elements is formed over the same time, the number of moles of aluminium is greater than that of iron because aluminium has smaller atomic mass. Hence, the rate of formation of aluminium is greater than that of iron.

(b)

TABLE OF RESULTS

Temperature (K)	K (sec ⁻¹)	Log k	$\frac{1}{T}$ (K ⁻¹)
273	7.9×10^{-7}	- 6.1	3.66×10^{-3}
298	3.5×10^{-5}	- 4.46	3.36×10^{-3}
303	1.41×10^{-4}	- 3.85	3.3×10^{-3}
312	5×10^{-4}	- 3.3	3.21×10^{-3}
318	1.5×10^{-3}	- 2.8	3.14×10^{-3}
320	4.9×10^{-3}	- 2.3	3.125×10^{-3}

Graph of $\log k$ against $\frac{1}{T}$



Hints:

- (i) To find activation energy:
- Firstly, find the slope of the graph, (m) by taking any two points from the graph (not given specific given points). In finding the slope don't forget to multiply the factor of 10^{-3} on denominator
 - Then take $m = -\frac{E_a}{2.303R}$ where $R = 8.314 \text{ J mol K}^{-1}$
- (ii) To find Arrhenius factor
- With obtained value of activation energy (E_a) and any one point on the graph; substitute them on simplified Arrhenius equation $\log k = -\frac{E_a}{2.303RT} + \log A$ to get A

Question 10

- (a) Half-life of zero order reaction varies inversely proportional to initial concentration of reactant while that of second order varies directly proportional to the initial concentration.
- (b) $T_1 = 317^\circ\text{C} = 590\text{K}$; $T_2 = 427^\circ\text{C} = 700\text{K}$

$$K_1 = 1.4 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}, K_2 = 6.4 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

$$\text{Using } \log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log\left(\frac{6.4 \times 10^{-2}}{1.4 \times 10^{-3}}\right) = \frac{E_a}{2.303 \times 8.314} \left(\frac{700 - 590}{700 \times 590}\right)$$

From which $E_a = 119339 \text{ J/mol}$ or 119.339 kJ/mol

The activation energy of the reaction is 119.339 kJ/mol

Question 11

- (a) There are various method which can be used to deduce order of chemical reaction from the kinetic data. This includes:
- Graphical method,
 - Half-life method,
 - Integral method and
 - Initial rate method
- (b) $R = k[Z]^x[Y]^y$

Then:

$$R_1 = 0.002 = k[0.1]^x[0.1]^y \dots\dots\dots (i)$$

$$R_2 = 0.00798 = k[0.1]^x[0.2]^y \dots\dots\dots (ii)$$

$$R_5 = 0.00601 = k[0.3]^x[0.1]^y \dots\dots\dots (iii)$$

$$\frac{R_2}{R_1} = \frac{0.00798}{0.002} = \left(\frac{0.2}{0.1}\right)^y$$

$$2^2 = 2^y \text{ or } y = 2$$

$$\frac{R_5}{R_1} = \frac{0.00601}{0.002} = \left(\frac{0.3}{0.1}\right)^x$$

$$3^1 = 3^x \text{ or } x = 1$$

(c) Hence:

- The order of reaction with respect to Z is 1
- The order of reaction with respect to Y is 2
- The overall order = $x + y = 1 + 2 = 3$

Thus the reaction is of the third order

(d) Substituting values of x and y to (i) $0.002 \text{ mol/dm}^{-3} \text{ min}^{-1} = k \times 0.1 \text{ mol/dm}^{-3} \times (0.1 \text{ mol/dm}^{-3})^2$

$$k = \frac{0.002}{0.001} = 2 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$$

Hence:

- Rate constant is $2 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$
- Units of rate constant is $\text{dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$

Question 12

- (a) For reaction (i):
- Disappearance of purple colouration of KMnO_4** (by noting the rate the change of the colour intensity).
 - Formation of carbon dioxide gas** (by measuring the rate of increase of volume of the gas)

For reaction (ii):

- Formation of white precipitate of AgCl** (by noting the rate of intensity of the colour formation).
- Disappearance of green colouration of CuCl_2** (by noting the rate of the change of the colour intensity).

(b) So using $t_{1/2} = \frac{0.683}{k}$ (half-life for first order chemical reaction)

From which $k = \frac{0.683}{t_{1/2}}$

Then rate constant at 27°C = $\frac{0.693}{5000} \text{sec}^{-1} = 1.386 \times 10^{-4} \text{sec}^{-1}$

Given that at 37°C: $t_{1/2} = 1000 \text{seconds}$

Then rate constant at 37°C: = $\frac{0.693}{1000} \text{sec}^{-1} = 6.93 \times 10^{-4} \text{sec}^{-1}$

Using: $\log\left(\frac{k_1}{k_2}\right) = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

From which $E_a = \frac{2.303RT_1T_2}{(T_1 - T_2)} \log\left(\frac{k_1}{k_2}\right)$

Then $E_a = \frac{2.303 \times 8.314 \times 300 \times 310}{(300 - 310)} \log\left(\frac{1.386 \times 10^{-4}}{6.93 \times 10^{-4}}\right) = 124464 \text{J/mol}$

Hence the activation energy of the reaction is 124.464 kJ/mol

Question 13

(a)

(i) By increasing frequency of collision between reactants.

(ii) Not true.

Explanation

The extent of which reaction rate will increase after increasing the reactant concentration is determined by order of chemical reaction; it is not the same for all reactions. For example; zero order reaction, the reaction rate will remain the same even after doubling the concentration of reactant. Or in the second order reaction, doubling the concentration of reactant will make the reaction rate quadruple. The given statement holds for the first order reactions only.

(b) An equation for first order chemical reaction is $k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$

But volume of KMnO_4 used varies directly proportional to the concentration of undecomposed hydrogen peroxide

Thus if V_0 is the volume of KMnO_4 used before decomposition of hydrogen peroxide and V_t is the volume of the manganate used after time, t then $\frac{a}{a-x} = \frac{V_0}{V_t}$

So in terms of volume of KMnO_4 ;

The equation: $k = \frac{2.303}{t} \log\left(\frac{V_0}{V_t}\right)$

Where $V_0 = 75 \text{cm}^3$

Volume of KMnO_4 used in cm^3	47	30	13	7.2
Time (minutes)	06	09	20	29
$k = \frac{2.303}{t} \log\left(\frac{V_0}{V_t}\right)$	0.0779	0.1018	0.0876	0.0808

If obtained values are written to one decimal place, they all give the same value of 0.1. That is the values are almost the same and hence the reaction is of the first order as it obeys first order equation.

The rate constant, $k = \frac{k_1 + k_2 + k_3 + k_4}{4} = \frac{0.0779 + 0.1018 + 0.0876 + 0.0808}{4} = 0.0870 \text{min}^{-1}$

The rate constant is 0.0870min^{-1}

Question 14

(a)

(i) High activation energy means low reaction rate and vice-versa.

(ii) There are two factors which affect activation energy as explained below:

1. **Nature of reactants:** Usually ionic reactants have low activation energy while covalent reactants have high activation energy.

2. **Catalyst:** Positive catalysts decreases the activation energy while negative catalyst increases activation energy.

(b) $R = k[A]^x[B]^y$ (i)

$2R = k(2[A])^x[B]^y$ (ii)

(When concentration of B was kept constant while that of A doubled, the rate of reaction doubled)

$3R = k[A]^x(3[B])^y$ (iii)

(When the concentration of A was kept constant while the concentration of B tripled, the rate of reaction was tripled).

(ii) ÷ (i) Gives: $2^1 = 2^x$ or $x = 1$

(iii) $\div$ (i) gives: $3^1 = 3^y$ or $y = 1$

Thus the reaction of first order with respect to both reactants A and B which can be deduced from the molecularity of reaction (1)

- (i) Hence reaction (1) is rate determining step and
(ii) The rate law for the reaction is $R = k[A][B]$

Question 15

- (a) For a change in total pressure to affect the reaction rate, it must affect partial pressure of reactants. The addition of helium which is noble gas does not affect partial pressure of reactants (nitrogen and hydrogen gas) and thus the reaction rate remains unchanged keeping the rate of formation the same.
(b) Let rate law of the reaction to be: $R = k[G]^x[F]^y$

$$\text{Then } 3.1 \times 10^{-3} = 3.44 \times 10^{-4} \times 2^x \times 3^y$$

$$9 = (2^x)(3^y) \dots \dots \dots (i)$$

$$\text{And } 7.75 \times 10^{-4} = 3.44 \times 10^{-4} \times 1^x \times 1.5^y$$

$$\text{But } 1^x = 1$$

$$\text{Then } 1.5^y = \frac{7.75}{3.44} \dots \dots \dots (ii)$$

$$\text{Then } y = \frac{\log\left(\frac{7.75}{3.44}\right)}{\log 1.5} = 2$$

Substituting $y = 2$ to (i)

$$9 = (2^x)3^2 \text{ or } x = 0$$

Then reaction is of the second order with respect to F and zero order with respect to G Overall order

$$= x + y = 0 + 2 = 2$$

Hence the overall order for the reaction is 2

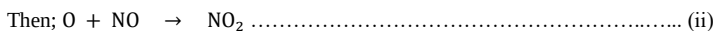
Question 16

- (a) Yes, it is possible.

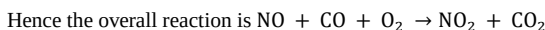
Explanation

Activation energy may be altered by adding (or removing) catalyst. Adding positive catalyst to the chemical system of chemical reaction, decreases activation energy while adding negative catalyst, increases activation energy.

- (b) (i) Reaction mechanism:



Adding (i),(ii) and (iii) and then cancelling like terms:



(ii) Intermediates are molecular entities which are formed from reactants (or another intermediates) and react further to give product either directly or indirectly

Thus from above reaction, intermediates are OOH and O

(iii) OH is catalyst because initially participated in converting oxygen molecule into more reactive oxygen atom and finally it was regenerated (remain unchanged)

Question 17

- (a) Zinc powder has greater surface area and thus it enables to achieve faster reaction than zinc wire.
(b) Disintegration of an isotope as result of its decomposition is the first order chemical reaction.

$$\text{For first order chemical reaction, } t_{1/2} = \frac{0.693}{k} \text{ or } k = \frac{0.693}{3 \text{ days}}$$

$$\text{But } 1 \text{ day} = 60 \times 60 \times 24 \text{ seconds}$$

$$\text{So } 3 \text{ days} = 3 \times 60 \times 60 \times 24 \text{ seconds}$$

$$\text{Then } k \text{ in } \text{sec}^{-1} = \frac{0.693}{3 \times 60 \times 60 \times 24} = 2.6736 \times 10^{-6} \text{sec}^{-1}$$

- (i) The rate constant is $2.6736 \times 10^{-6} \text{sec}^{-1}$

$$\text{From } k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

$$t = \frac{2.303}{2.6736 \times 10^{-6}} \log \left(\frac{0.031}{0.001} \right) \text{ seconds or } 14.87 \text{ days}$$

- (ii) Thus 14.87 days are required to x – 210 to disintegrate from 0.031mg to 0.001mg

Question 18

- (a) As the reaction proceeds, concentration of reactants decreases while concentration products are increases. Hence like velocity, reaction rate may take both negative values (for reactants) and positive values (for products) unlike speed which takes positive values only.
- (b)
- (i) Rate equation is deduced from stoichiometric coefficients of reactants of the slowest step which is the rate determining step whereby concentration of each reactant in the equation is raised to the coefficient.
Rate equation is $R = k[Z][W]$
- (ii) In the slow step, **two** molecules react (collide);

Hence the molecularity of the slow step is 2.

Question 19

- (a) By providing alternative mechanism with lower activation energy.
- (b) From the simplified Arrhenius equation: $\log k = -\frac{E_a}{2.303RT} + \log A$

Thus the slope of the graph $\log k$ against $\frac{1}{T}$, m is given by: $m = -\frac{E_a}{2.303R}$

Or $E_a = -2.303mR$

But $m = -9.8 \times 10^3 K$

And $R = 8.314 J mol^{-1} K^{-1}$

So $E_a = -2.303 \times 9.8 \times 10^3 \times \frac{8.314 J}{mol} = 187.6 kJ/mol$

The value of activation energy is 187.6 kJ/mol

(ii) Using $\log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

With $T_1 = 409 K, T_2 = 389 K$

$\log \left(\frac{k_2}{k_1} \right) = \frac{187.6 \times 10^3}{2.303 \times 8.314} \left(\frac{389 - 409}{409 \times 389} \right)$

From which $\frac{k_2}{k_1} = 0.0587$

Thus the new rate constant is 5.87% of the original rate constant and hence the rate constant is decreased by 94.13% when the temperature is lowered from 409K to 389K

Question 20

- (a) From given data:
- When concentration of B is doubled while that of A is kept constant, the rate of reaction is doubled and hence the reaction is of the first order with respect to B.
 - When concentration of A is doubled while that of B is kept constant, the rate of reaction is doubled and hence the reaction is of the first order with respect to A.
- (i) Hence the rate equation for the reaction is: $R = k[A][B]$
- (ii) From (i) above $R = k[A][B]$

So using data of first row in a given table:

$1 \times 10^2 M sec^{-1} = k(2 \times 10^{-2} M)(1 \times 10^{-2} M)$

From which $k = 5 \times 10^5 M^{-1} sec^{-1}$

(b) $\Delta H^\theta = E_{af} - E_{ab}$

Where ΔH^θ is the standard heat of reaction

E_{af} is the activation energy for forward reaction

E_{ab} is the activation energy for backward reaction

Then $50 = 200 - E_{ab}$

$E_{ab} = (200 - 50) kJ/mol = 150 kJ/mol$

Activation energy of backward reaction is 150 kJ/mol

Question 21

- (a) An increase in concentration of that reactant, decreases rate of the chemical reaction.
- (b) $R = k[X]^m[Y]^n$ (i)

When $[X]$ is increased to $3[X]$ the rate of reaction, R become 9R

That is $9R = k(3[X]^m[Y]^n)$ (ii)

Taking (ii) $\div$ (i) gives; $9 = 3^2 = 3^m$ or $m = 2$

Hence the reaction is of the second order with respect to X.

Question 22

- (a) The initial rate will decrease to one-third.
 (b) $R = k[A][B]$ (Second order chemical reaction)

Substituting given values:

$$8 \times 10^{-3} \text{ moldm}^{-3} \text{ sec}^{-1} = k \times 0.2 \text{ moldm}^{-3} \times 0.2 \text{ moldm}^{-3}$$

$$k = 0.2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Question 23

- (a) The evidences are:
 1. Exothermic reactions may be slow. Example, rusting of iron.
 2. Exothermic reaction may not start without suitable initiating conditions. Example, wood does not burn (combust) at room temperature unless it is ignited.

(b) $R = k[\text{CH}_3\text{CHO}]^x$

$$R_1 = 1.04 = k(0.46)^x$$

$$R_2 = 2.05 \times 10^{-4} = k(0.2)^x$$

$$\text{Then } \frac{R_1}{R_2} = \frac{1.04}{2.05 \times 10^{-4}} = \left(\frac{0.46}{0.2}\right)^x$$

$$5073.17 = 2.3^x$$

Introducing logarithms to base ten both sides gives; $x = \frac{\log(5073.17)}{\log(2.3)} = 10$

Thus the reaction is of tenth order and its rate law is: $R = k[\text{CH}_3\text{CHO}]^{10}$

$$\text{From which } k = \frac{R}{[\text{CH}_3\text{CHO}]^{10}}$$

When $[\text{CH}_3\text{CHO}]$ is equivalent to pressure of 0.46atm, $R = 1.04 \text{ atmsec}^{-1}$

$$\text{Then } k = \frac{1.04 \text{ atmsec}^{-1}}{(0.46 \text{ atm})^{10}} = 2451.63 \text{ atm}^{-9} \text{ sec}^{-1}$$

The rate constant for the reaction is $2451.63 \text{ atm}^{-9} \text{ sec}^{-1}$

Question 24

(a)

Substance added to an excess of zinc and 100 cm ³ of 0.2M HCl	Volume of hydrogen /cm ³	Effect on initial rate of reaction
100 cm ³ water	240	Decreased
10g zinc	240	No change
50 cm ³ 0.2M hydrochloric acid	360	No change

If you have not got how the above table has been filled, the explanation below will be of big help to you!

- 100cm³ water decrease concentration of HCl but does not change number of moles of it. So because number of mole of HCl remain unchanged (240cm³). Also because concentration of HCl is decrease (after dilution of 100cm³ water), the rate of reaction will be decreased.
- 10g zinc has no effect on both volume of H₂ produced and rate of chemical reaction because zinc is already present in excess. More addition of it (10g zinc) is just increasing amount of unreacted zinc.
- 50cm³ 0.2MHCl (1×10^{-2} mol of HCl) is the half amount of 100cm³ 0.2MHCl (2×10^{-2} mol of HCl) originally used in the reaction mixture which produced 240cm³ of H₂. So this extra amount of HCl will produce extra $\frac{1}{2} \times 240 \text{ cm}^3$ or 120 cm³ of hydrogen gas making a total of 360cm³ (240cm³ + 120cm³) produced. However the concentration of HCl remain unchanged (it is still 0.2MHCl) and therefore the rate of chemical reaction remain unchanged too.

(b) If $R = K[A]^m[B]^n = 5 \times 10^{-5}$

$$R_1 = K(0.16)^m (0.2)^n = 5 \times 10^{-5}$$

$$R_2 = K(0.24)^m (0.2)^n = 7.5 \times 10^{-5}$$

$$R_3 = K(0.32)^m (0.1)^n = 5 \times 10^{-5}$$

$$\frac{R_2}{R_1} = \frac{(0.24)^m (0.2)^n}{(0.16)^m (0.2)^n} = \left(\frac{0.24}{0.16}\right)^m = \frac{7.5 \times 10^{-5}}{5 \times 10^{-5}}$$

$$\text{From which } \left(\frac{3}{2}\right)^m = \left(\frac{3}{2}\right)^1 \text{ or } m = 1$$

Hence the order of reaction with respect to A is 1

$$\frac{R_3}{R_2} = \frac{K(0.32)^m (0.1)^n}{(0.26)^m (0.2)^n} = \frac{5}{7.5} \left(\frac{0.32}{0.24}\right)^m \left(\frac{0.1}{0.2}\right)^n = \frac{5 \times 10^{-5}}{7.5 \times 10^{-5}}$$

$$\text{From which } \left(\frac{4}{3}\right)^1 \left(\frac{1}{2}\right)^n = \frac{2}{3}$$

Then $\left(\frac{1}{2}\right)^n = 2/3 \times 3/4 = 1/2$ or $n = 1$

Hence the order of reaction with respect to B is 1

Thus the rate equation is $R = k[A][B]$

Then $R_4 = k(0.12)(0.15)$

And $R_3 = k(0.32)(0.1) = 5 \times 10^{-5}$

So $\frac{R_4}{R_3} = \frac{0.12 \times 0.15}{0.32 \times 0.1} = \frac{R_4}{5 \times 10^{-5}}$; $R_4 = 2.8 \times 10^{-5}$

Hence the rate of the fourth experiment is $2.8 \times 10^{-5} \text{ Ms}^{-1}$

Question 25

- (i) The intermediate, firstly is formed as product and then is consumed as reactant while the catalyst, firstly is used as reactant and then is regenerated as product.
 (ii) Using $R = k[N]^n$ where n is the overall order of reaction

From which $k = \frac{R}{[N]^n}$

Thus units of $k = \frac{\text{units of } R}{(\text{units of } [N]^n)} = \frac{\text{Ms}^{-1}}{\text{M}^n} = \text{s}^{-1}$

Then $\text{M}^{1-n} \text{ s}^{-1} = \text{s}^{-1}$ or $\text{M}^{1-n} = 1$ or M^0

Then $1 - n = 0$ or $n = 1$

Hence the overall of the reaction is 1

T is greater than 700K because the rate constant at T is greater than rate constant at 700K and the value of rate constant increase with the increase in temperature.

Question 26

- (a) Does not affect.

Explanation

Titration experiments involve reactions between liquid solutions. Since liquids are incompressible, pressure has no effect in such reactions and hence the time taken to observe end-point is not affected by pressure.

- (b) Five times the average molecular energy $5 \times 1.3 \text{ kJ/mol} = 6.5 \text{ kJ/mol} = 6500 \text{ J/mol}$

Fraction of miles with energy equal to or greater than 6500J/mol

$$e^{-E/RT} = e^{\frac{-6500}{8.314 \times 298}} = 0.0725$$

But total number of molecules $= nN_A = 1 \text{ mol} \times 6.02 \times 10^{23} \text{ molecule/mol} = 6.02 \times 10^{23} \text{ molecules}$

Thus number of moles with energy equal to or greater than 6500J/mol

$$\begin{aligned} &= 0.0725 \times 6.02 \times 10^{23} \text{ molecules} \\ &= 4.3645 \times 10^{22} \text{ molecules} \end{aligned}$$

Hence the number of molecules is $4.3645 \times 10^{22} \text{ molecules}$

Question 27

- (a) The initial rate will increase

Explanation:

Addition of hydrogen gas increases its concentration thus increasing the frequency of collision between hydrogen and iodine molecules.

- (b) The initial rate will decrease

Explanation

Increase in volume of reaction vessel decreases concentration of the reactants ($\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$) and thus the frequency of collisions between them is decreased.

- (c) The initial rate will increase

Explanation

The catalyst provides the alternative route of the reaction which has lower activation energy.

Refer to the text for the diagram.

- (d) The initial rate will increase

Explanation

Increase in temperature:

- Increases number of molecules with kinetic energy greater than activation energy (In other words it makes collisions between reactant more energetic).
- Increases frequency of collisions between reactants (because the speed of particles increases with increase in temperature).

Refer to the text for the diagram.

Question 28

(a)

(i) The reaction is second order with respect to Cl^- **Justification:**

Tripling $[\text{Cl}^-]$ between trials 1 and 2 with no change in $[\text{MnO}_4^-]$ or $[\text{H}^+]$ results in a nine-fold increase in the rate. (Alternatively you may justify by using calculation –just show the calculation of deducing the order of the reaction).

(ii) The reaction is first order with respect to $[\text{MnO}_4^-]$ **Justification:**

Doubling $[\text{MnO}_4^-]$ between trials 3 and 2 with no change in $[\text{Cl}^-]$ or $[\text{H}^+]$ results in a doubling of the rate.

(b)

(i) $\text{Rate} = k[\text{Cl}^-]^2 [\text{MnO}_4^-] [\text{H}^+]^3$ (ii) $1.93 \times 10^{-3} \text{ M}^{-5} \text{ s}^{-1}$

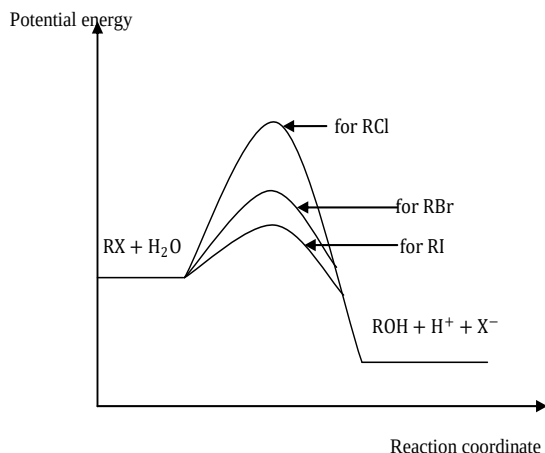
(c) It is not single step reaction

Justification

- The orders of the reaction with respect to reactants do not correspond to the coefficients in the balanced equation
- The reaction requires the simultaneous collision of many reactant particles which is practically impossible

Question 29(a) $R = k[\text{RX}]$

(b)

**Note:**

The overall reaction equation which is $\text{RX} + \text{H}_2\text{O} \rightarrow \text{ROH} + \text{H}^+ + \text{X}^-$ is obtained by combining (through addition) the given two steps in the question.

Question 30

- Increase in pressure; decrease the volume of gaseous reactants (C_2H_4 and H_2) thus increasing their concentrations. The increase in concentration leads to more frequent collisions between C_2H_4 and H_2 and hence the reaction rate is increased
- Increase in temperature increase frequency of collision between C_2H_4 and H_2 through increasing their speed. It also increases the number of molecules (collisions) with activation energy through increasing their kinetic energy. As result, number of molecules with activation energy is increased making more collisions between C_2H_4 and H_2 result in the formation of activated complex and hence the rate of reaction is increased.
- Nickel is the catalyst for the reaction. It provides alternative route for the reaction with lower action and thus number of molecules with kinetic energy equal to or greater than activation energy is increased and hence the rate of reaction is increased.
- Powdered nickel has greater surface area than a single piece of nickel of the same mass. Greater surface area of catalyst means more catalytic sites and hence greater rate of the reaction.

PART FOUR

Question 1

- (a) According to Arrhenius equation ($k = Ae^{\frac{-E_a}{RT}}$); an increase in magnitude of rate constant at given temperature rise becomes high as the activation energy (E_a) becomes high too. For exothermic reactions, the activation energy of backward reaction is higher than that of forward reaction making the increase in K_b value greater than that of K_f value at the given temperature rise and hence the K_c value decreases as the temperature increases.

- (b) Initially: Number of moles of $PCl_5 = \frac{2}{208.5} \text{ mol} = 0.00959 \text{ mol}$

Equation for the reaction: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

At equilibrium $0.00959 - x \quad x \quad x$

$$K_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{0.00959 - x}{v}\right)} = \frac{x^2}{(0.00959 - x)v}$$

$$x^2 + 0.008x - 0.00007672 = 0 \quad \text{or} \quad x = 0.005629$$

Degree of dissociation of PCl_5 :

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Original number of moles before dissociation}}$$

$$= \frac{0.005629}{0.00959} = 0.587 \quad \text{or} \quad 58.7\%$$

Hence degree of dissociation of PCl_5 is 58.7%

Question 2

- (a) Because $K_c = \frac{k_f}{k_r} = 57$, the rate constant for the formation of HI (forward reaction) is larger than the rate constant for the decomposition of HI (reverse reaction) by a factor of 57.

- (b) $K_c = \frac{k_f}{k_r}$

$$\text{Substituting; } 57 = \frac{k_f}{1.16 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}}$$

$$\text{From which } K_f = 6.61 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$$

- (c) A catalyst lowers the activation energy barrier for the forward and reverse reactions by the same amount, thus increasing the rate constants k_f and k_r by the same factor. Because equilibrium constant, K_c equals to the ratio of k_f to k_r the value of K_c is unaffected by addition of catalyst.
- (d) Because the reaction is endothermic, the activation energy for the forward reaction is greater than activation energy for the reverse reaction. Consequently, as the temperature increases, k_f increases more than k_r , and therefore $K_c = \frac{k_f}{k_r}$ increases, consistent with Le – Chatelier's principle.

Question 3

- (a) Reaction 1

Explanation

The forward reaction is endothermic. So according to Le-Chatelier's principle, increase in temperature (which in turn increases heat at initial stage) will shift the position of equilibrium to the right hand side so as to absorb the added heat energy.

- (b) Reaction 1

Explanation

The reaction is not accompanied with change in number of moles of gas molecules which in turn means the reaction does neither increase nor decrease the pressure and hence pressure has no effect on the equilibrium.

- (c)

- (i) None
(ii) Reaction 3

Explanation

The reaction has greatest enthalpy change and hence more affected with the change in temperature

Question 4

- (a) It is the balance of the rate of the two reactions (forward and reverse reaction) which are proceeding at the same time in opposite directions. It is an equilibrium involving the constant interchange of particles in motion in opposite directions of forward and reverse reaction.
- (b) System of chemical equilibrium opposes the change. So increase in pressure shifts the position of chemical equilibrium to the side with fewer moles (NH_3 – side) so as to decrease the pressure.
- (c) Too expensive to generate such high pressure (50MPa) and therefore is not economic.
- (d)

- (i) Yield of ammonia increases

Explanation

The forward reaction is exothermic. So according to the Le-Chatelier's principle, the decrease in temperature will shift the position of equilibrium to the NH_3 – side so as to increase the temperature.

- (ii) Increase the rate of producing NH_3 .

- (iii) Balance between **rate** of producing NH_3 and **yield** of NH_3 (This means good yield of NH_3 is obtained at reasonable rate).

Question 5

- (a) Depends on temperature only.

- (b) Mass of CO in 100g of the mixture = 90.55g

Thus mass of CO_2 in the gaseous mixture = $(100 - 90.55) \text{ g} = 9.45 \text{ g}$

$$\text{Number of moles of CO} = \frac{90.55}{28} \text{ mol} = 3.24 \text{ mol}$$

$$\text{Number of moles of CO}_2 = \frac{9.45}{44} \text{ mol} = 0.215 \text{ mol}$$

$$P_{\text{CO}} = X_{\text{CO}} P_T; P_{\text{CO}} = \left(\frac{3.234}{3.234 + 0.215} \right) \times 1 \text{ atm} = 0.94 \text{ atm}$$

$$P_{\text{CO}_2} = P_T - P_{\text{CO}} \text{ (From Dalton's law of partial pressure)}$$

$$P_{\text{CO}_2} = (1 - 0.94) \text{ atm} = 0.06 \text{ atm}$$

$$\text{Then } K_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} = \frac{(0.94 \text{ atm})^2}{0.06 \text{ atm}} = 14.73 \text{ atm}$$

$$\text{Using } K_c = K_p (RT)^{m-n}$$

Where:

m is the number of molecules in the reactant side = 1 (for gases only).

n is the number of molecules in the product side = 2.

$$\text{Then; } K_c = 14.73 \times (0.082 \times 1127)^{1-2} \text{ mol dm}^{-3} = 0.159 \text{ mol dm}^{-3}$$

Hence the equilibrium constant, $K_c = 0.159 \text{ mol dm}^{-3}$

Question 6

- (a)

- (i) Is the state that occurs in the reversible reaction when the rate forward reaction is equal to the rate of backward reaction.

- (ii) Is the direction to which the reversible reaction proceeds so as to establish the equilibrium and therefore acting as the measure of relative concentrations of reacting substances at equilibrium.



$$\text{Initially (t = 0)} \quad \quad \quad 1 \quad \quad 3 \quad \quad 0$$

$$\text{At equilibrium} \quad \quad \quad 1 - x \quad 3 - 3x \quad 2x$$

And total number of moles of gases at equilibrium,

$$n_T = (1 - x) + (3 - 3x) + 2x = (4 - 2x) \text{ moles}$$

But from Avogadro's law; Mole ratio = volume ratio

Thus; percentage by volume of the gas = percentage by moles

$$\text{Then } \left(\frac{n_{\text{NH}_3}}{n_T} \right) = 0.15 \text{ or } \frac{2x}{4-2x} = 0.15 \text{ or } x = 0.26$$

$$X_{\text{H}_2} = \frac{3-(3 \times 0.26)}{4-(2 \times 0.26)} = 0.64$$

$$X_{\text{N}_2} = \frac{1-0.26}{4-(2 \times 0.26)} = 0.21$$

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{(X_{\text{NH}_3} P_T)^2}{(X_{\text{N}_2} P_T)(X_{\text{H}_2} P_T)^3} = \frac{(X_{\text{NH}_3})^2}{(X_{\text{N}_2})(X_{\text{H}_2})^3 P_T^2}$$

$$K_p = \frac{(0.15)^2}{0.21 \times (0.64)^3 (1.01 \times 10^6)^2} = 4 \times 10^{-13} \text{ Pa}^{-2}$$

Hence the equilibrium constant, K_p is $4 \times 10^{-13} \text{ Pa}^{-2}$

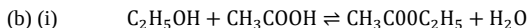
Question 7

(a)

(i)

- Catalyses the reaction thus increasing the rate of production of the compound.
- Dehydrate (remove) water which makes the reaction to be more forward thus increasing percentage yield of the compound (ethylethanoate).

(ii) No significant production of ethylethanoate will be observed (Alkaline solution like NaOH is good catalyst for reverse reaction in the production of carboxylic acid like ethanoic acid).



Initially 0.18 1 0 0

At equilibrium 0.18 - x 1 - x x x

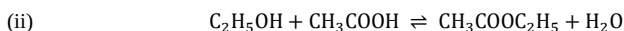
$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.18-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{(0.18-x)(1-x)}$$

But 1 - x = 0.829 (0.829 moles of CH₃COOH remained at equilibrium)

x = 0.171 moles

$$K_c = \frac{0.171^2}{(0.18 - 0.171)(1 - 0.171)} = 3.919$$

Hence the value of K_c is 3.919



Initially 0.3 0.2 0 0

At equilibrium 0.3 - x 0.2 - x x x

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.3-x}{V}\right)\left(\frac{0.2-x}{V}\right)} = \frac{x^2}{(0.3-x)(0.2-x)} = 3.919$$

$$x^2 = 3.919x^2 - 1.9595x + 0.23514$$

x = 0.156 moles (x = 0.515 is not practical solution because it exceeds initial amount of reactants present in the system).

Hence number of moles of ethylethanoate (CH₃COOC₂H₅) formed in a dm³ was 0.156 moles.

But molar mass of ethylethanoate = 88g /mole using m = nM_r

Mass of the ethylethanoate = 0.156 × 88g = 13.728g

Hence mass of ethylethanoate in 1dm³ of equilibrium mixture is 13.728g

Question 8

(a) This is the temperature dependent fixed ratio which is obtained as the quotient of the product of the equilibrium concentration of products to that of reactants raised to powers equal to their stoichiometric coefficients.

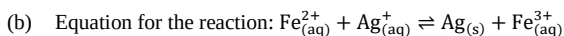
It is the fixed ratio which is obtained according to the equilibrium law.

For the reaction: Aa + bB ⇌ cC + dD

Then Equilibrium constant, $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Significance

The value of equilibrium constant K_c is important in predicting the extent of forward reaction or backward reaction of which a particular reaction proceeds. If K_c is too large then the reaction is more forward while small value of K_c implies that the reaction is more backward.

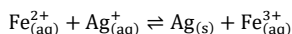


As we are given with all reagents at the beginning of the reaction; we must firstly find reaction quotient (R_Q) so as to determine the direction to which the reaction proceed.

$$R_Q = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^+]} = \frac{0.3}{0.2 \times 0.1} = 15$$

But K_c = 2.98

So Q_c > K_c and hence the reaction **proceed backward** to establish the equilibrium.



Initially 0.1 0.2 0.3

At equilibrium 0.1 + x 0.2 + x 0.3 - x

$$K_c = \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^+]}$$

$$\text{Then } \frac{0.3 - x}{(0.2 + x) \times (0.1 + x)} = 2.98$$

$$\text{Or } 2.98x^2 + 1.894x - 0.2404 = 0 \text{ or } x = 0.10843$$

Hence at equilibrium:

$$[\text{Fe}^{3+}] = 0.19157\text{M}$$

$$[\text{Ag}^+] = 0.30843\text{M}$$

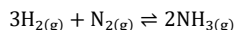
$$[\text{Fe}^{2+}] = 0.20843$$

Question 9

(a) **Name of the law:** Equilibrium law

It states that: This is the temperature dependent fixed ratio which is obtained as the quotient of the product of the equilibrium concentration of products to that of reactants raised to powers equal to their stoichiometric coefficients.

(b)



$$\text{Initially} \quad 0 \quad 0 \quad 1$$

$$\text{At equilibrium} \quad 3x \quad x \quad 1 - 2x$$

$$n_T \text{ at equilibrium } 3x + x + 1 - 2x = (1 + 2x) \text{ moles}$$

Where $2x$ is numerically equal to the degree of dissociation.

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{H}_2})^3 (P_{\text{N}_2})} = \frac{(X_{\text{NH}_3} P_T)^2}{(X_{\text{H}_2} P_T)^3 (X_{\text{N}_2} P_T)} = \frac{(X_{\text{NH}_3})^2}{(X_{\text{H}_2})^3 (X_{\text{N}_2}) P_T^2}$$

$$\text{But } 2x = 0.95 \text{ (95\% NH}_3 \text{ of dissociated into its elements); } x = 0.475$$

Then:

$$X_{\text{NH}_3} = \frac{1 - 2x}{1 + 2x} = 0.026$$

$$X_{\text{H}_2} = \frac{3x}{1 + 2x} = 0.731$$

$$X_{\text{N}_2} = \frac{x}{1 + 2x} = 0.244$$

$$\text{Then } 2 \times 10^{-14} = \frac{0.026^2}{0.731^3 \times 0.244 P_T^2} \text{ or } P_T = 5.955 \times 10^5 \text{ Pa}$$

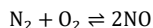
Hence the pressure is $5.955 \times 10^5 \text{ Pa}$

(c) K_p will remain the same as the constant does not depend on the concentration of the reagents present in the system (like K_c , K_p is only temperature dependent).

Question 10

(a) Increase in temperature and decrease in temperature favour forward reaction for endothermic reaction and exothermic reaction respectively and vice versa.

(b)



$$\text{Initially} \quad 4 \quad 1 \quad 0$$

$$\text{At equilibrium} \quad 4 - x \quad 1 - x \quad 2x$$

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{4-x}{v}\right)\left(\frac{1-x}{v}\right)} = \frac{4x^2}{x^2 - 5x + 4} = 8 \times 10^{-4}$$

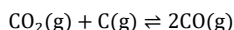
$$3.9992x^2 + 0.004x - 0.0032 = 0 \text{ or } x = 0.0278$$

$$\% \text{NO} = \frac{n_{\text{NO}}}{n_T} \times 100\% = \left(\frac{2x}{5}\right) \times 100\% = 1.112\%$$

Hence the percentage of nitrogen monoxide by volume is 1.112%

Question 11

- (a) Equilibrium constant is the reaction quotient of the chemical system at equilibrium.
 (b) Reaction equation;



From which; $K_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}}$

But by Dalton's law of partial pressure; $P_T = 4 = P_{\text{CO}} + P_{\text{CO}_2}$

From which; $P_{\text{CO}_2} = 4 - P_{\text{CO}}$

Then; $K_p = 10 = \frac{(P_{\text{CO}})^2}{4 - P_{\text{CO}}}$; $(P_{\text{CO}})^2 + 10P_{\text{CO}} - 40 = 0$

Solving the above quadratic equation with P_{CO} as the unknown gives;

$P_{\text{CO}} = 3\text{atm}$ and therefore $P_{\text{CO}_2} = 4 - P_{\text{CO}} = (4 - 3)\text{atm} = 1\text{atm}$

Then; $X_{\text{CO}} = \frac{P_{\text{CO}}}{P_T} = \frac{3\text{atm}}{4\text{atm}} = 0.75$ and $X_{\text{CO}_2} = \frac{P_{\text{CO}_2}}{P_T} = \frac{1\text{atm}}{4\text{atm}} = 0.25$

The mole fraction of CO is 0.75

The mole fraction of CO₂ is 0.25

For gases; Volume ratio = Mole ratio (Avogadro's law)

It follows that; $\frac{V_{\text{CO}_2}}{V_T} \times 100 = \frac{n_{\text{CO}_2}}{n_T} \times 100 = 6$

But; $\frac{n_{\text{CO}_2}}{n_T} = X_{\text{CO}_2}$; so $X_{\text{CO}_2} = 0.06$ and $X_{\text{CO}} = 1 - X_{\text{CO}_2} = 1 - 0.06 = 0.94$

Then; $K_p = 10 = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} = \frac{(X_{\text{CO}}P_T)^2}{X_{\text{CO}_2}P_T} = \frac{(X_{\text{CO}})^2P_T}{X_{\text{CO}_2}} = \frac{(0.94)^2P_T}{0.06}$

From which the total pressure (P_T) is 0.68atm

Question 12

- (a)
 (i) Reaction for contact process

Reason

The reaction is accompanied with greater heat change.

- (ii) Reaction for Haber process

Reason

Reaction is accompanied with greater change of number of gas molecules.



At equilibrium $2 - x \quad 3 - x \quad 2x$

$$K_c = \frac{[\text{C}]^2}{[\text{A}][\text{B}]} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{3-x}{v}\right)\left(\frac{2-x}{v}\right)} = \frac{4x^2}{x^2 - 5x + 6}$$

But $K_c = 4$

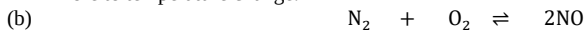
Then $4 = \frac{4x^2}{x^2 - 5x + 6}$

Solving above equation gives $x = 1.2$ and $2x = 2 \times 1.2 = 2.4\text{moles}$

Hence number of moles of C at equilibrium is 2.4 moles

Question 13

- (a) The reaction for contact process has smaller change of number of gas molecules implying that high pressure has less effect (compared to Haber process) while the higher heat change in the contact process ensures that the contact process respond more to temperature change.



At equilibrium $4 - x \quad 1 - x \quad 2x$

n_T at equilibrium $(4 - x) + (1 - x) + (2x) = 5\text{moles}$

$$K_p = \frac{(P_{\text{NO}})^2}{(P_{\text{N}_2})(P_{\text{O}_2})} = \frac{(X_{\text{NO}}P_T)^2}{(X_{\text{N}_2}P_T)(X_{\text{O}_2}P_T)} = \frac{(X_{\text{NO}})^2}{(X_{\text{N}_2})(X_{\text{O}_2})}$$

But $X_{\text{NO}} = \frac{2x}{5}$, $X_{\text{N}_2} = \frac{4-x}{5}$, $X_{\text{O}_2} = \frac{1-x}{5}$

Then $0.0008 = \frac{4x^2}{(4-x)(1-x)} = \frac{4x^2}{4-5x+x^2}$

Solving above equation gives $x = 0.028$

$\% \text{ NO} = \left(\frac{2x}{5}\right) \times 100\% = \frac{2 \times 0.028}{5} \times 100\% = 1.12\%$

Hence the percentage of nitric oxide is 1.12%

Question 14

(a)

1. It increases the percentage yield of ammonia.
2. It increases the rate of producing ammonia (ammonia is produced in shorter time).

(b) Equation for dissociation of N_2O_4 into NO_2 : $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2(\text{g})$

$$K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{(0.3\text{atm})^2}{(0.7\text{atm})} = 0.1286\text{atm}$$

If $P_T = 10\text{atm}$

By Dalton's law of partial pressure; $P_{\text{NO}_2} + P_{\text{N}_2\text{O}_4} = 10\text{atm}$

Then $0.1286 = \frac{(P_{\text{NO}_2})^2}{10 - P_{\text{NO}_2}}$

$$(P_{\text{NO}_2})^2 + 0.1286P_{\text{NO}_2} - 1.286 = 0$$

This is the quadratic equation in P_{NO_2} ; thus solving the equation gives $P_{\text{NO}_2} = 1.07\text{atm}$.

$$P_{\text{N}_2\text{O}_4} = 10 - P_{\text{NO}_2} = 8.93\text{atm}$$

Hence:

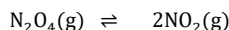
The partial pressure of NO_2 is 1.07atm

The partial pressure of N_2O_4 is 8.93atm

Alternative solution

$$K_p = \frac{(X_{\text{NO}_2}P_T)^2}{(X_{\text{N}_2\text{O}_4}P_T)} = \frac{(X_{\text{NO}_2})^2 P_T}{(X_{\text{N}_2\text{O}_4})}$$

Where $P_T = 10\text{atm}$



At equilibrium $1 - \alpha \qquad 2\alpha$

$$X_{\text{NO}_2} = \frac{2\alpha}{1 + \alpha} \quad \text{and} \quad X_{\text{N}_2\text{O}_4} = \frac{1 - \alpha}{1 + \alpha}$$

Then $K_p = \frac{4\alpha^2 P_T}{1 - \alpha^2} = \frac{4 \times 10 \alpha^2}{1 - \alpha^2} = 0.1286$

Solving above equation gives $\alpha = 0.0568$

$$P_{\text{N}_2\text{O}_4} = \left(\frac{1 - \alpha}{1 + \alpha}\right) P_T = \left(\frac{1 - 0.0568}{1 + 0.0568}\right) 10\text{atm}$$

$$P_{\text{NO}_2} = \left(\frac{2\alpha}{1 + \alpha}\right) P_T = \left(\frac{2 \times 0.0568}{1 + 0.0568}\right) 10\text{atm} = 1.07\text{atm}$$

Hence

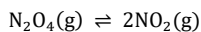
The partial pressure of NO_2 is 1.07atm

The partial pressure of N_2O_4 is 8.93atm

Question 15

(a) Temperature only.

(b) Increase in temperature increases the magnitude of equilibrium constant for endothermic reaction while it decreases the magnitude of equilibrium constant for exothermic reaction and vice-versa.



At equilibrium $0.28\text{atm} \qquad 1.1\text{atm}$

$$K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{(1.1\text{atm})^2}{(0.28\text{atm})} = 4.32\text{atm}$$

Total pressure, P_1 at equilibrium = $P_{N_2O_4} + P_{NO_2}$ (By Dalton's law of partial pressure)

If the volume is doubled from V_1 to V_2 such that $V_2 = 2V_1$

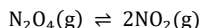
By Boyle's law; $P_1V_1 = P_2V_2$

$$P_2 = \frac{P_1V_1}{V_2} = \frac{P_1V_1}{2V_1} = \frac{P_1}{2}$$

$$\text{For } N_2O_4; P_2 = \frac{0.28\text{atm}}{2} = 0.14\text{atm}$$

$$\text{For } NO_2; P_2 = \frac{1.1\text{atm}}{2} = 0.55\text{atm}$$

The decrease in pressure will shift equilibrium position to the NO_2 side.



At new equilibrium $0.14 - x \quad 0.55 + 2x$

$$\text{Then; } 4.32 = \frac{(0.55+2x)^2}{0.14-x}$$

$$\text{From which; } 4x^2 + 6.52x - 0.3023 = 0; x = 0.045$$

Hence at new equilibrium:

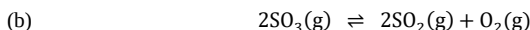
$$\text{Partial pressure of } N_2O_4 = 0.14 - 0.045 = (0.14 - 0.045)\text{atm} = 0.095\text{atm}$$

$$\text{Partial pressure of } NO_2 = 0.55 + 2x = (0.55 + 2 \times 0.045)\text{atm} = 0.64\text{atm}$$

Question 16

(a)

- (i) No effect.
- (ii) The percentage yield will increase.
- (iii) No effect.



At equilibrium $1 - 2x \quad 2x \quad x$

$$\text{Where } \alpha = \frac{2x}{1} = 0.5, x = 0.25$$

$$P_{O_2} = X_{O_2} P_T = \left(\frac{x}{1+x} \right) 1\text{atm} = 0.2\text{atm}$$

$$P_{SO_2} = X_{SO_2} P_T = \left(\frac{2x}{1+x} \right) 1\text{atm} = 0.4\text{atm}$$

$$P_{SO_3} = X_{SO_3} P_T = \left(\frac{1-2x}{1+x} \right) 1\text{atm} = 0.4\text{atm}$$

$$K_p = \frac{(P_{SO_2})^2 (P_{O_2})}{(P_{SO_3})^2} = \frac{0.2 \times 0.4^2}{0.4^2} = 0.2\text{atm}$$

Hence K_p is 0.2atm

$$K_c = K_p (RT)^{m-n} \quad \text{for } m = 2 \text{ and } n = 3$$

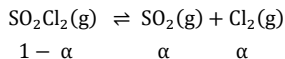
$$K_c = K_p (RT)^{2-3} = K_p (RT)^{-1} \quad \text{or } K_c = \frac{K_p}{RT} = \frac{0.2}{0.082 \times 523} = 4.66 \times 10^{-3} \text{mol dm}^{-3}$$

Hence K_c is $4.66 \times 10^{-3} \text{mol dm}^{-3}$

Question 17

(a)

- (i) It increases the rate of both forward and backward reaction by the same amount.
- (ii) A: To increase the production rate of ammonia.
B: To reduce the production cost of ammonia.



Where α is numerically equal to the degree of dissociation = 0.9

$$P_{SO_2} = X_{SO_2} P_T = \left(\frac{\alpha}{1+\alpha} \right) P_T = \left(\frac{0.9}{1+0.9} \right) 1\text{atm} = 0.474\text{atm} = P_{Cl_2}$$

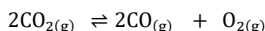
$$P_{SO_2Cl_2} = \left(\frac{1-\alpha}{1+\alpha} \right) P_T = \left(\frac{1-0.9}{1+0.9} \right) \times 1\text{atm} = 0.053\text{atm}$$

$$K_p = \frac{(P_{SO_2})(P_{Cl_2})}{(P_{SO_2Cl_2})} = \frac{0.474 \times 0.474}{0.053} = 4.239 \text{atm}$$

Hence numerical value of K_p is 4.239

Question 18

- (a) Catalyst affect chemical equilibrium by enabling the equilibrium to be reached earlier. It has no effect on the **position** of chemical equilibrium (not chemical equilibrium in general).
(b)



At equilibrium



But $\alpha = \frac{2x}{1} = 0.4$ or $x = 0.2$

Atmospheric pressure = 1 atm

$$P_{\text{CO}} = X_{\text{CO}} P_T = \left(\frac{2x}{1+x} \right) \times 1 \text{ atm} = 0.33 \text{ atm}$$

$$P_{\text{O}_2} = X_{\text{O}_2} P_T = \left(\frac{x}{1+x} \right) \times 1 \text{ atm} = 0.17 \text{ atm}$$

$$P_{\text{CO}_2} = X_{\text{CO}_2} P_T = \left(\frac{1-2x}{1+x} \right) \times 1 \text{ atm} = 0.5 \text{ atm}$$

$$K_p = \frac{(P_{\text{CO}})^2 (P_{\text{O}_2})}{(P_{\text{CO}_2})^2} = \frac{(0.33)^2 (0.17)}{(0.5)^2} = 7.4 \times 10^{-2} \text{ atm}$$

Hence the dissociation constant (K_p) for the reaction is $7.4 \times 10^{-2} \text{ atm}$

Question 19

(a) $K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]}$

At the equilibrium; rate of forward reaction = rate of backward reaction

That is $K_f [\text{NO}]^2 [\text{O}_2] = K_b [\text{NO}_2]^2$

From which $\frac{K_f}{K_b} = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]} = K_c$

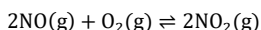
Substituting $\frac{2.6 \times 10^3 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}}{4.1 \text{ L mol}^{-1} \text{ s}^{-1}} = K_c$

- (b) Hence the value of equilibrium constant is $634.15 \text{ L mol}^{-1}$

(c) $\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = R = K[\text{NO}]^2 [\text{O}_2]$
 $= 2.6 \times 10^3 \times (0.006)^2 \times 0.29 \text{ or } 0.027 \text{ Ms}^{-1}$

Then $\frac{d[\text{NO}_2]}{dt} = 2R = 2 \times 0.027 \text{ Ms}^{-1}$

Hence the rate of the production of NO_2 is 0.054 Ms^{-1}



0 0 0.2

2x x 0.2 - 2x

But $\frac{2x}{0.2} = 0.15$ or $x = 0.015 \text{ mol}$

Then $[\text{NO}_2] = \frac{(0.2 - 2 \times 0.015)}{5 \text{ L}} \text{ mol} = 0.034 \text{ M}$

$[\text{O}_2] = \frac{0.015 \text{ mol}}{5 \text{ L}} = 0.003 \text{ M}$

$[\text{NO}] = \frac{2 \times 0.015 \text{ mol}}{5 \text{ L}} = 0.006 \text{ M}$

Then using $K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]} = \frac{(0.034 \text{ M})^2}{(0.006 \text{ M})^2 \times 0.003 \text{ M}} = 1.07 \times 10^4 \text{ M}^{-1}$

Hence the value of the equilibrium constant is $1.07 \times 10^4 \text{ M}^{-1}$

Question 20

- (a) (i) It explains effect of different factors on the position of chemical equilibrium.

(ii) It describes the relationship between concentration of reactants and that of products when the chemical system of reversible reaction is allowed to attain the equilibrium. .

(b) (i) $K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2 \text{O}_4]}$ (ii) $K_p = \frac{(\text{NO}_2)^2}{(\text{N}_2 \text{O}_4)}$

(iii) $K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2 \text{O}_4})} = \frac{(P_{\text{NO}_2})^2}{2.71 \text{ atm}} = 0.133 \text{ atm}$

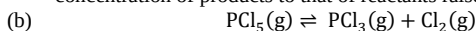
$(P_{\text{NO}_2})^2 = 0.36043 \text{ atm}^2$; $P_{\text{NO}_2} = \sqrt{0.36043 \text{ atm}^2} = 0.6 \text{ atm}$

Equilibrium pressure of NO_2 is 0.6atm

Question 21

(a)

- (i) Represents the ratio of product of concentration of products to that of reactants raised to powers equal to their stoichiometric coefficients obtained in the course of the chemical reaction.
 (ii) Represents the temperature dependent fixed ratio which is obtained as the quotient of the product of equilibrium concentration of products to that of reactants raised to powers equal to their stoichiometric coefficient.



Pressure at $t = 0$ P_0 0 0

Pressure at equilibrium $P_0 - P$ P P

(Since pressure is directly proportional to the number of moles, pressure ratio is equal to the mole ratio and therefore pressure can be treated as moles in the equation).

Also from, pressure-mole relationship:

Degree of dissociation, $\alpha = \frac{P}{P_0}$

And $\alpha = 20\% = 0.2$ (PCl_5 dissociated to 80%)

Thus $0.2 = \frac{P}{P_0}$ or $P = 0.2P_0$

Total pressure at equilibrium; $P_0 - P + P + P = 1.5$ or $P_0 + P = P_0 + 0.2P_0 = 1.2P_0 = 1.5$

From which $P_0 = 1.25$ atm

And $P = 0.2P_0 = 0.2 \times 1.25 \text{ atm} = 0.25 \text{ atm}$

Hence:

Partial pressure of $\text{PCl}_5 = P_0 - P = (1.25 - 0.25)\text{atm} = 1 \text{ atm}$

Partial pressure of $\text{PCl}_3 = P = 0.25 \text{ atm}$

Partial pressure of $\text{Cl}_2 = P = 0.25 \text{ atm}$

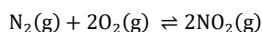
Question 22

(a) By adding hydrogen gas.

Explanation:

Decreasing volume of the container has no effect on the position of chemical equilibrium. This is because the decrease in volume will increase the total pressure of the system and since the reaction is not accompanied with change in number of gas molecules, the change in pressure has no effect on the position of equilibrium and thus no effect on the yield of HI too. However according to Le-Chatelier's principle, the increase in concentration of hydrogen gas shift the position of equilibrium to HI side and therefore increasing the yield of HI.

(b) For gases, the most common method of representing equilibrium constant is K_p . So the given value of Equilibrium constant is K_p value.



At $t = 0$ 2 2 0

At equilibrium $2 - x$ $2 - 2x$ $2x$

$K_p = 4.3 \times 10^{-3}$

$$K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2})(P_{\text{O}_2})^2} = \frac{(X_{\text{NO}_2}P_T)^2}{(X_{\text{N}_2}P_T)(X_{\text{O}_2}P_T)^2} = \frac{(X_{\text{NO}_2})^2}{(X_{\text{N}_2})(X_{\text{O}_2})^2 P_T}$$

Using $X = \frac{n}{n_T}$

Where $n_T = 2 - x + 2 - 2x + 2x = 4 - x$

Then; $K_p = \frac{\left(\frac{2x}{4-x}\right)^2}{\left(\frac{2-x}{4-x}\right)\left(\frac{2-2x}{4-x}\right)^2 \times 1} = 4.3 \times 10^{-3}$

$\frac{4x^2(4-x)}{(2-x)(2-2x)^2} = 4.3 \times 10^{-3}$

$\frac{16x^2 - 4x^3}{8 - 20x + 16x^2 - 4x^3} = 4.3 \times 10^{-3}$

From which; $3.982x^3 - 15.9312x^2 - 0.086x + 0.0344 = 0$

Solving the above equation, gives the practical value of x which is 0.044.

Hence the composition of each is as follows:

Number of moles of $\text{N}_2 = 2 - x = 1.956 \text{ mol}$.

Number of moles of $O_2 = 2 - 2x = 1.912 \text{ mol}$.

Number of moles of $NO_2 = 2x = 0.088 \text{ mol}$.

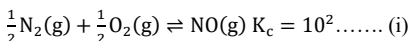
Question 23

(a)

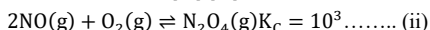
(i) White fumes (of hydrogen chloride gas).

(ii) HCl being gaseous is removed from the equilibrium system and thus the position of equilibrium shifts to the right.

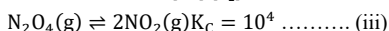
(b) Given that:



From which: $K_c = \frac{[NO]}{[N_2]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}} = K_1 = 10^2$



From which: $K_c = \frac{[N_2O_4]}{[NO]^2[O_2]} = K_2 = 10^3$



From which: $K_c = \frac{[NO_2]^2}{[N_2O_4]} = K_3 = 10^4$

Taking 2(i) + (ii) + (iii) gives



Thus the K_c of the given equation will be given by the following relationship:

$$\text{Required } K_c = (K_1)^2 K_2 K_3 = (10^2)^2 \times 10^3 \times 10^4 = 10^{11}$$

Hence the equilibrium constant is 10^{11}

Question 24

(a) "When a chemical system is allowed to reach the equilibrium at a particular temperature, there is a fixed ratio of product of concentration of products to that of reactants raised to powers equals to stoichiometric coefficients regardless to the original concentration of the reagents present in the system."

For the hypothetical reaction: $aA + bB \rightleftharpoons cC + dD$

Then according to equilibrium law; $\frac{[C]^c[D]^d}{[A]^a[B]^b} = \text{Constant } (K_c)$

(b)

$$(i) \quad K_c = \frac{[R]^2}{[P][Q]^2}$$

$$(ii) \quad [P] = \frac{3.82 \text{ mol}}{10 \text{ dm}^3} = 0.382 \text{ mol dm}^{-3}; [R] = \frac{5.24 \text{ mol}}{10 \text{ dm}^3} = 0.524 \text{ mol dm}^{-3}$$

$$K_c = 68.0 \text{ mol}^{-1} \text{ dm}^3 = \frac{(0.524 \text{ mol dm}^{-3})^2}{0.382 \text{ mol dm}^{-3} \times [Q]^2}$$

From which; $[Q] = 0.103 \text{ mol dm}^{-3}$

(iii) The equilibrium amount of P will increase while the K_c value will decrease.

(iv) The equilibrium amount of P will increase.

$$(v) \quad K_c = \frac{[P][Q]^2}{[R]^2} = \frac{1}{\frac{[R]^2}{[P][Q]^2}} = \frac{1}{68.0 \text{ mol}^{-1} \text{ dm}^3} = 0.0147 \text{ mol dm}^{-3}$$

Question 25

(a)

(i)

First feature: Rate of forward reaction is equal to the rate of backward reaction.

Second feature: Concentration of reagents present in the system remain unchanged.

(ii) Heating will force the system to resist the change by absorbing the heat and therefore favouring forward reaction which is endothermic and hence more NO_2 which appears in brown colouration will be formed.

(iii) Increasing the pressure will force the system to resist the change by shifting the equilibrium position to the side with fewer gas molecules (N_2O_4 side) and hence the amount of NO_2 decreases.

(b) Using $n = \frac{m}{M_r}$;

$$\text{Initial number of moles of } CH_3COOH = \frac{24.4 \text{ g}}{60 \text{ g mol}^{-1}} = 0.4 \text{ mol}$$

$$\text{Initial number of moles of } CH_3CH_2OH = \frac{24.3 \text{ g}}{46 \text{ g mol}^{-1}} = 0.53 \text{ mol}$$

CH_3COOH reacts with $NaOH$ according to the following equation; $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

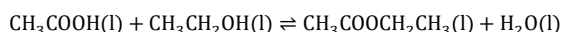
From which mole ratio of $NaOH$ to CH_3COOH is 1:1

Thus $n_{\text{NaOH}} = n_{\text{CH}_3\text{COOH}} = \frac{26.5}{1000} \times 0.4 \text{ mol} = 0.0106 \text{ mol}$

Whence number of moles of CH_3COOH in 25 cm^3 of the solution is 0.0106 mol .

Then number of moles of CH_3COOH in 250 cm^3 of the solution = $\frac{0.0106 \times 250}{25} \text{ mol} = 0.106 \text{ mol}$

Hence number of moles of CH_3COOH at equilibrium was 0.106 mol



Initially

0.4 0.53 0 0

At equilibrium

$0.4 - x$ $0.53 - x$ x x

$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$$

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.4-x}{V}\right)\left(\frac{0.53-x}{V}\right)} = \frac{x^2}{(0.4-x)(0.53-x)}$$

But $0.4 - x = 0.106$; $x = 0.294$

Substituting; $K_c = \frac{0.294^2}{(0.4-0.294)(0.53-0.294)} = 3.46$

Hence the equilibrium constant is 3.46

Question 26

- (a) **In terms of Le-Chatelier's principle:** To decrease the applied high pressure the equilibrium position will shift to the side with fewer gas particles (ammonia side) by producing more ammonia and hence high pressure has an advantage of increasing the ammonia yield in the Haber process.

In terms of behaviour of particles: High pressure makes gases to be more compressed into smaller volume and therefore more concentrated leading to greater collision frequency and hence higher reaction rate. So high pressure has another advantage of increasing the rate of ammonia production in the Haber process.

(b)

$$(i) \quad K_c = \frac{[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$$

(ii) At equilibrium:

$$n_{\text{Acid}} = 1 - x; \quad n_{\text{Ethanol}} = 2 - x$$

$$n_{\text{Ester}} = x; \quad n_{\text{Water}} = 5 + x$$

But $n_{\text{Ester}} = x = 0.54 \text{ mol}$;

Thus $n_{\text{Water}} = 5 + x = (5 + 0.54) = 5.54 \text{ mol}$

The number of moles of water is 5.54 mol

$$(iii) \quad K_c = \frac{[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]} = \frac{\left(\frac{x}{V}\right)\left(\frac{5+x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{2-x}{V}\right)} = \frac{x^2+5x}{x^2-3x+2}$$

Substituting; $K_c = \frac{0.54^2+5(0.54)}{0.54^2-3(0.54)+2} = 4.45$

The value for K_c is 4.45

The K_c value has no units because there is an equal number of molecules in either side (reactants side and products side) of the reaction equation.

- (iv) A: The amount will decrease.
B: The time will decrease.
C: The value will decrease.

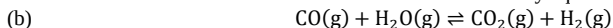
Question 27

(a)

- (i) *Is the condition which occurs in the reversible reaction when the rate of forward reaction is equal to the rate of reverse reaction.* In this case the equilibrium occurs when the rate of consumption of 3-menthylbutanoic acid and ethanol is equal to the rate of producing ester and water at which concentration of all reagents (acid, ethanol, ester and water) remain unchanged.

- (ii) In order to increase the yield of ester. This is because, according to Le-Chatelier's principle; using high concentration of ethanol shifts equilibrium position to ester side (side with lower concentration) and therefore forming more ester.

- (iii) Catalyst enable the equilibrium to be reached in shorter time. However, it has no effect in equilibrium position because it increases the rate of both forward and reverse reaction by equal amount.



Number of moles (At = 0) 3 1 0 0

Number of moles (at equilibrium) $3 - x$ $1 - x$ x x

$$K_p = \frac{(P_{\text{CO}_2})(P_{\text{H}_2})}{(P_{\text{CO}})(P_{\text{H}_2\text{O}})} = \frac{(X_{\text{CO}_2} P_T)(X_{\text{H}_2} P_T)}{(X_{\text{CO}} P_T)(X_{\text{H}_2\text{O}} P_T)}$$

$$K_p = \frac{(X_{\text{CO}_2})(X_{\text{H}_2})}{(X_{\text{CO}})(X_{\text{H}_2\text{O}})} = \frac{\left(\frac{n_{\text{CO}_2}}{n_T}\right)\left(\frac{n_{\text{H}_2}}{n_T}\right)}{\left(\frac{n_{\text{CO}}}{n_T}\right)\left(\frac{n_{\text{H}_2\text{O}}}{n_T}\right)} = \frac{n_{\text{CO}_2} \times n_{\text{H}_2}}{n_{\text{CO}} \times n_{\text{H}_2\text{O}}}$$

$$K_p = 0.65 = \frac{(x)(x)}{(3-x)(1-x)} = \frac{x^2}{x^2 - 4x + 3}$$

$$\text{From which } 0.37x^2 + 2.52x - 1.89x = 0$$

Solving above equation gives practical value of x which is 0.68

(i) Hence the number of moles of H_2 is 0.68mol

(ii) $n_T = (3-x) + (1-x) + x + x = 4\text{mol}$

$$P_{\text{CO}} = X_{\text{CO}} P_T = \left(\frac{n_{\text{CO}}}{n_T}\right) P_T = \left(\frac{3-x}{4}\right) P_T$$

$$\text{Substituting; } P_{\text{CO}} = \left(\frac{3-0.68}{4}\right) 2\text{atm} = 1.16\text{atm}$$

$$\text{Similarly; } P_{\text{H}_2\text{O}} = \left(\frac{n_{\text{H}_2\text{O}}}{n_T}\right) P_T = \left(\frac{1-x}{4}\right) P_T = \left(\frac{1-0.68}{4}\right) \times 2\text{atm} = 0.16\text{atm}$$

$$P_{\text{H}_2} = P_{\text{CO}_2} = \left(\frac{x}{4}\right) P_T = \left(\frac{0.68}{4}\right) \times 2\text{atm} = 0.34\text{atm}$$

Hence:

Partial pressure of $\text{CO} = 1.16\text{atm}$

Partial pressure of $\text{H}_2\text{O} = 0.16\text{atm}$

Partial pressure of $\text{H}_2 = 0.34\text{atm}$

Partial pressure of $\text{CO}_2 = 0.34\text{atm}$

Question 28

(a) Lower temperature.

Reason

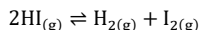
K_p is larger at the lower temperature.

(b)

$$(i) K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]}$$

(ii) V cancels in the K_c expression (as the reaction is not accompanied by change in number of moles of reagents present in the system).

(iii)



Initially

$$0.218 \quad 0 \quad 0$$

At equilibrium

$$0.218 - 2x \quad x \quad x$$

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.218-2x}{V}\right)^2} = \frac{x^2}{(0.218-2x)^2}$$

But $x = 0.023$ (Amount of hydrogen at equilibrium)

$$K_c = \frac{(0.023)^2}{(0.218 - 2(0.023))^2} = 0.0179$$

The value of K_c is 0.0179

$$(iv) K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{F}_2]} = \frac{1}{\frac{[\text{H}_2][\text{F}_2]}{[\text{HI}]^2}} = \frac{1}{0.0179} = 55.9$$

The value of K_c is 55.9

Question 29

(a) $\text{I} < \text{II} < \text{III}$

Increase in tendency of forming products

$$(b) K_c = \frac{K_f}{K_r} = \frac{0.13^{-1}\text{s}^{-1}}{6.02 \times 10^{-4}\text{s}^{-1}} = 215.9\text{M}^{-1}$$

The value of equilibrium constant is 215.9M^{-1}

(c) From the given reaction equation;

$$(i) \quad K_p = P_{CO_2} = 0.236 \text{ atm}$$

$$(ii) \quad \Delta n = 1 - 0 = 1$$

$$\text{Then } K_p = K_c(RT)^{\Delta n} = K_c(RT)^1$$

$$\text{Substituting; } 0.236 \text{ atm} = K_c \times 0.082 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 1073 \text{ K}$$

$$\text{From which } K_c = 2.68 \times 10^{-3} \text{ mol dm}^{-3}$$

Question 30

(a)

(i) Remain the same

(ii) Decrease

(iii) Increase

(iv) Remain the same

(v) Increase

(b) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

Pressure at $t = 0$ 1.66 0 0

Pressure at equilibrium 1.66 - x x x

$$K_p = \frac{(P_{\text{PCl}_3})(P_{\text{Cl}_2})}{(P_{\text{PCl}_5})}$$

$$\text{Substituting; } 0.497 = \frac{(x)(x)}{1.66-x} = \frac{x^2}{1.66-x}$$

$$\text{From which; } x^2 + 0.497x - 0.82502 = 0; x = 0.693$$

Hence:

$$\text{Partial pressure of } P_{\text{PCl}_3} = x = 0.693 \text{ atm}$$

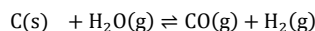
$$\text{Partial pressure of } \text{Cl}_2 = x = 0.693 \text{ atm}$$

$$\text{Partial pressure of } P_{\text{PCl}_5} = 1.66 - x = 0.967 \text{ atm}$$

Question 31

(a) From ideal gas equation; $P = \frac{nRT}{V}$

$$\text{Then; } P_{\text{initial}} = \frac{n_{\text{H}_2\text{O}}RT}{V} = \frac{0.1 \times 0.082 \times 1153 \text{ atm}}{1} = 9.4546 \text{ atm}$$



Initial pressure 9.4546 0 0

Equilibrium pressure 9.4546 - x x x

$$K_p = 14.1 = \frac{(P_{\text{CO}})(P_{\text{H}_2})}{(P_{\text{H}_2\text{O}})} = \frac{x^2}{9.4546 - x}$$

$$\text{From which; } x^2 + 14.1x - 133.3 = 0; x = 6.5$$

Hence:

$$\text{Partial pressure of CO} = x = 6.5 \text{ atm}$$

$$\text{Partial pressure of H}_2 = x = 6.5 \text{ atm}$$

$$\text{Partial pressure of H}_2\text{O} = 9.4546 - x = 2.95 \text{ atm}$$

(b) Amount of $\text{H}_2\text{O(g)}$ reacted is equivalent to the pressure of 6.5 atm (decrease in pressure)

$$\text{Using; } n = \frac{PV}{RT}$$

$$n_{\text{H}_2\text{O reacted}} = \frac{6.5 \times 1 \text{ mol}}{0.082 \times 1153} = 0.069 \text{ mol}$$

From the reaction equation, mole ratio of C(s) to $\text{H}_2\text{O(g)}$ is 1:1

So number of moles of C(s) required to react with 0.069 mol was also 0.069 mol.

Using $m = nM_r$;

$$\text{Minimum amount of C(s) required is } 0.069 \text{ mol} \times 12 \text{ g mol}^{-1} = 0.83 \text{ g}$$

Question 32

(a) Exothermic

Explanation:

K_f increases more than K_r when temperature is increased. This means that E_a of reverse reaction is greater than E_a of forward reaction. The reaction is exothermic when $E_a(\text{reverse}) > E_a(\text{forward})$.

(b)

	$\text{SO}_2(\text{g})$	$+$	$\text{NO}_2(\text{g})$	$\rightleftharpoons$	$\text{SO}_3(\text{g})$	$+$	$\text{NO}(\text{g})$
At equilibrium	0.8		0.1		0.6		0.4

$$K_c = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = \frac{\left(\frac{0.6}{V}\right)\left(\frac{0.4}{V}\right)}{\left(\frac{0.8}{V}\right)\left(\frac{0.1}{V}\right)} = 3$$

Addition of 1 mole of NO to the equilibrium mixture will favour reverse reaction.

	$\text{SO}_2(\text{g})$	$+$	$\text{NO}_2(\text{g})$	$\rightleftharpoons$	$\text{SO}_3(\text{g})$	$+$	$\text{NO}(\text{g})$
After addition of 1mol of NO	0.8		0.1		0.6		1.4
At new equilibrium	$0.8 + x$		$0.1 + x$		$0.6 - x$		$1.4 - x$

Then;

$$K_c = 3 = \frac{\left(\frac{0.6 - x}{V}\right)\left(\frac{1.4 - x}{V}\right)}{\left(\frac{0.8 + x}{V}\right)\left(\frac{0.1 + x}{V}\right)}$$

From which; $2x^2 + 4.7x - 0.6 = 0$; $x = 0.12$

Hence at new equilibrium (by substituting $x = 0.12$):

Number of moles of $\text{SO}_2 = 0.8 + x = 0.92\text{mol}$

Number of moles of $\text{NO}_2 = 0.1 + x = 0.22\text{mol}$

Number of moles of $\text{SO}_3 = 0.6 - x = 0.48\text{mol}$

Number of moles of $\text{NO} = 1.4 - x = 1.28\text{mol}$

Question 33

(a)

	$\text{PCl}_5(\text{g})$	$\rightleftharpoons$	$\text{PCl}_3(\text{g})$	$+$	$\text{Cl}_2(\text{g})$
Initially	1		0		0
At equilibrium	$1 - \alpha$		α		α

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\left(\frac{\alpha}{V}\right)\left(\frac{\alpha}{V}\right)}{\left(\frac{1 - \alpha}{V}\right)} = \frac{\alpha^2}{(1 - \alpha)V}$$

But $\alpha = \frac{78.5}{100} = 0.785$ and $V = 5\text{L}$

$$K_c = \frac{0.785^2}{(1 - 0.785) \times 5} \text{mol/L} = 0.573\text{mol/L}$$

$K_p = K_c(\text{RT})^{\Delta n}$ where $\Delta n = 2 - 1 = 1$

$$K_p = 0.573\text{molL}^{-1} \times 0.082\text{atmLmol}^{-1}\text{K}^{-1} \times 500\text{K} = 23.5\text{atm}$$

The value of K_p is 23.5atm

(b) $Q_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{0.15\text{M} \times 0.6\text{M}}{0.5\text{M}} = 0.18\text{M}$

So $Q_c(0.18) < K_c(0.573\text{M})$ and hence **the reaction will proceed in forward direction to reach the equilibrium.**

	$\text{PCl}_5(\text{g})$	$\rightleftharpoons$	$\text{PCl}_3(\text{g})$	$+$	$\text{Cl}_2(\text{g})$
At new equilibrium	$0.5 - x$		$0.15 + x$		$0.6 + x$

$$K_c = 0.573 = \frac{(0.15 + x)(0.6 + x)}{(0.5 - x)}$$

From which: $x^2 + 1.323x - 0.1965 = 0$; $x = 0.135$

Hence at the new equilibrium (by substituting $x=0.135$):

$$[\text{PCl}_5] = 0.5 - x = 0.365\text{M}$$

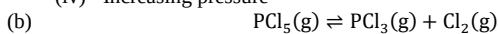
$$[\text{PCl}_3] = 0.15 + x = 0.285\text{M}$$

$$[\text{Cl}_2] = 0.6 + x = 0.735\text{M}$$

Question 34

(a)

- (i) Increasing concentration of N_2 (adding N_2)
- (ii) Increasing concentration of H_2 (adding H_2)
- (iii) Increasing temperature
- (iv) Increasing pressure



Initially 1 0 0

At equilibrium $1 - \alpha$ α α

$$K_p = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})} = \frac{(X_{PCl_3}P_T)(X_{Cl_2}P_T)}{(X_{PCl_5}P_T)}$$

$$K_p = \frac{\left(\frac{n_{PCl_3}}{n_T}\right)\left(\frac{n_{Cl_2}}{n_T}\right)P_T}{\left(\frac{n_{PCl_5}}{n_T}\right)P_T} = \frac{(n_{PCl_3})(n_{Cl_2})P_T}{(n_{PCl_5})(n_T)}$$

$$K_p = 1.78 = \frac{\alpha \times \alpha}{(1 - \alpha)(1 + \alpha)} (n_T = 1 - \alpha + \alpha + \alpha = 1 + \alpha)$$

$$= \frac{\alpha^2}{1 - \alpha^2}$$

From which; $2.78\alpha^2 = 1.78$; $\alpha = 0.8$

Thus the degree of dissociation (α) is 0.8

Then using $\alpha = \frac{i-1}{N-1}$

Where: i is the Van't Hoff's factor,

N is the number of molecules formed after dissociation of 1 molecule of $PCl_5 = 2$

Substituting $0.8 = \frac{i-1}{2-1}$; $i = 1.8$

But also; $i = \frac{\text{Expected } M_r}{\text{Observed } M_r}$

Where; expected M_r = Molar mass of PCl_5 before dissociation = $(31 + (5 \times 35.5))\text{gmol}^{-1} = 208.5\text{gmol}^{-1}$

Then $1.8 = \frac{208.5\text{gmol}^{-1}}{\text{Observed } M_r}$; Observed $M_r = 115.8\text{gmol}^{-1}$

From ideal gas equation; $\rho = \frac{PM_r}{RT}$

Thus density of the mixture (density of PCl_5 after dissociation) = $\frac{1\text{atm} \times 115.8\text{gmol}^{-1}}{0.082\text{atmLmol}^{-1}\text{K}^{-1} \times 523\text{K}} = 2.7\text{gL}^{-1}$

Density of the equilibrium mixture is 2.7g/L

Question 35

(a) $K_p = \frac{(P_{CO_2})^4}{(P_{C_2H_6})^2(P_{O_2})^7}$

But from ideal gas equation; $P = []RT$

Then $K_p = \frac{([CO_2]RT)^4}{([C_2H_6]RT)^2([O_2]RT)^7}$

$$K_p = \frac{[CO_2]^4}{[C_2H_6]^2[O_2]^7} \times (RT)^{4-(2+7)}$$

But $\frac{[CO_2]^4}{[C_2H_6]^2[O_2]^7} = K_c$

Hence $K_p = K_c(RT)^{-5}$

(b) Initial total pressure = $P_{H_2} = \frac{n_{H_2}RT}{V} = \frac{0.2 \times 0.082 \times 363}{1} \text{atm} = 5.9532\text{atm}$



Initial pressure 5.9532 0

Equilibrium pressure 5.9532 - x x

$$K_p = \frac{P_{H_2S}}{P_{H_2}} = \frac{x}{5.9532 - x} = 6.8 \times 10^{-2}$$

From which ; $1.068x = 0.4048$; $x = 0.379$

The partial pressure of H_2S is 0.379atm

Question 36

- (a) This is because the increase in temperature does not increase values of K_f and K_b by the same amount due to the difference in activation energy of forward and backward reaction. If the activation energy of forward reaction is greater than that of backward reaction (for endothermic reactions), the increase in K_f value will be greater than that of K_b and therefore the K_c value will increase while the K_c value will decrease if the activation energy of forward reaction is smaller (for exothermic reactions).

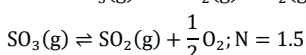
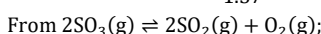
- (b) From ideal gas equation: $M_r = \frac{mRT}{VP} = \frac{\rho RT}{P}$

$$\text{Then } M_{\text{mixture}} = \frac{3.2 \times 0.0821 \times 800}{3.6} \text{ g/mol} = 58.3822 \text{ g/mol}$$

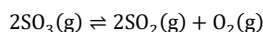
$$i = \frac{\text{Expected } M_r}{\text{Observed } M_r} = \frac{80 \text{ g/mol}}{58.3822 \text{ g/mol}} = 1.37$$

$$\text{But also } i = \frac{P_{\text{observed}}}{P_{\text{expected}}} = \frac{3.6}{P_{\text{expected}}} = 1.37$$

$$\text{From which } P_{\text{expected}} = \frac{3.6}{1.37} \text{ atm} = 2.63 \text{ atm}$$



$$\alpha = \frac{i - 1}{N - 1} = \frac{1.37 - 1}{1.5 - 1} = 0.74$$



Initial pressure	2.63	0	0

Equilibrium pressure	$2.63 - 2x$	$2x$	x

$$\text{But } \alpha = \frac{2x}{2.63} = 0.74; x = 0.9731$$

Equilibrium pressure for each:

$$P_{\text{SO}_2} = 2.63 - 2x = 0.6838 \text{ atm}$$

$$P_{\text{SO}_2} = 2x = 1.9462 \text{ atm},$$

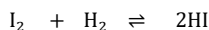
$$P_{\text{O}_2} = x = 0.9731 \text{ atm}$$

$$K_p = \frac{(P_{\text{SO}_2})^2 \times P_{\text{O}_2}}{(P_{\text{SO}_3})^2} = \frac{(1.9462 \text{ atm})^2 \times 0.9731 \text{ atm}}{(0.6838 \text{ atm})^2} = 7.88 \text{ atm}$$

The K_p value is 7.88atm.

Question 37

- (a) Yes; it is correct. When the system is at equilibrium, the reaction quotient becomes equal to an equilibrium constant which is constant at given temperature.
- (b)



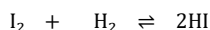
At equilibrium	$2.98 - x$	$8.1 - x$	$2x$

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{4x^2}{(2.98 - x)(8.1 - x)}$$

$$\text{But } 2x = 5.64 \text{ (Amount of HI at equilibrium); } x = 2.82$$

Substituting the value of x to above K_c expression gives $K_c = 37.65$

If we start with 5.3 moles of I_2 and 7.94 moles of H_2



At equilibrium	$5.3 - x$	$7.94 - x$	$2x$

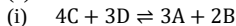
$$\text{Then; } 37.65 = \frac{4x^2}{(5.3 - x)(7.94 - x)}$$

Solving above equating gives; $x = 4.62 \text{ mol}$ and $2x = 2 \times 4.62 \text{ mol} = 9.24 \text{ mol}$

Hence number of moles of HI formed is 9.24moles

Question 38

(a)

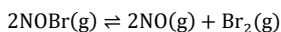


(ii) Units of $K_c = \frac{(\text{Units of } [A])^3 (\text{Units of } [B])^2}{(\text{Units of } [C])^4 (\text{Units of } [D])^3}$

$$\text{Units of } K_c = \frac{(\text{mol dm}^{-3})^3 (\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^4 (\text{mol dm}^{-3})^3} = (\text{mol dm}^{-3})^{-3} = \mathbf{dm^9 mol^{-3}}$$

(iii) The reaction is exothermic.

(b) Reaction equation:



Initial pressure P 0 0

Pressure at equilibrium P - 2x 2x x

Where $P_T = P - 2x + 2x + x = P + x = 0.28\text{atm}$

But $\frac{2x}{P} \times 100 = 33.33$; $x = 0.16665P$

Then $P + x = P + 0.16665P = 0.28\text{atm}$; $P = 0.24\text{atm}$

Thus at equilibrium:

$$P_{\text{NOBr}} = P - 2x = 0.24\text{atm} - (2 \times 0.16665 \times 0.24)\text{atm} = 0.16\text{atm}$$

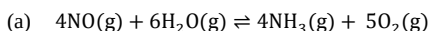
$$P_{\text{NO}} = 2x = 2 \times 0.16665 \times 0.24\text{atm} = 0.08\text{atm}$$

$$P_{\text{Br}_2} = x = 0.16665 \times 0.24\text{atm} = 0.04\text{atm}$$

$$K_p = \frac{(P_{\text{NO}})^2 \times P_{\text{Br}_2}}{(P_{\text{NOBr}})^2} = \frac{(0.08\text{atm})^2 \times 0.04\text{atm}}{(0.16\text{atm})^2} = 0.01\text{atm}$$

The K_p is 0.01atm

Question 39



(b)

(i) $K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}}$

(ii) From $M_r = \frac{mRT}{PV}$

Where: $m = 2.585\text{g}$, $V = 1\text{dm}^3 = 10^{-3}\text{ m}^3$, $R = 8.314$,

$P = 1.01 \times 10^5\text{ N/m}^2$; $T = 60^\circ\text{C} = (60 + 273)\text{ K} = 333\text{K}$

Then observed molar of the gas $= \frac{2.585 \times 8.314 \times 333}{1.01 \times 10^5 \times 10^{-3}}\text{ g/mol} = 70.86\text{g/mol}$

$$i = \frac{\text{Expected molar mass of the gas}}{\text{observed molar mass of the gas}}$$

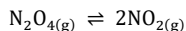
But expected molar mass of N_2O_4 is 92g/mol

Thus $i = \frac{92}{70.86} = 1.3$

Using $\alpha = \frac{i-1}{N-1}$ where $N = 2$

$$\alpha = \frac{1.3 - 1}{2 - 1} = 0.3 \text{ or } 30\%$$

Hence degree of dissociation of N_2O_4 is 30%



At equilibrium 1 - α 2 α

$$n_T = (1 - \alpha) + 2\alpha = (1 + \alpha)\text{moles}$$

$$P_{\text{N}_2\text{O}_4} = \left(\frac{1 - \alpha}{1 + \alpha}\right) P_T = \left(\frac{1 - 0.3}{1 + 0.3}\right) \times 1.01 \times 10^5 = 5.44 \times 10^4\text{Nm}^{-2}$$

$$P_{\text{NO}_2} = \left(\frac{2\alpha}{1 + \alpha}\right) P_T = \left(\frac{2 \times 0.3}{1 + 0.3}\right) \times 1.01 \times 10^5 = 4.66 \times 10^4\text{Nm}^{-2}$$

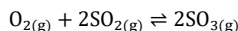
Using K_p expression in (i) above:

$$K_p = \frac{(4.66 \times 10^4)^2}{5.44 \times 10^4}\text{ Nm}^{-2} = 3.99 \times 10^4\text{Nm}^{-2}$$

Question 40

- (a) The amount of CaCO_3 must be so small that even after its complete decomposition it produces small amount of CO_2 with partial pressure which is less than K_p .

(b)



Initially 0.1 0.2 0

At equilibrium 0.1 - x 0.2 - 2x 2x

At equilibrium $n_T = (0.1 - x) + (0.2 - 2x) + 2x = (0.3 - x)$ moles

$$\text{But } \frac{(n_{\text{O}_2} + n_{\text{SO}_2})}{n_T} \times 100 = 10$$

$$\frac{(0.1-x)+(0.2-2x)}{0.3-x} = 0.1 \text{ or } 0.3 - 3x = 0.03 - 0.1x \text{ or } x = 0.093 \text{ moles}$$

Hence at equilibrium:

Amount of $\text{O}_2 = 0.1 - x = 0.0069$ moles

Amount of $\text{SO}_2 = 0.2 - 2x = 0.0138$ moles

Amount of $\text{SO}_3 = 2x = 0.1862$ moles

By Dalton's law of partial pressure: $P_T = P_{\text{O}_2} + P_{\text{SO}_2} + P_{\text{SO}_3}$

$$P_T = \frac{n_{\text{O}_2}RT}{V} + \frac{n_{\text{SO}_2}RT}{V} + \frac{n_{\text{SO}_3}RT}{V}$$

$$P_T = (n_{\text{O}_2} + n_{\text{SO}_2} + n_{\text{SO}_3}) \frac{RT}{V}$$

$$P_T = \frac{n_T RT}{V}$$

But of equilibrium $n_T = (0.3 - x) = 0.2069$ moles

$$\text{Then; } P_T = \frac{0.2069 \times 0.082 \times 311}{0.2} \text{ atm} = 26.38 \text{ atm}$$

Hence the pressure of the system at equilibrium is 26.38 atm.

Question 41

- (a) 100% yield implies that the magnitude of equilibrium constant is **infinitely large**.

(b) Initially:

$$\text{Number of moles of } [\text{SOCl}_2] = \frac{23.8}{119} = 0.2 \text{ moles}$$

$$\text{Number of moles of } [\text{SO}] = \frac{19.2}{48} = 0.4 \text{ moles}$$

$$\text{Number of moles of } [\text{Cl}_2] = \frac{142}{71} = 2 \text{ moles}$$

Thus at the beginning of the reaction:

$$\text{Using } [\] = \frac{n}{V} \text{ where } V = 1 \text{ dm}^3$$

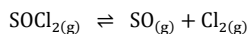
$$[\text{SOCl}_2] = 0.2 \text{ M}$$

$$[\text{SO}] = 0.4 \text{ M}$$

$$[\text{Cl}_2] = 2 \text{ M}$$

$$Q_c = \frac{[\text{SO}][\text{Cl}_2]}{[\text{SOCl}_2]} = \frac{0.4 \times 2}{0.2} = 4 \text{ M}$$

But $K_c = 1.2 \text{ M}$. So $Q_c > K_c$ and hence the reaction will proceed in reverse direction to establish the equilibrium.



Initially 0.2 0.4 2

At equilibrium: 0.2 + x 0.4 - x 2 - x

$$K_c = \frac{[\text{SO}][\text{Cl}_2]}{[\text{SOCl}_2]}$$

$$\text{Then } \frac{(0.4-x)(2-x)}{(0.2+x)} = 1.2$$

At equilibrium $n_T = (0.2 + x) + (0.4 - x) + (2 - x) = 2.437$ moles

Number of moles of $\text{SOCl}_2 = 0.2 + x = 0.363$ moles

Number of moles of $\text{SO} = 0.4 - x = 0.237$ moles

Number of moles of $\text{Cl}_2 = (2 - x) = 1.837$ moles

$$\% \text{SOCl}_2 = \frac{n_{\text{SOCl}_2}}{n_T} \times 100\% = \frac{0.363}{2.437} \times 100\% = 14.9\%$$

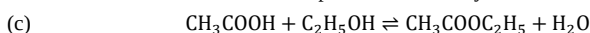
$$\% \text{SO} = \frac{n_{\text{SO}}}{n_T} \times 100\% = \frac{0.237}{2.437} \times 100\% = 9.7\%$$

$$\% \text{Cl}_2 = \frac{n_{\text{Cl}_2}}{n_T} \times 100\% = \frac{1.837}{2.437} \times 100\% = 75.4\%$$

Hence the equilibrium composition of each gas is 14.9%, 9.7% and 75.4% by volume for SOCl_2 , SO , and Cl_2 respectively.

Question 42

- (a) Is the state that occurs in the reversible reaction when the rate forward reaction is equal to the rate of backward reaction. It is the state in which both reactants and products are simultaneously consumed and produced by the same speed such that their concentrations remain unchanged.
- (b) Conditions which favour the formation of chemical equilibrium are:
- The system (reaction) must be reversible.
 - The reaction should take place in a closed system, that is; no material is allowed to enter or to leave the system.



Initially 1 1 0 0

At equilibrium $1-x$ $1-x$ x x

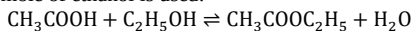
$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{(\frac{x}{V})(\frac{x}{V})}{(\frac{1-x}{V})(\frac{1-x}{V})}$$

$$K_c = \frac{x^2}{x^2 - 2x + 1}$$

But $1-x = \frac{1}{3}$ or $x = \frac{2}{3}$ (One third of ethanoic acid remains at equilibrium).

Substituting $x = \frac{2}{3}$ in above equilibrium constant expression gives, $K_c = 4$.

If three quarters of one mole of ethanol is used:



Initially 1 $\frac{3}{4}$ 0 0

At equilibrium $1-x$ $\frac{3}{4}-x$ x x

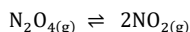
$$K_c = \frac{(\frac{x}{V})(\frac{x}{V})}{(\frac{3/4-x}{V})(\frac{1-x}{V})} = \frac{x^2}{x^2 - 1.75x + 0.75} = 4 \quad \text{or } x = 0.57$$

And $1-x = 1 - 0.57 = 0.43$ moles

Hence the amount of ethanoic acid which would remain is 0.43 moles.

Question 43

- (a)
- (i) Yellow colouration of CrO_4^{2-} .
(Addition of NaOH is equivalent to removal of H^+ thus shifting the position of equilibrium to the right).
- (ii) Orange colouration of $\text{Cr}_2\text{O}_7^{2-}$ (Addition of HCl(aq) shift the position of chemical equilibrium to the left).
- (iii) Orange colouration of $\text{Cr}_2\text{O}_7^{2-}$ (Anhydrous CaCl_2 absorbs thus shifting position of chemical equilibrium to the left).
- (b)



Initially 1 0

At equilibrium $1-\alpha$ 2α

Where α is numerically equal to the degree of dissociation.

$$K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})} = \frac{(X_{\text{NO}_2} P_T)^2}{(X_{\text{N}_2\text{O}_4} P_T)} = \frac{(X_{\text{NO}_2})^2 P_T}{(X_{\text{N}_2\text{O}_4})}$$

But $X_{\text{NO}_2} = \frac{2\alpha}{1+\alpha}$ Where $n_T = (1-\alpha) + 2\alpha = 1+\alpha$

And $X_{\text{N}_2\text{O}_4} = \frac{1-\alpha}{1+\alpha}$

Then $K_p = \frac{4\alpha^2 P_T}{1-\alpha^2}$

When $\alpha = 0.5$ and $P_T = 1 \text{ atm}$

$$K_p = \frac{4 \times 0.5^2 \times 1}{1 - 0.5^2} \text{ atm} = \frac{4}{3} \text{ atm}$$

Hence the equilibrium constant in terms of pressure is $\frac{4}{3}$ atm

When the pressure, P_T is changed to 10 atm

$$\text{From } K_p = \frac{4\alpha^2 P_T}{1 - \alpha^2}$$

When $P_T = 10 \text{ atm}$

Since temperature is kept constant, K_p remain unchanged.

$$\text{Then } \frac{4}{3} = \frac{4 \times 10 \alpha^2}{1 - \alpha^2} \text{ or } \alpha = 0.18 \text{ or } 18\%$$

Hence when the pressure is 10 atm, degree of dissociation of the gas becomes 18%.

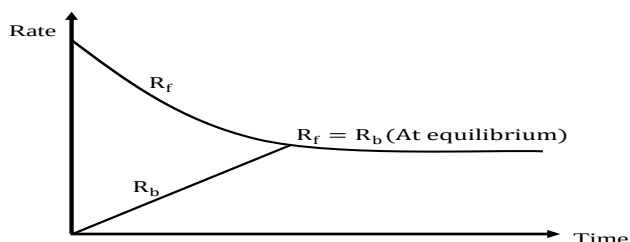
Question 44

(a)

(i) Chemical equilibrium involves balance of the rate of the two reactions which are **proceeding at the same time** in **opposite directions**. So it involves the **constant interchange of particles in motion**, moving in opposite direction of forward and reverse reaction and hence the equilibrium is said to be dynamic.

(ii) Consider the reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

Initially the rate of forming HI (forward reaction) is maximum while that of dissociation of HI to form H_2 and I_2 (backward reaction) is zero because at the beginning, only H_2 and I_2 are present. As the reaction proceed concentration of H_2 and I_2 start to decrease and thus lowering the rate of forward reaction while HI is formed leading to backward reaction. Thus as the reaction proceed, the rate of forming HI is continuously decreasing while that of dissociation of HI is continuously increasing until they become equal where it said that the equilibrium has been attained as illustrated in the following graph:



Where:

R_f is the rate of formation of HI (forward reaction rate)

R_b is the rate of dissociation of HI (backward reaction)

(b) Equation for the reaction: $\text{I}_2 \rightleftharpoons \text{I} + \text{I}$

Simplified equation after combining two I atoms is;



Initially

$$1 \quad 0$$

At equilibrium

$$1 - \alpha \quad 2\alpha$$

$$K_p = \frac{(P_I)^2}{(P_{I_2})} = \frac{(X_I P_T)^2}{(X_{I_2} P_T)} = \frac{(X_I)^2 P_T}{(X_{I_2})}$$

$$X_I = \frac{2\alpha}{1 + \alpha} \quad \text{and} \quad X_{I_2} = \frac{1 - \alpha}{1 + \alpha}$$

$$\text{Then } K_p = \frac{4\alpha^2 P_T}{1 - \alpha^2} \text{ But } \frac{2\alpha}{1 + \alpha} = 0.4 \text{ (iodine vapour contains 40\% by volume of iodine atoms) or } \alpha = 0.25$$

And it is given that $P_T = 1 \text{ atm}$

$$K_p = \frac{4 \times 0.25^2 \times 1}{1 - 0.25^2} = \frac{4}{15} \text{ atm}$$

If the pressure is reduced to 20%

$$\frac{2\alpha}{1 + \alpha} = 0.2 \text{ or } \alpha = \frac{1}{9}$$

$$\text{Substituting } \alpha = \frac{1}{9} \quad \text{and } K_p = \frac{4}{15}$$

$$\frac{4}{15} = \frac{4 \left(\frac{1}{9}\right)^2 P_T}{1 - \left(\frac{1}{9}\right)^2} \text{ or } P_T = 5.33 \text{ atm}$$

Thus the percentage will be reduced to the given amount when the total pressure is 5.33 atm.

Question 45

- (a) The value of equilibrium constant for the titration reaction is infinitely large.
 (b)



$$K_p = \frac{(P_{\text{NO}})^2}{(P_{\text{O}_2})(P_{\text{N}_2})} = \frac{(X_{\text{NO}} P_T)^2}{(X_{\text{O}_2} P_T)(X_{\text{N}_2} P_T)} = \frac{(X_{\text{NO}})^2}{(X_{\text{O}_2})(X_{\text{N}_2})}$$

$$\text{But } n_T = (1 - \alpha) + (1 - \alpha) + 2\alpha = 2 \text{ moles}$$

$$\text{Then } X_{\text{NO}} = \frac{2\alpha}{2} = \alpha$$

$$X_{\text{N}_2} = X_{\text{O}_2} = \frac{1 - \alpha}{2}$$

$$\text{So } 3.6 \times 10^{-3} = \frac{4\alpha^2}{(1-\alpha)^2} = \frac{4\alpha^2}{\alpha^2 - 2\alpha + 1}$$

$$\text{Or } 3.9964\alpha^2 - 0.0072\alpha - 0.0036 = 0 \text{ or } \alpha = 0.029$$

Hence the fraction of original nitrogen which is used in the reaction is 0.029

The fraction by volume of nitric oxide in the mixture = $X_{\text{NO}} = \alpha = 0.029$

Hence the fraction of nitric oxide in the mixture is also 0.029

Question 46

- (a) No. For the equilibrium to be achieved, reaction rates (not rate constant) for forward and reverse reactions must be the same. Rate constants for forward and reverse reactions are different and they are not changing in the course of chemical reaction.
 (b) $X_{\text{PCl}_3} = X_{\text{Cl}_2} = 0.407$ (Both PCl_3 and Cl_2 are produced from the decomposition of the phosphorous pentachloride introduced in the vessel and their mole ratio is 1:1).

$$X_{\text{PCl}_3} + X_{\text{Cl}_2} + X_{\text{PCl}_5} = 1$$

$$\text{Thus; } X_{\text{PCl}_5} = 1 - (X_{\text{Cl}_2} + X_{\text{PCl}_3}) = 1 - (0.407 + 0.407) = 0.186$$

$$\text{Using; } P' = X P_T$$

$$\text{Partial pressure of } \text{PCl}_3, P_{\text{PCl}_3} = 0.407 \times 202 \text{ kPa} = 82.214 \text{ kPa}$$

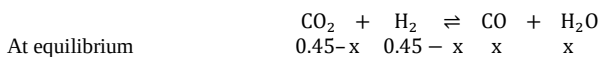
$$\text{Partial pressure of } \text{PCl}_5, P_{\text{PCl}_5} = 0.186 \times 202 \text{ kPa} = 37.572 \text{ kPa}$$

$$P_{\text{PCl}_3} = P_{\text{Cl}_2} = 82.214 \text{ kPa} \text{ (They have the same mole fraction)}$$

$$K_p = \frac{(P_{\text{PCl}_3})(P_{\text{Cl}_2})}{(P_{\text{PCl}_5})} = \frac{82.214 \text{ kPa} \times 82.214 \text{ kPa}}{37.572 \text{ kPa}} = 179.9 \text{ kPa}$$

Question 47

- (a)
 (i) At the beginning of the chemical reaction where there are only reactants (with zero amount of products).
 (ii) At the completion of the chemical reaction whereby all reactants have been converted to products.
 (b)



$$K_c = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = \frac{x^2}{(0.45 - x)^2} = 0.11$$

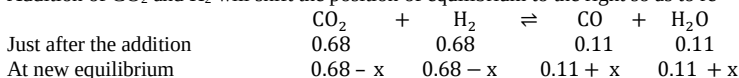
$$\text{Solving above equation gives } x = 0.11$$

Hence at equilibrium:

$$\text{Numbers of moles } \text{CO}_2 = \text{Number of moles of } \text{H}_2 = 0.45 - x = 0.34 \text{ moles}$$

$$\text{Number of moles of } \text{CO} = \text{Number of moles of } \text{H}_2\text{O} = x = 0.11 \text{ moles}$$

Addition of CO_2 and H_2 will shift the position of equilibrium to the right so as to re-establish the equilibrium:



Then $0.11 = \frac{(0.11+x)^2}{(0.68-x)^2}$ or $x = 0.0869$

From which $x = 0.0869$

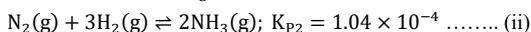
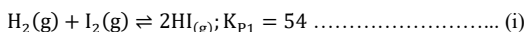
Hence at new equilibrium:

Number of moles of $\text{CO}_2 = \text{Number of moles of } \text{H}_2 = 0.68 - x = 0.5931 \text{ moles}$

Number of moles of $\text{CO} = \text{Number of moles of } \text{H}_2\text{O} = 0.11 + x = 0.1969 \text{ moles}$

Question 48

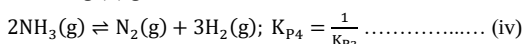
(a) Given that:



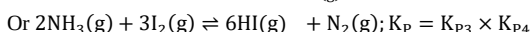
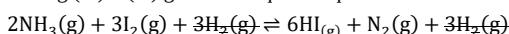
Taking $3 \times (i)$ gives:



Reversing (ii) gives;



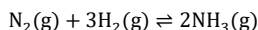
Taking (iii) + (iv) gives the required equation which is:



Thus the required $K_P = (K_{P1})^3 \times \frac{1}{K_{P2}} = 54^3 \times \frac{1}{1.04 \times 10^{-4}} = 1.51 \times 10^9$

The value of K_P is 1.51×10^9

(b)



Initially $\quad \quad \quad 1 \quad \quad \quad 3 \quad \quad \quad 0$

At equilibrium $\quad \quad \quad 1 - x \quad \quad \quad 3 - 3x \quad \quad \quad 2x$

$$n_T = (1 - x) + (3 - 3x) + 2x = 4 - 2x$$

But $\left(\frac{2x}{4-2x}\right) \times 100 = 1.2$ (molar percent of NH_3 is 1.2)

From which $x = 0.024 \text{ moles}$

At equilibrium:

Number of moles of $\text{N}_2 = 1 - x = 0.97 \text{ moles}$

Number of moles of $\text{H}_2 = 3 - 3x = 2.928 \text{ moles}$

Number of moles of $\text{NH}_3 = 2x = 0.048 \text{ moles}$

Total number of moles, $n_T = 4 - 2x = 3.952 \text{ moles}$

$$P_{\text{NH}_3} = X_{\text{NH}_3} P_T = \frac{0.048 \times 10 \text{ atm}}{3.952} = 0.12 \text{ atm}$$

$$P_{\text{H}_2} = X_{\text{H}_2} P_T = \frac{2.928 \times 10 \text{ atm}}{3.952} = 7.4 \text{ atm}$$

$$P_{\text{N}_2} = X_{\text{N}_2} P_T = \frac{0.976 \times 10 \text{ atm}}{3.952} = 2.47 \text{ atm}$$

$$K_P = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{0.12^2}{2.47 \times 7.4^3} = 1.44 \times 10^{-5} \text{ atm}^{-2}$$

Hence K_P for the reaction is $1.44 \times 10^{-5} \text{ atm}^{-2}$

Molar percent of NH_3 is 10.4

Then $\left(\frac{2x}{4-2x}\right) \times 100 = 10.4$

From which $x = 0.188$

Then at new equilibrium:

Number of moles of $\text{N}_2 = 1 - x = 0.812 \text{ moles}$

Number of moles of $\text{H}_2 = 3 - 3x = 2.436 \text{ moles}$

Number of moles of $\text{NH}_3 = 2x = 0.376 \text{ moles}$

Total number of moles, $n_T = 4 - 2x = 3.624 \text{ moles}$

$$P_{\text{NH}_3} = X_{\text{NH}_3} P_T = \frac{0.376 P_T}{3.624} = 0.1 P_T$$

$$P_{\text{H}_2} = X_{\text{H}_2} P_T = \frac{2.436 P_T}{3.624} = 0.672 P_T$$

$$P_{\text{N}_2} = X_{\text{N}_2} P_T = \frac{0.812 P_T}{3.624} = 0.224 P_T$$

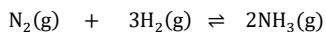
$$K_P = \frac{(0.1 P_T)^2}{(0.224 P_T)(0.672 P_T)^3} = \frac{0.147}{(P_T)^2} = 1.44 \times 10^{-5}; \quad P_T = 101 \text{ atm}$$

Thus the required pressure for molar percent of NH_3 to be 10.4 is 101 atm.

Question 49

- (a) No. At equilibrium, concentrations of products and reactants do not change; this does not mean they are equal. The equality exists in the reaction rate of forward and reverse reaction; this also does not mean equal concentration of reactants and products due to difference of rate constants and reaction orders (for forward and reverse reactions).
- (b) Let required number of moles of NH_3 be a

Then:



Initially 0 0 0

At equilibrium x $3x$ $a - 2x$

But at equilibrium $[\text{H}_2] = 6\text{M}$

Thus $3x = 6$ or $x = 2$

Hence concentration of each at equilibrium is as follows:

$[\text{NH}_3] = a - 2x = (a - 4)\text{M}$, $[\text{N}_2] = x = 2\text{M}$ and $[\text{H}_2] = 6\text{M}$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(a - 4)^2}{(2) \times (6)^3}$$

$$\text{Or } a - 4 = \sqrt{(1.8) \times (2) \times (6)^3} = 27.9 \quad \text{or } a = 31.9 \text{ moles}$$

Hence 31.9 moles of ammonia must be placed in 1 litre container.

Question 50

- (a) In the open container, carbon dioxide (another product of the decomposition) being a gas escapes to atmosphere, leaving the system and therefore the reverse reaction (between carbon dioxide and calcium oxide) will not occur. Consequently, the decomposition will continue until there is zero amount calcium carbonate in the container.

- (b) From the given reaction equation: $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$

If number of moles SO_2 = number of moles of SO_3 ;

Then $[\text{SO}_2] = [\text{SO}_3]$ and $K_c = \frac{1}{[\text{O}_2]}$

$$[\text{O}_2] = \frac{1}{K_c} = \frac{1}{100} = 0.01\text{M};$$

Then using $n = V[\quad]$;

Number of moles in 10L flask = $10 \times 0.01 \text{ moles} = 0.1 \text{ moles}$

Hence 0.1 moles of O_2 present in the flask

If number of moles of $\text{SO}_3 = 2 \times$ number of moles of SO_2

Then $2[\text{SO}_2] = [\text{SO}_3]$

$$\text{So } K_c = \frac{(2[\text{SO}_2])^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{4}{[\text{O}_2]}$$

$$[\text{O}_2] = \frac{4}{K_c} = \frac{4}{100} = 0.04$$

Thus number of moles of O_2 in 10L flask = $10 \times 0.04 \text{ moles} = 0.4 \text{ moles}$

Hence 0.4 moles of O_2 present in the flask.

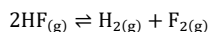
Question 51

- (a) Reaction quotient is obtained from concentration of reactants and products at any time in the reaction course and therefore it may take any value from zero (when concentrations of reactants are non-zero while those of products are zero; at the beginning of chemical reaction) to infinitely large (when concentrations of reactants are zero while those of products are non-zero; at the completion of chemical reaction). This is different to equilibrium constant which is obtained at a particular time in the reaction course when the equilibrium has been achieved; that is, its value is specific for concentration of reactants and products at equilibrium only.
- (b) Calculating the value of reaction quotient to know the reaction direction:

$$Q_c = \frac{[H_2][F_2]}{[HF]^2} = \frac{\left(\frac{0.5}{V}\right)\left(\frac{0.75}{V}\right)}{\left(\frac{5}{V}\right)^2} = 0.015 = 1.5 \times 10^{-2}$$

But the given K_c value is 1×10^{-2} which is smaller than the reaction quotient (1.5×10^{-2})

Since $Q_c > K_c$, the reaction will proceed in reverse direction to establish the equilibrium.



Initial (At $t = 0$)

$$\begin{array}{ccc} 5 & 0.5 & 0.75 \\ 5 + x & 0.5 - x & 0.75 - x \end{array}$$

At equilibrium

$$K_c = \frac{[H_2][F_2]}{[HF]^2} = \frac{\left(\frac{0.5-x}{V}\right)\left(\frac{0.75-x}{V}\right)}{\left(\frac{5+x}{V}\right)^2}$$

Then;

$$1 \times 10^{-2} = \frac{x^2 - 1.25x + 0.375}{x^2 + 10x + 25}$$

From which; $0.99x^2 - 1.35x + 0.125 = 0$; $x = 0.1$

Hence:

$$[HF] = \frac{5+x}{V} = \frac{(5+0.1)\text{mol}}{5L} = 1.02M$$

$$[H_2] = \frac{0.5-x}{V} = \frac{[0.5-0.1]\text{mol}}{5L} = 0.08M$$

$$[F_2] = \frac{0.75-x}{V} = \frac{[0.75-0.1]\text{mol}}{5L} = 0.13M$$

Question 52

(a) Agree

Explanation:

Equilibrium constant determines relative concentration of products to that of reactants at equilibrium whereby very large value of equilibrium constant implies that equilibrium concentrations of products are high compared to equilibrium concentrations of reactants and vice-versa. On another hand if the equilibrium constant is close to 1 means that equilibrium concentrations of reactants and products do not differ much.

(b) For gases, pressure ratio = mole ratio.

So, if initially was only solid ammonium carbamate in the vessel, at the first equilibrium; $P_{NH_3} = 2P_{CO_2}$

Thus if we let $P_{CO_2} = P$, then $P_{NH_3} = 2P$

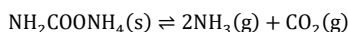
And if P_{CO_2} at new equilibrium is P'

Then P_{NH_3} at new equilibrium will be P'' (Not $2P'$ because after the addition of ammonia the mole ratio is disturbed).

But P_{NH_3} at new equilibrium = Total pressure in the first equilibrium

$$= P + 2P = 3P$$

$$\text{Thus } P'' = 3P \text{ or } P'' = \frac{3}{2}P$$



At the first equilibrium

$$2P \quad P$$

At the final equilibrium

$$3P \quad P'$$

$$K_p = (P_{NH_3})^2 \times P_{CO_2} = (2P)^2 \times P = (3P)^2 \times P'$$

$$\text{From which } P' = \frac{4}{9}P$$

Original total pressure = $2P + P = 3P$

Final total pressure = $3P + P'$

$$\frac{\text{Final total pressure}}{\text{Original total pressure}} = \frac{3P + P'}{3P} = \frac{3P + \frac{4}{9}P}{3P} = \frac{31}{27}$$

Hence the ratio is $\frac{31}{27}$

PART FIVE**Question 1****(a) Reason:**

The reaction produces acidic salt which undergoes cationic hydrolysis to give acidic solution.

Explanation

Anion which is the conjugate base of strong acid is the weak base while cation which is the conjugate acid of weak base is the strong acid. So the given reaction, gives a salt containing strong acid cation and weak base anion which undergoes cationic hydrolysis.

$$(b) \text{ Number of moles of base (NaOH)} = \frac{27.1}{1000} \times 0.1 \text{ mol} = 0.00271 \text{ mol}$$

Thus 0.00271 mole of NaOH reacts with 0.16g of the acid

$$\text{And } \frac{0.16 \times 1}{0.00271} \text{ g} = 59 \text{ g of acid reacts with 1 mole of NaOH}$$

Whence 59g of the acid reacts with 1 mole of NaOH

But 59g is a half mole of acid (one mole of acid has mass of 118g), therefore 1 mole of the acid reacts with 2 moles of NaOH and hence the acid is dibasic.

Question 2

(a) Acidic salts: FeCl_3 and NH_4Br

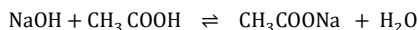
Basic salts: K_2CO_3 and HCOOK

Neutral salts: KClO_4 and KCl

(b) Number of moles of NaOH in 16.9 cm^3 of its solution

$$= \frac{16.9}{1000} \times 0.5 \text{ moles} = 8.45 \times 10^{-3} \text{ moles}$$

NaOH reacts with CH_3COOH according to the following equation:



From which mole ratio of CH_3COOH to NaOH is 1:1

Thus number of moles of CH_3COOH (in 25 cm^3) reacted was also 8.45×10^{-3} moles

It follows that: Number of moles of CH_3COOH in 250 cm^3 of its solution (dilute solution formed by mixing 100 cm^3 of vinegar and distilled water) = $\frac{8.45 \times 10^{-3} \times 250}{25}$ moles = 0.0845 moles

Thus number of moles of CH_3COOH in 100 cm^3 of vinegar was 0.0845 moles.

Using $m = nM_r$;

Mass of ethanoic acid in 100 cm^3 of vinegar = $0.0845 \text{ mol} \times 60 \text{ g mol}^{-1} = 5.07 \text{ g}$

Using mass = Volume $\times$ Density;

Total mass of vinegar in 100 cm^3 of its volume = $100 \text{ cm}^3 \times 1.02 \text{ g cm}^{-3} = 102 \text{ g}$

Thus the percentage of CH_3COOH = $\frac{5.07}{102} \times 100\% = 4.97\%$

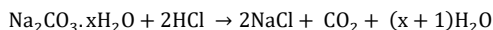
Hence the percentage by mass of the acid was 4.97%

Question 3

(a) Both cations and anions in salts coming from strong base and strong acid are weak acid and weak base respectively and hence they are incapable of combining with H^+ and OH^- from water, making solution of those salts neutral.

(b) Number of moles of HCl reacted with washing soda = $\frac{30}{1000} \times 0.2 \text{ moles} = 6 \times 10^{-3} \text{ moles}$

HCl reacts with washing soda ($\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$) according to the following equation:



From which mole ratio of washing soda to HCl is 1:2;

Thus number of moles (in 25 cm^3) of washing soda reacted = $\frac{6 \times 10^{-3}}{2} = 0.003 \text{ mol}$

So number of moles of the soda in 250 cm^3 = $\frac{0.003 \times 250}{25} \text{ mol} = 0.03 \text{ mol}$

Using $M_r = \frac{m}{n}$;

Molar mass of washing soda = $\frac{8.58 \text{ g}}{0.03 \text{ mol}} = 286 \text{ g mol}^{-1}$

It follows that: $(2 \times 23) + 12 + (16 \times 3) + 18x = 286$ or $x = 10$

Hence the value of x is 10

Question 4(a) PbCO_3 and CaF_2

(b) The potassium salt is tribasic (presence of three H's) so the mole ratio of the salt to NaOH is 1:3

But number of moles of NaOH reacted = $\frac{22.7}{1000} \times 1\text{mol} = 0.0227\text{mol}$ Thus number of moles of the salt reacted = $\frac{0.0227}{3}\text{mol} = 0.00757\text{mol}$ Using $M_r = \frac{m}{n}$;Molar mass of the salt = $\frac{1.923\text{g}}{0.00757\text{mol}} = 254\text{g/mol}$ Then $2 + 24 + 64 + 39 + 1 + 24 + 64 + 18x = 254$ or $x = 2$

Hence the value of x is 2.

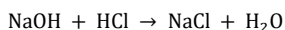
Question 5

(a) Salt dissolve slowly in water if:

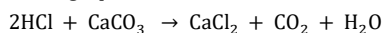
- 1) The water is cold.
- 2) The water already contains high concentration of salt.
- 3) The salt has not been finely ground.
- 4) The mixture of salt and water is not stirred.

(b) Since the resulting solution was neutralised by the base (NaOH), the solution was acidic and HCl was excess in its reaction with CaCO_3 of limestone.Number of moles of NaOH reacted = $\frac{21.05}{1000} \times 0.1\text{mol} = 2.105 \times 10^{-3}\text{moles}$

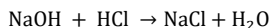
NaOH reacts with HCl according to the following equation:



From which mole ratio of NaOH to HCl is 1:1

Thus number of moles HCl in 25cm^3 to the solution is also $2.105 \times 10^{-3}\text{moles}$.And number of moles of the unreacted HCl in the reaction with CaCO_3 was $\frac{2.105 \times 10^{-3} \times 250}{25}\text{mol} = 0.02105\text{mol}$.But total number of moles of HCl before the reaction with $\text{CaCO}_3 = \frac{50}{1000} \times 1\text{mol} = 0.05\text{mol}$ Then number of moles of HCl reacted with $\text{CaCO}_3 = (0.05 - 0.02105)\text{mol} = 0.02895\text{mol}$ CaCO_3 reacts with HCl according to the following equation:From which mole ratio of HCl to CaCO_3 is 2:1Thus number of moles of CaCO_3 reacted = $\frac{0.02895}{2}\text{mol} = 0.014475\text{mol}$ Using $m = nM_r$;Mass of CaCO_3 in 1.5g of limestone = $0.014475 \times 100\text{g} = 1.4475\text{g}$ So % $\text{CaCO}_3 = \frac{1.4475}{1.5} \times 100\% = 96.5\%$ Hence the percentage of CaCO_3 present was 96.5%**Question 6**(a) NaCl contains weak acid cation and weak base anion as it is formed from strong base and strong acid. Consequently, neither Na^+ can react with base nor Cl^- can react with base and hence NaCl is incapable of eliminating added acid or base so to resist pH change which is the main purpose of buffer.(b) Number of moles of NaOH reacted with excess acid = $\frac{30}{1000} \times 1\text{mol} = 0.03\text{mol}$

NaOH reacts with HCl according to the following equation:

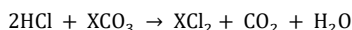


From which mole ratio of NaOH to HCl is 1:1

Thus number of moles of excess acid was also 0.03mol

But number of moles of HCl before the reaction with carbonate = $\frac{50}{1000} \times 1\text{mol} = 0.05\text{mol}$ Thus number of moles of HCl reacted with the carbonate = $(0.05 - 0.03)\text{mol} = 0.02\text{mol}$ If X is divalent metal, the formula of its carbonate is XCO_3

The carbonate reacts with HCl according to the following equation:



From which mole ratio of HCl to XCO_3 is 2:1

Therefore number of mole of XCO_3 reacted = $\frac{0.02}{2}$ mol = 0.01 mol

Using $M_r = \frac{m}{n}$;

Molar mass of the carbonate = $\frac{1\text{g}}{0.01\text{mol}} = 100\text{g/mol}$

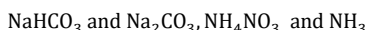
The molecular mass of X is 100g/mol

Then $X + 12 + (16 \times 3) = 100$ or $X = 40$

Hence the relative atomic mass of X is 40

Question 7

(a) Combinations which gives buffer are:



(b) Number of moles of HCl reacted with excess alkali = $\frac{25.4}{1000} \times 0.1 \text{ mol} = 0.00254 \text{ mol}$

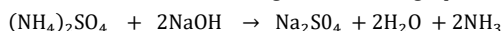
NaOH reacts with HCl such that their mole is 1:1;

Thus number of moles of excess alkali (NaOH) was also 0.00254 mol

But number of moles of NaOH before reaction with $(\text{NH}_4)_2\text{SO}_4 = \frac{50}{1000} \times 0.1 \text{ mol} = 0.005 \text{ mol}$

So number of moles of NaOH reacted with $(\text{NH}_4)_2\text{SO}_4 = (0.005 - 0.00254) \text{ mol} = 0.00246 \text{ mol}$

NaOH reacts with $(\text{NH}_4)_2\text{SO}_4$ according to the following equation:



From which mole ratio of $(\text{NH}_4)_2\text{SO}_4$ to NaOH is 1:2

Thus number of moles of $(\text{NH}_4)_2\text{SO}_4$ in 25cm^3 reacted with NaOH = $\frac{0.00246}{2} \text{ mol} = 0.00123 \text{ mol}$

So number of moles of $(\text{NH}_4)_2\text{SO}_4$ in $250\text{cm}^3 = \frac{0.00123 \times 250}{25} \text{ mol} = 0.0123 \text{ mol}$

And mass of ammonium sulphate = $0.0123 \times 132\text{g} = 1.6236\text{g}$

$\%(\text{NH}_4)_2\text{SO}_4 = \frac{1.6236}{1.65} \times 100\% = 98.4\%$

Hence the percentage of ammonium sulphate is 98.4%.

Question 8

(a) It is incapable of producing enough concentration of conjugate base to eliminate added acid.

(b) From related equations of reactions of previous related problems:

Volume of acid required to titrate $\text{Na}_2\text{CO}_3 = 2(22.7 - 18.6)\text{cm}^3 = 8.2\text{cm}^3$

Volume of acid required to titrate NaOH = $(22.7 - 8.2)\text{cm}^3 = 14.5\text{cm}^3$

Number of moles of HCl reacted with $\text{Na}_2\text{CO}_3 = \frac{8.2}{1000} \times 0.1 \text{ mol} = 0.00082 \text{ mol}$

But mole ratio of Na_2CO_3 to HCl is 1:2

Thus number of moles of Na_2CO_3 reacted = $\frac{0.00082 \text{ mol}}{2} = 0.00041 \text{ mol}$

Mass concentration of $\text{Na}_2\text{CO}_3 = \frac{0.00041 \times 1000 \times 106 \text{ gdm}^{-3}}{25} = 1.7384 \text{ gdm}^{-3}$

Hence mass concentration of sodium carbonate was 1.7384 gdm^{-3}

Number of moles of acid (HCl) reacted with NaOH = $\frac{14.5}{1000} \times 0.1 \text{ mol} = 0.00145 \text{ mol}$

But mole ratio of NaOH to HCl is 1:1

Thus number of moles of NaOH reacted was also 0.00145 mol

And its mass concentration = $\frac{0.00145 \times 1000 \times 40}{25} \text{ gdm}^{-3} = 2.32 \text{ gdm}^{-3}$

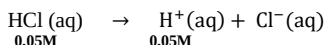
Hence mass concentration of sodium hydroxide was 2.32 gdm^{-3}

And mass concentration of sodium carbonate was 1.7384 gdm^{-3}

Question 9

(i) For CH_3COOH : $[\text{H}^+] = \alpha C = \sqrt{CK_a}$; $\text{pH} = -\log[\text{H}^+] = -\log \sqrt{0.05 \times 1.8 \times 10^{-5}} = 3$
Thus the pH of 0.05M CH_3COOH is 3

(ii) For HCl:



$\text{pH} = -\log[\text{H}^+] = -\log 0.05 = 1.3$

Thus the pH of 0.05M HCl is 1.3

Comment: pH of HCl is smaller than that of CH_3COOH because HCl is stronger acid and ionises completely in the solution to give greater concentration of hydrogen ions.

Question 10

From Ostwald dilution's law; $\alpha = \sqrt{\frac{K_b}{C}}$

(a) From which; $K_b = \alpha^2 C = \left(\frac{1.4}{100}\right)^2 \times 0.1\text{M} = 1.96 \times 10^{-5}$

Thus the dissociation constant of the base is 1.96×10^{-5}

$\text{p}K_b = -\log K_b = -\log 1.96 \times 10^{-5} = 4.7$

Hence $\text{p}K_b$ of the base is 4.7

(b) When $C = 0.002\text{M}$:

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.96 \times 10^{-5}}{0.002}} = 0.099 \text{ or } 9.9\%$$

Thus the degree of dissociation of $0.002\text{M NH}_3(\text{aq})$ is 9.9%

$[\text{OH}^-] = \alpha C$; then $\text{pOH} = -\log[\text{OH}^-] = -\log(0.002 \times 0.099) = 3.7$

But $\text{pH} = 14 - \text{pOH} = 14 - 3.7 = 11.3$

Hence pH of the ammonia solution is 10.3.

Question 11

(a) Sulphuric acid being strong acid ionises completely in the aqueous solution and hence in such mixture there is no formation of dynamic equilibrium which is the fundamental requirement for buffer to function.

(b) CH_3COO^- is conjugate base of CH_3COOH ; so their K_b and K_a respectively are related by the following equation:

$$K_a K_b = 10^{-14}$$

From which, K_a of $\text{CH}_3\text{COOH} = \frac{10^{-14}}{K_b \text{ of } \text{CH}_3\text{COO}^-} = \frac{10^{-14}}{5.025 \times 10^{-10}} = 1.99 \times 10^{-5}$

Then from Ostwald dilution law: $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.99 \times 10^{-5}}{0.01}} = 0.045 \text{ or } 4.5\%$

Thus the degree of ionisation of CH_3COOH is 4.5%

Using; $[\text{H}^+] = \alpha C$, then $\text{pH} = -\log[\text{H}^+] = -\log \alpha C = -\log(0.045 \times 0.01) = 3.35$

Hence pH of the solution is 3.35.

Question 12

(a) Yes, it affects.

Explanation

Both K_a and K_b values increase as temperature increases. This implies that $\text{p}K_a$ and $\text{p}K_b$ values decrease as temperature increases and hence the increase in temperature decreases pH of acidic buffer solution and increases pH of basic buffer solution.

(b) "Solubility of benzoic acid in water at 0°C is 2.44g dm^{-3} " means saturated solution of benzoic acid in water contains 2.44g benzoic acid in 1dm^3 .

Taking density of water as 1g/cm^3 or 1000g/dm^3 ; mass of water in dm^3 of its volume is;

$$\rho V = 1000\text{g dm}^{-3} \times 1\text{dm}^3 = 1000\text{g or } 1\text{kg}.$$

And molar mass of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) is 122g/mol

Then number of moles of the acid in 1kg of the solvent (water) = $\frac{2.44\text{g}}{122\text{g mol}^{-1}} = 0.02\text{mol}$

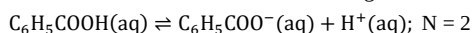
Hence molality of the saturated solution of benzoic acid is 0.02mol/kg

Freezing point depression, ΔT of water in the solution = $0^\circ\text{C} - (-0.0392^\circ\text{C}) = 0.0392^\circ\text{C}$

When there is dissociation of the solute in the solvent:

$$\Delta T = i K_f m \text{ or } i = \frac{\Delta T}{K_f m} = \frac{0.0392}{1.86 \times 0.02} = 1.054$$

But in the solution benzoic acid ionises according to the following equation:



Then $\alpha = \frac{i-1}{N-1} = \frac{1.054-1}{2-1} = 0.054 \text{ or } 5.4\%$

Thus the degree of dissociation of benzoic acid in the saturated is 0.054 or 5.4%

From Ostwald's dilution law: $\alpha = \sqrt{\frac{K_a}{C}}$

From which $K_a = \alpha^2 C$

But for very dilute solution of the water as a solvent: Molality = Molarity

Thus Molarity of saturated solution of the acid is 0.02M

Then $K_a = (0.054)^2 \times 0.02 \text{ mol dm}^{-3} = 5.832 \times 10^{-5} \text{ mol dm}^{-3}$

Hence dissociation constant for the acid is $5.832 \times 10^{-5} \text{ mol dm}^{-3}$

Question 13

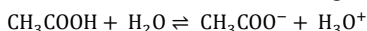
(a) It is possible.

Explanation

CH_3COONa reacts with HCl to give CH_3COOH . Thus when CH_3COONa present in excess, the unreacted CH_3COONa and the produced CH_3COOH will form acidic buffer solution.



(b) In the solution, ethanoic acid ionises according to the following equation:



From which: $K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$ or $[\text{H}_3\text{O}^+] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$

Introducing $-\log$ both sides; $-\log[\text{H}_3\text{O}^+] = -\log \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$

Or $-\log[\text{H}_3\text{O}^+] = -\log K_a + -\log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$

Thus $\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$

When $[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}]$, $\log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \log 1 = 0$ and therefore $\text{pH} = \text{p}K_a$

Hence pH of ethanoic acid solution will be equal to its $\text{p}K_a$, if the concentration of undissociated ethanoic acid is equal to the concentration of the dissociated acid i.e. if the acid has dissociated to 50%.

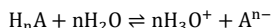
Question 14

(a) A buffer is a solution that contains either a large amount of weak acid and its conjugate base or a large amount of weak base and its conjugate acid.

Both of these buffers use the same principle such as: in a weak acid- conjugate base buffer solution, if an acid is added, the conjugate base neutralizes it. If a base is added to the buffer, then, the weak acid neutralizes it and vice-versa.

If at the end, the conjugate base/weak acid ratio does not change much, the value of the pH of the solution does not change much.

(b) H_nA being weak acid ionises according to the following equation:



From which mole ratio of A^{n-} to H_3O^+ is 1: n;

Thus $[\text{A}^{n-}] = \frac{1}{n}[\text{H}_3\text{O}^+]$

And $K_a = \frac{[\text{A}^{n-}][\text{H}_3\text{O}^+]^n}{[\text{H}_n\text{A}]} = \frac{[\text{H}_3\text{O}^+][\text{H}_3\text{O}^+]^n}{n[\text{H}_n\text{A}]}$ or $K_a = \frac{[\text{H}_3\text{O}^+]^{n+1}}{n[\text{H}_n\text{A}]}$ or $[\text{H}_3\text{O}^+]^{n+1} = nK_a[\text{H}_n\text{A}]$

But $[\text{H}_n\text{A}] = C$; then $[\text{H}_3\text{O}^+]^{n+1} = nK_a C$

Hence $[\text{H}_3\text{O}^+] = \sqrt[n+1]{nCK_a}$

Question 15

(a) When sparingly soluble substance dissolves heat is absorbed from the surroundings. So the equilibrium reaction $\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ is endothermic. Being endothermic, the rise in temperature shifts position of equilibrium to the right by dissolving more AgCl(s) and this is reflected by the increase in value of K_{sp} .

(b) The mixture of ethanoic acid and sodium ethanoate is acidic of a buffer solution whose p^H value is given by the following equation: $\text{p}^H = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

But $[\text{Salt}] = [\text{CH}_3\text{COONa}] = 0.2\text{M}$, $[\text{Acid}] = [\text{CH}_3\text{COOH}] = 0.02\text{M}$

And $\text{p}K_a = -\log K_a = -\log(1.8 \times 10^{-5}) = 4.7$; then $\text{pH} = 4.7 + \log \left(\frac{0.2}{0.02} \right) = 5.7$

Hence pH of the solution 5.7

Question 16

(a) (i) Buffer solution cannot maintain its pH value in any amount of acid/base. Buffer solution can only maintain its pH on addition of small amount of acid or base without exceeding its buffer capacity.

(ii) Basically common ion effect is the depression of ionization of weak electrolyte which is not necessary accompanied with depression in solubility. Adding strong electrolyte like HCl and NaOH in weak acid or weak base like CH_3COOH and NH_3

merely depress their ionization without affecting their solubility because their dissolution process is not based on ionisation. (Only for salts decrease in ionisation leads to decrease in solubility).

(b) Let the required volume in cm^3 be V

Then by using;

$$\text{pH} = \text{pK}_a + \log \frac{\text{Number of moles of HCOONa (Salt)}}{\text{Number of moles of HCOOH (Acid)}}, 5 = -\log 1.6 \times 10^{-4} + \log \frac{0.1V}{100 \times 0.01}$$

From which $V = 160$

Hence volume of HCOONa is 160cm^3

Question 17

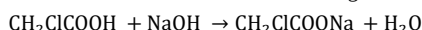
(a) Acid is any hydrogen containing specie which is capable of donating one or more hydrogen proton to a base.

Base is any specie which is capable of accepting one or more hydrogen proton from an acid.

Advantages of Bronsted-Lowry theory

1. It expands the list of potential acids and bases to include positive and negative ions as well as species with lone pair.
2. It explains the role of water in acid-base reaction where it accepts H^+ from acid to form H_3O^+ .
3. It expands to include solvent other than water and reactions which occur in the gas or solid phase.
4. It explains the difference in relative strength of a pair of acid and a pair of base.

(b) Chloroethanoic acid reacts with NaOH according to the following equation:



From which mole ratio of the acid to NaOH is 1:1

$$\text{Number of moles of NaOH taken} = \frac{100}{1000} \times 0.25 \text{ moles} = 2.5 \times 10^{-2} \text{ moles}$$

$$\text{Number of moles of CH}_2\text{ClCOOH taken} = \frac{100}{1000} \times 0.5 \text{ moles} = 5 \times 10^{-2} \text{ moles}$$

Thus CH_2ClCOOH is in excess and $(5 \times 10^{-2} - 2.5 \times 10^{-2})$ moles = 2.5×10^{-2} moles of it remain unreacted at the end of the reaction.

Number of moles of $\text{CH}_2\text{ClCOONa}$ formed is 2.5×10^{-2} moles

(NaOH is limited reactant, so amount of $\text{CH}_2\text{ClCOONa}$ formed is deduced from it).

So at the end of chemical reaction, there are 2.5×10^{-2} moles of formed $\text{CH}_2\text{ClCOONa}$ and

2.5×10^{-2} moles of unreacted CH_2ClCOOH .

The formed $\text{CH}_2\text{ClCOONa}$ and unreacted CH_2ClCOOH forms acidic buffer solution whose pH value is given by the following equation: $\text{pH} = \text{pK}_a + \log \frac{\text{Number of moles of salt (CH}_2\text{ClCOONa)}}{\text{Number of moles of acid (CH}_2\text{ClCOOH)}}$

$$\text{Substituting pH} = 2.86 + \log \left(\frac{2.5 \times 10^{-2}}{2.5 \times 10^{-2}} \right) = 2.86$$

Hence pH of the buffer solution is 2.86.

Question 18

$$(a) \text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-; K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$$

$$\text{From which } [\text{H}_3\text{O}^+] = \frac{K_a[\text{HCN}]}{[\text{CN}^-]}$$

Where $[\text{CN}^-] = [\text{NaCN}]$, because the salt is fully ionised while HCN being very weak acid is only partially ionised to give CN^-

$$\text{Substituting } [\text{H}_3\text{O}^+] = \frac{4.93 \times 10^{-10} \times 0.1}{0.8} \text{ M} = 6.1625 \times 10^{-11} \text{ M}$$

Hence the concentration of H_3O^+ is $6.1625 \times 10^{-11} \text{ M}$

Alternative solution

$$\text{Using pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}; \text{Where } [\text{Salt}] = [\text{NaCN}] = 0.8 \text{ M}, [\text{Acid}] = [\text{HCN}] = 0.1 \text{ M}$$

$$\text{And } \text{pK}_a = -\log K_a = -\log 4.93 \times 10^{-10} = 9.3; \text{ So } \text{pH} = 9.3 + \log \frac{0.8}{0.1} = 10.2$$

$$\text{But } [\text{H}_3\text{O}^+] = \log^{-1}(-\text{pH}) = \log^{-1}(-10.2) = 6.31 \times 10^{-11} \text{ M}$$

Thus the concentration of H_3O^+ is $6.31 \times 10^{-11} \text{ M}$

(b) After addition of 0.1 mole of HCl :

$$[\text{CN}^-] = \frac{(0.8-0.1)\text{mol}}{1\text{dm}^3} = 0.7 \text{ M} \text{ and } [\text{HCN}] = \frac{(0.1+0.1)\text{mol}}{1\text{dm}^3} = 0.2 \text{ M}$$

$$\text{Then from } [\text{H}_3\text{O}^+] = \frac{K_a[\text{HCN}]}{[\text{CN}^-]}$$

$$\text{Then new } [\text{H}_3\text{O}^+] = \frac{4.93 \times 10^{-10} \times 0.2}{0.7} \text{ M} = 1.41 \times 10^{-10} \text{ M}$$

After addition of 0.02 mole of NaOH :

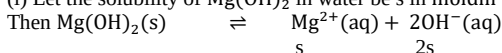
$$[\text{CN}^-] = \frac{(0.8+0.02)\text{mol}}{1\text{dm}^3} = 0.82 \text{ M} \text{ and } [\text{HCN}] = \frac{(0.1-0.02)\text{mol}}{1\text{dm}^3} = 0.08 \text{ M}$$

$$\text{Using } \text{pH} = \text{pK}_a + \log \frac{[\text{CN}^-]}{[\text{HCN}]} = 9.3 + \log \left(\frac{0.82}{0.08} \right) = 10.31$$

Hence the pH after addition of the NaOH is 10.31

Question 19

(i) Let the solubility of $\text{Mg}(\text{OH})_2$ in water be s in mol dm^{-3}



$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^{-}]^2$$

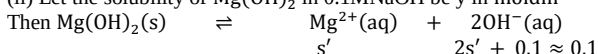
$$\text{Substituting } 1.1 \times 10^{-11} = (s)(2s)^2 = 4s^3$$

$$\text{Or } s = \sqrt[3]{\frac{1.1 \times 10^{-11}}{4}} = 1.4 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{Solubility in g dm}^{-3} = 1.4 \times 10^{-4} \times 58 \text{ g dm}^{-3} = 8.12 \times 10^{-3} \text{ g dm}^{-3}$$

Thus the solubility of $\text{Mg}(\text{OH})_2$ in H_2O is $8.12 \times 10^{-3} \text{ g dm}^{-3}$

(ii) Let the solubility of $\text{Mg}(\text{OH})_2$ in 0.1M NaOH be y in mol dm^{-3}



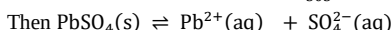
$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^{-}]^2$$

$$\text{Substituting } 1.1 \times 10^{-11} = y \times 0.1^2 \text{ or } y = 1.1 \times 10^{-9} \text{ mol dm}^{-3}$$

$$\text{Solubility in g dm}^{-3} = 1.1 \times 10^{-9} \times 58 \text{ g dm}^{-3} = 6.38 \times 10^{-8} \text{ g dm}^{-3}$$

Question 20

$$\begin{aligned} \text{(i) Molar solubility of } \text{PbSO}_4 &= \frac{\text{Solubility of PbSO}_4 \text{ in g dm}^{-3}}{\text{Molar mass of PbSO}_4} \\ &= \frac{0.4}{303} \text{ mol dm}^{-3} = 1.32 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$



$$\text{From which } [\text{Pb}^{2+}] = [\text{SO}_4^{2-}] = 1.32 \times 10^{-3} \text{ mol dm}^{-3}$$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = (1.32 \times 10^{-3} \text{ mol dm}^{-3})^2 = 1.7424 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$$

(ii) Hence the solubility product of PbSO_4 was $1.7424 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$

Let the solubility of PbSO_4 in 0.01M Na_2SO_4 be s

$$\text{Then } [\text{Pb}^{2+}] = s$$

$$[\text{SO}_4^{2-}] = s + 0.01 \approx 0.01$$

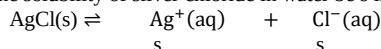
$$\text{Then } 1.7424 \times 10^{-6} = 0.01s \text{ or } s = 1.7424 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{But solubility in g dm}^{-3} = \text{Molar solubility} \times \text{Molar mass} = 1.7424 \times 10^{-4} \times 303 \text{ g dm}^{-3} = 0.053 \text{ g dm}^{-3}$$

Hence the solubility of PbSO_4 in 0.01M Na_2SO_4 is 0.053 g dm^{-3}

Question 21

(a) Let the solubility of silver chloride in water be s in mol dm^{-3}



$$K_{\text{sp}} = [\text{Ag}^{+}][\text{Cl}^{-}]$$

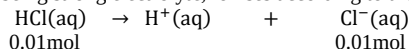
$$\text{Then } 1 \times 10^{-10} = s^2 \text{ or } s = \sqrt{1 \times 10^{-10}} = 10^{-5} \text{ mol dm}^{-3}$$

$$\text{Solubility AgCl in g dm}^{-3} = 10^{-5} \times 143.5 \text{ g dm}^{-3} = 1.435 \times 10^{-3} \text{ g dm}^{-3}$$

$$\begin{aligned} \text{Thus maximum mass of AgCl which goes into solution as ions in } 1 \text{ dm}^3 \\ = 1.435 \times 10^{-3} \text{ g dm}^{-3} \times 1 \text{ dm}^3 = 1.435 \times 10^{-3} \text{ g} \end{aligned}$$

Hence maximum loss from the precipitate is $1.435 \times 10^{-3} \text{ g}$

(b) HCl being strong electrolyte, ionises according to the following equation:



Thus if s' is the molar solubility of AgCl in 0.01M HCl;

$$[\text{Ag}^{+}] = s'; [\text{Cl}^{-}] = s' + 0.01 \approx 0.01$$

$$\text{Then } 10^{-10} = 0.01s' \text{ or } s' = 10^{-8} \text{ mol dm}^{-3}$$

$$\text{Solubility of AgCl in g dm}^{-3} = 10^{-8} \times 143.5 = 1.435 \times 10^{-6} \text{ g dm}^{-3}$$

Thus, the maximum mass of AgCl which goes into the solution as dissolved ions in 1 dm^3 of the solution

$$= 1.435 \times 10^{-6} \text{ g dm}^{-3} \times 1 \text{ dm}^3 = 1.435 \times 10^{-6} \text{ g}$$

Hence the mass of silver chloride lost by washing with 1 dm^3 of 0.01M HCl is $1.435 \times 10^{-6} \text{ g}$

Question 22

(a) In molten state (anhydrous form), AlCl_3 has no enough concentration of ions for doing electrolytic conduction as result of its high degree of polarisation. But in aqueous solution the salt undergoes cationic hydrolysis yielding enough concentration of free ions ($\text{H}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$) which are responsible for electrolytic conduction.

i.e. $\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{H}^+(\text{aq}) + 3\text{Cl}^-(\text{aq})$

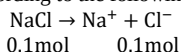
(b) If s is the solubility of AgCl in water (before addition of NaCl);

Then K_{sp} of $\text{AgCl} = [\text{Ag}^+][\text{Cl}^-] = s^2$

$$\begin{aligned}\text{From which } x = \sqrt{K_{\text{sp}}} &= \sqrt{1.69 \times 10^{-10}} = 1.3 \times 10^{-5} \text{M} = 1.3 \times 10^{-5} \times 143.5 \text{gdm}^{-3} \\ &= 1.8655 \times 10^{-3} \text{gdm}^{-3}\end{aligned}$$

$$\text{Number of moles of NaCl in 5.85g of its mass} = \frac{5.85\text{g}}{58.5\text{g mol}^{-1}} = 0.1\text{mol}$$

NaCl being strong electrolyte ionises completely according to the following equation:



Then new: $[\text{Cl}^-] = s' + 0.1 \approx 0.1\text{M}$; $[\text{Ag}^+] = s'$

Where y is the solubility of AgCl after introducing AgCl to the solution

$$\begin{aligned}K_{\text{sp}} &= [\text{Ag}^+][\text{Cl}^-] = 0.1y = 1.69 \times 10^{-10}; y = 1.69 \times 10^{-9}\text{M} = 1.69 \times 10^{-9} \times 143.5 \text{gdm}^{-3} \\ &= 2.42515 \times 10^{-7} \text{gdm}^{-3}\end{aligned}$$

Thus the solubility of AgCl decreased from $1.8655 \times 10^{-3} \text{gdm}^{-3}$ to $2.42515 \times 10^{-7} \text{gdm}^{-3}$ after introducing 5.85g of NaCl . The difference is the mass of AgCl precipitate formed in a litre of solution.

That is $(1.8655 \times 10^{-3} - 2.42515 \times 10^{-7})\text{g} = 1.865 \times 10^{-3} \text{g}$ of AgCl precipitate was formed

Hence $1.865 \times 10^{-3} \text{g}$ of silver chloride will be precipitated in a litre of the solution

Question 23

In aqueous solution, NaF undergoes anionic salt hydrolysis according to the following equation: $\text{NaF} + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{NaOH}$

The above equation can be written ionically as: $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$

$$\text{From which } K = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]}$$

Where K stands for dissociation constant.

$$\text{But } [\text{HF}] = [\text{OH}^-]$$

$$\text{Then } K = \frac{[\text{OH}^-]^2}{[\text{F}^-]}$$

$$[\text{OH}^-] = \sqrt{K[\text{F}^-]}$$

$$\text{Then } \text{pOH} = -\log[\text{OH}^-] = -\log\sqrt{K[\text{F}^-]}$$

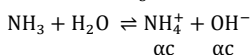
Where $[\text{F}^-] = [\text{NaF}] = 0.25\text{M}$ (Since K is very small)

$$\text{pOH} = -\log\sqrt{1.5 \times 10^{-11} \times 0.25} = 5.7$$

$$\begin{aligned}\text{Using } \text{pH} &= 14 - \text{pOH} \quad (\text{pH} + \text{pOH} = 14) \\ &= 14 - 5.7 = 8.3\end{aligned}$$

Hence the pH of 0.25M NaF is 8.3

In solution, NH_3 ionises according to the following equation:



Where $[\text{OH}^-] = \alpha\text{C}$ and $\text{pOH} = -\log[\text{OH}^-]$

$$\text{But from Ostwald's dilution law; } \alpha = \sqrt{\frac{K_b}{C}}$$

$$\text{Then } [\text{OH}^-] = C \sqrt{\frac{K_b}{C}} = \sqrt{CK_b}$$

$$\text{pOH} = -\log\sqrt{CK_b}$$

where $K_b = 1.77 \times 10^{-5}$ and $C = 0.01\text{M}$

$$\text{Substituting } \text{pOH} = -\log\sqrt{0.01 \times 1.77 \times 10^{-5}} = 3.34$$

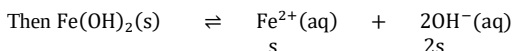
$$\begin{aligned}\text{Then } \text{pH} &= 14 - \text{pOH} \quad (\text{pH} + \text{pOH} = 14) \\ &= 14 - 3.38 = 10.62\end{aligned}$$

Hence the pH of 0.01M $\text{NH}_3(\text{aq})$ is 10.62

Question 24

(a) Molar solubility of $\text{Fe}(\text{OH})_2 = \frac{0.6 \times 10^{-3} \text{ g dm}^{-3}}{90 \text{ g mol}^{-1}} = 6.67 \times 10^{-6} \text{ mol dm}^{-3}$

If s is the molar solubility of $\text{Fe}(\text{OH})_2$



(b) From which $K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^{-}]^2 = s(2s)^2 = 4s^3$

But $s = 6.67 \times 10^{-6} \text{ mol dm}^{-3}$

Thus $K_{\text{sp}} = 4 \times (6.67 \times 10^{-6} \text{ mol dm}^{-3})^3 = 1.19 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$

There fore K_{sp} value of $\text{Fe}(\text{OH})_2$ is $1.19 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$

From $K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^{-}]^2$; $[\text{OH}^{-}] = \sqrt{\frac{K_{\text{sp}}}{[\text{Fe}^{2+}]}}$

But $[\text{Fe}^{2+}] = \frac{10^{-6}}{56} \text{ M} = 1.786 \times 10^{-8} \text{ M}$

Then $[\text{OH}^{-}] = \sqrt{\frac{1.19 \times 10^{-15}}{1.786 \times 10^{-8}}} = 2.58 \times 10^{-4} \text{ M}$

$\text{pOH} = -\log [\text{OH}^{-}] = -\log(2.58 \times 10^{-4}) = 3.6$

And $\text{pH} = 14 - \text{pOH} = 14 - 3.6 = 10.4$

Hence the minimum pH required is 10.4

Question 25

(a) Since the solubility product BaSO_4 is smaller than that of CaSO_4 and the two compounds (salts) have similar formula with the same proportions of constituent then BaSO_4 will first precipitate.

(b) The first solid to precipitate is BaSO_4 whose K_{sp} is given by; $K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$

From which; $[\text{SO}_4^{2-}] = \frac{K_{\text{sp}}}{[\text{Ba}^{2+}]}$; but $[\text{Ba}^{2+}] = 0.1 \text{ M}$

Whence $[\text{SO}_4^{2-}] = \frac{1.1 \times 10^{-10}}{0.1} \text{ M} = 1.1 \times 10^{-9} \text{ M}$

Thus the molar concentration of SO_4^{2-} at the instant the first solid precipitate is $1.1 \times 10^{-9} \text{ M}$

(c) For CaSO_4 ; $K_{\text{sp}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$

From which $[\text{SO}_4^{2-}] = \frac{K_{\text{sp}}}{[\text{Ca}^{2+}]} = \frac{2.4 \times 10^{-5}}{0.1} = 2.4 \times 10^{-4} \text{ M}$

But from $K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$

Thus $[\text{SO}_4^{2-}]$ when first precipitate of CaSO_4 occurs is $2.4 \times 10^{-4} \text{ M}$

$$[\text{Ba}^{2+}] = \frac{K_{\text{sp}}}{[\text{SO}_4^{2-}]} = \frac{1.1 \times 10^{-10}}{2.4 \times 10^{-4}} = 4.58 \times 10^{-7} \text{ M}$$

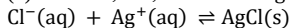
Hence concentration of Ba^{2+} present when the first precipitate of CaSO_4 occurs is $4.58 \times 10^{-7} \text{ M}$

Question 26

(a)

- Solubility is the ability of a certain solute to be dissolved in a given solvent which is given as the amount of substance dissolved in one litre of saturated solution at given temperature.
- Saturated solution is the solution which cannot dissolve more solute without forming a precipitate at given temperature.
- Saturated point is the point at which a liquid cannot take up more of the solute at given temperature.
- Supersaturated solution is the solution with more solute beyond its saturated point.
- Fractional precipitation is the method for separating elements or compounds with similar solubility by a series of analytical precipitations, each one improving the purity of the desired element.

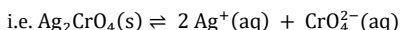
(b) Chloride, Cl^{-} , reacts with Ag^{+} (from AgNO_3) according to the following equation:



The end point is obtained when $[\text{Ag}^{+}][\text{Cl}^{-}] = K_{\text{sp}}$ of AgCl at which $[\text{Ag}^{+}] = [\text{Cl}^{-}]$

Thus K_{sp} of $\text{AgCl} = [\text{Ag}^{+}]^2$

Using potassium chromate (K_2CrO_4) as an indicator, the end point is obtained when the precipitate of Ag_2CrO_4 (silver chromate) starts to form.

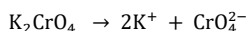


From which K_{sp} of $\text{Ag}_2\text{CrO}_4 = [\text{Ag}^{+}]^2 [\text{CrO}_4^{2-}]$

Taking; $\frac{K_{\text{sp}} \text{ of } \text{Ag}_2\text{CrO}_4}{K_{\text{sp}} \text{ of } \text{AgCl}} = \frac{[\text{Ag}^{+}]^2 [\text{CrO}_4^{2-}]}{[\text{Ag}^{+}]^2}$

Substituting $[\text{CrO}_4^{2-}] = \frac{1 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}}{1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}} = 10^{-2} \text{ mol dm}^{-3}$

But potassium chromate (K_2CrO_4) ionises according to the following equation:

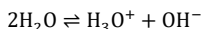


From which mole ratio of K_2CrO_4 to CrO_4^{2-} is 1:1 and therefore; $[K_2CrO_4] = [CrO_4^{2-}]$

Hence the concentration of potassium chromate at the end point is $10^{-2} \text{ mol dm}^{-3}$.

Question 27

(i) Water undergo self-ionization according to the following equation:



Where $[OH^-] = [H_3O^+]$

Then $K_w = [OH^-][H_3O^+] = [H_3O^+]^2$; $[H_3O^+] = \sqrt{K_w}$

And $pH = -\log[H_3O^+] = -\log\sqrt{K_w}$

But at 30°C ; $K_w = 1.471 \times 10^{-14}$

Substituting $pH = -\log\sqrt{1.471 \times 10^{-14}} = 6.9$

Hence the pH of water at 30°C is 6.9

(ii) Since both KOH and HCl are strong base and acid respectively, they give **neutral solution** at the equivalence point.

And for neutral solution; $[OH^-] = [H_3O^+]$

Then $K_w = [OH^-][H_3O^+] = [H_3O^+]^2$; $[H_3O^+] = \sqrt{K_w}$

And $pH = -\log[H_3O^+] = -\log\sqrt{K_w}$

Where at 10°C , $K_w = 0.293 \times 10^{-14}$

Substituting $pH = -\log\sqrt{0.293 \times 10^{-14}} = 7.3$

Hence the pH at equivalence point is 7.3.

Question 28

(i) HA reacts with NaOH according to the following equation: $HA + NaOH \rightarrow NaA + H_2O$

To make the solution with $pH = 6$ (acidic solution), the acid HA must be in excess.

But if the weak acid HA and produced NaA forms acidic buffer solution whose pH value is given by the following equation:

$pH = pK_a + \log \frac{[Salt]}{[Acid]}$, where $[Salt] = [NaA]$ and $[Acid] = [HA]$

Thus $pH = pK_a + \log \frac{[NaA]}{[HA]}$; $6 = 6 + \log \frac{[NaA]}{[HA]}$

From which $\frac{[NaA]}{[HA]} = \log^{-1}(0) = 1$

Whence $[NaA] = [HA]$ (after the reaction) for the solution to have pH of 6

Let volume of HA taken be V_{HA} and volume of NaOH taken to V_{NaOH}

Using $n = MV$; $n_{HA} = 0.1V_{HA}$ and $n_{NaOH} = 0.1V_{NaOH}$

Then from mole ratio of the reaction equation:

$n_{NaA} \text{ produced} = 0.1V_{NaOH}$

$n_{HA} \text{ unreacted} = 0.1V_{HA} - 0.1V_{NaOH}$

Using $[\] = \frac{n}{V}$ and $[HA] \text{ unreacted} = [NaA] \text{ produced}$

$$\frac{0.1V_{HA} - 0.1V_{NaOH}}{V_{HA} + V_{NaOH}} = \frac{0.1V_{NaOH}}{V_{HA} + V_{NaOH}}$$

From which; $0.1V_{HA} = 0.2V_{NaOH}$ or $V_{HA} = 2V_{NaOH}$

Hence to prepare the solution with pH of 6, the volume of HA solution mixed must be twice the volume of NaOH mixed.

(ii) Also from $pH = pK_a + \log \frac{[NaA]}{[HA]}$

If $pH = 5$; $5 = -\log(1 \times 10^{-6}) + \log \frac{[NaA]}{[HA]}$

$-1 = \log \frac{[NaA]}{[HA]}$; $\frac{[NaA]}{[HA]} = 0.1$

Whence after the reaction; $[NaA] = 0.1[HA]$; for the pH to be 5; $n_{HA} \text{ mixed} = 0.1V_{HA}$

$n_{NaOH} \text{ mixed} = 0.1V_{NaOH} = n_{NaA} \text{ produced}$ (NaOH was limited reactant)

$n_{HA} \text{ unreacted} = (0.1V_{HA} - 0.1V_{NaOH})$

But $[NaA] \text{ produced} = 0.1 \times [HA] \text{ unreacted}$

$$\text{Thus } \frac{0.1V_{\text{NaOH}}}{V_{\text{HA}} + V_{\text{NaOH}}} = \left(\frac{0.1V_{\text{HA}} - 0.1V_{\text{NaOH}}}{V_{\text{HA}} + V_{\text{NaOH}}} \right) \times 0.1$$

$$\text{From which } V_{\text{HA}} = 11V_{\text{NaOH}}$$

Hence to prepare the solution with pH of 5, the volume of HA solution mixed must be 11 times the volume of NaOH mixed

The best buffer solution is the solution with pH = 6 because at pH = 6, [salt]([NaA]) = [Acid]([HA]) making pH = pK_a where the buffer becomes most efficient with maximum buffer range.

Question 29

(a)

(i) The concentration of solid (Mg(OH)₂(s)) is constant (unchanged).

(ii) From; K_{sp} = [Mg²⁺(aq)][OH⁻(aq)]²

$$\text{Units of } K_{\text{sp}} = \text{Units of } [\text{Mg}^{2+}(\text{aq})] \times (\text{Units of } [\text{OH}^{-}(\text{aq})])^2$$

$$\text{Units of } K_{\text{sp}} = \text{mol dm}^{-3} \times (\text{mol dm}^{-3})^2 = \text{mol}^3 \text{ dm}^{-9}$$

(b) Given that:

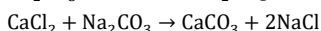
$$\text{Volume of CaCl}_2 = \text{Volume of Na}_2\text{CO}_3 = V \text{ dm}^3$$

Then using n = MV;

$$\text{Number of moles of CaCl}_2 = 0.1V \text{ mol}$$

$$\text{Number of moles of Na}_2\text{CO}_3 = 0.1V \text{ mol}$$

Na₂CO₃ reacts with CaCl₂ to give CaCO₃ according to the following equation:



From which mole ratio is 1:1 and because number of moles of CaCl₂ is equal to the number of moles of Na₂CO₃ (0.1V mol); nothing present in excess.

Also from the reaction equation; mole ratio of CaCl₂ (or Na₂CO₃) to CaCO₃ is 1:1; thus number of moles of CaCO₃ produced was also 0.1V mol.

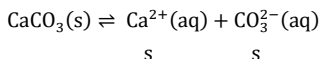
$$\text{Using } \left[\right] = \frac{n}{V};$$

$$\text{Number of moles of CaCO}_3 \text{ produced in } 1 \text{ dm}^3 \text{ of the solution} = \frac{0.1V \text{ mol}}{(V+V) \text{ dm}^3} = 0.05 \text{ mol dm}^{-3}$$

Then using mass concentration in gdm⁻³ = Molar concentration × Molar mass

$$\begin{aligned} \text{Mass of solid CaCO}_3 \text{ produced (just before being dissolved in the solution)} \\ = 0.05 \times 100 = 5 \text{ g dm}^{-3} \end{aligned}$$

The produced CaCO₃ dissolves only slightly according to the following equation:



where s is the molar solubility of CaCO₃

$$\text{Then using } K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = s^2$$

$$\text{From which } s = \sqrt{K_{\text{sp}}} = \sqrt{1.69 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}} = 1.3 \times 10^{-4} \text{ mol dm}^{-3}$$

Then using mass solubility = Molar solubility × Molar mass

$$\text{Mass solubility of CaCO}_3 = 1.3 \times 10^{-4} \times 100 = 0.013 \text{ g dm}^{-3}$$

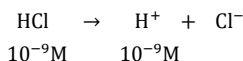
$$\text{And therefore mass of the precipitation in } 1 \text{ dm}^{-3} \text{ of the solution} = (5 - 0.013) \text{ g dm}^{-3} = 4.987 \text{ g dm}^{-3}$$

Hence the mass concentration of CaCO₃ precipitate 4.987 gdm⁻³

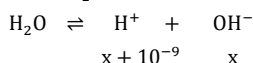
Question 30

(a) Since dissolving sparingly soluble substance is endothermic process, the value of solubility product increases with an increase in temperature.

(b) HCl ionises according to the following equation:



If x moles of H₂O are ionised to its respective ions in 1 dm³ of the solution;



$$\text{Then } K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} = (x + 10^{-9})x$$

$$\text{From which: } x^2 + 10^{-9}x - 10^{-14} = 0; x = 9.95 \times 10^{-8}$$

$$\text{Thus } [\text{H}^+] = (9.95 \times 10^{-8} + 10^{-9}) \text{ M}$$

$$= 1.005 \times 10^{-7} \text{ M}$$

$$\text{And pH} = -\log[\text{H}^+] = -\log(1.005 \times 10^{-7})$$

$$= 6.9978$$

Hence pH of the solution is 6.9978

Question 31

(a) Yes (It is possible).

Explanation:

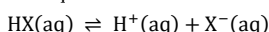
For the solution to be neutral, $[\text{H}_3\text{O}^+]$ must just be equal to $[\text{OH}^-]$. Only at 25°C , the equality occurs when $[\text{H}_3\text{O}^+] = 10^{-7} \text{ M}$ which intum gives the value of pH of 7, because at 25°C , $K_w = 10^{-14} \text{ M}^2$. However the K_w being an equilibrium constant, it is temperature dependent whose value increases with an increase in temperature. So at higher temperature than 25°C , the K_w value will be greater than 10^{-14} therefore making pH of neutral solution to be less than 7 (for example if $K_w = 10^{-12} \text{ M}^2$, pH of the neutral solution will be 6).

(b) Using $\text{pH} = -\log[\text{H}^+]$

$$\text{From which } [\text{H}^+] = \log^{-1}(\text{pH}) = \log^{-1}(-2.69) = 2.042 \times 10^{-3} \text{ M}$$

Hence $[\text{H}^+]$ is $2.042 \times 10^{-3} \text{ M}$

The equation to show ionisation of HX in solution:



$$\text{From which } K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$

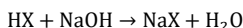
$$\text{But } [\text{H}^+] = [\text{X}^-]$$

$$\text{Thus } K_a = \frac{[\text{H}^+]^2}{[\text{HX}]}$$

$$\text{Substituting } K_a = \frac{(2.042 \times 10^{-3} \text{ M})^2}{0.15 \text{ M}} = 2.78 \times 10^{-5} \text{ M}$$

Hence the value of K_a is $2.78 \times 10^{-5} \text{ M}$

HX reacts with NaOH according to the following equation:



Since only half of HX has neutralized, after the reaction there are following compounds;

HX (unreacted) and NaX (produced) in water (solution)

Since HX is weak acid, the mixture of HX and NaX (NaX is strong salt containing conjugate base of the weak acid, HX) forms acidic buffer solution whose pH value is given by the following equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{X}^-]}{[\text{HX}]}$$

$$\text{Where } [\text{X}^-] = [\text{NaX}] = [\text{Salt}]$$

$$\text{And } [\text{HX}] = [\text{Acid}] \text{ but } [\text{X}^-] = [\text{HX}]$$

$$\text{Thence } \text{pH} = \text{p}K_a + \log(2.78 \times 10^{-5}) = 4.56$$

Hence the pH of the solution is 4.56

Question 32

(a) Bronsted acids: HCO_3^- , H_2O

Bronsted bases: S^{2-} , HCO_3^- , H_2O , NH_3

(b) Given that: $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$

$$\text{From which } K_c = \frac{[\text{NH}_3]}{[\text{NH}_4^+][\text{OH}^-]} = \frac{1}{\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}}$$

$$\text{But } \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = K_b(\text{NH}_3)$$

$$\text{Then } K_c = \frac{1}{K_b(\text{NH}_3)} = \frac{K_f}{K_r}; \text{ From which: } K_r = K_f \times K_b(\text{NH}_3)$$

Where;

K_r is the required rate constant of reverse reaction which involves proton transfer from water to NH_3

K_f is the rate constant of forward reaction $= 3.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$

But because NH_4^+ and NH_3 form conjugate pair;

$$K_a(\text{NH}_4^+)K_b(\text{NH}_3) = K_w = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

And ionisation constant of NH_4^+ in water is actually K_h (hydrolysis constant) of NH_4^+ which is equal to $k_a(\text{NH}_4^+)$

That is $K_a(\text{NH}_4^+) = 5.6 \times 10^{-10} \text{ mol dm}^{-3}$

Thence from $K_a K_b = K_w = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

$$K_b(\text{NH}_3) = \frac{10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{5.6 \times 10^{-10} \text{ mol dm}^{-3}} = 1.7857 \times 10^{-5} \text{ mol dm}^{-3}$$

The substituting this value of $K_b(\text{NH}_3)$ and given value of K_f to $K_r = K_f \times K_b(\text{NH}_3)$

$$K_r = 3.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \times 1.7857 \times 10^{-5} \text{ mol dm}^{-3} = 6.1 \times 10^5 \text{ sec}^{-1}$$

Hence the rate constant is $6.1 \times 10^5 \text{ sec}^{-1}$

Question 33

(a) **First component:** Weak electrolyte

Explanation:

This is either weak acid or weak base which is used to provide the dynamic system of the chemical equilibrium and to eliminate added base or added acid respectively.

Second component: Strong salt

Explanation:

The salt must contain either conjugate base of the acid or conjugate acid of the base of the first component. The strong salt which contain conjugate base of the weak acid, provides enough concentration of anions to combine with H^+ on addition of strong acid while strong salt which contain conjugate acid of the weak base provides enough concentration of cations to combine with OH^- on addition of strong acid.

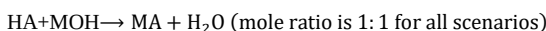
(b) After adding 10mL of strong base, the solution was still acidic suggesting that the acid was excess.

The unreacted weak acid and produced salt forms **acidic buffer solution** whose pH is given by the following equation:

$$\text{pH} = \text{pKa} + \log \frac{[\text{Salt}]}{[\text{Acid}]}; \text{pH} = \text{pKa} + \log \frac{\text{Number of moles of salt}}{\text{Number of moles of acid}}$$

$$\text{Where } \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 10^{-5} = 5$$

If the base is monoacid, MOH, and the acid is monobasic, HA, then the reaction equation will be:



Number of moles of base in 10mL of its solution

= Number of moles of produced salt

$$= \frac{10}{100} \times M_b \text{ (} M_b \text{ is unknown concentration of base)} = 0.01 M_b$$

Volume of base used to neutralize the acid in the buffer solution

$$= (22.22 - 10) \text{ mL} = 12.22 \text{ mL}$$

Number of moles of acid in the buffer = Number of moles of base used to neutralize it

$$= \frac{12.22}{1000} \times M_b = 0.01222 M_b$$

Then from $\text{pH} = \text{pKa} + \log \frac{\text{Number of moles of salt}}{\text{Number of moles of acid}}$

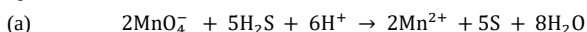
$$5 = \text{pKa} + \log \frac{0.01 M_b}{0.01222 M_b}; \text{From which } \text{pKa} = 5.087$$

$$K_a = \log^{-1}(-\text{pKa}) = \log^{-1}(-5.087) = 8.18 \times 10^{-6}$$

Dissociation constant for the acid is 8.18×10^{-6}

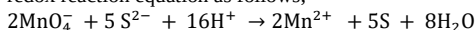
PART SIX

Question 1



The student should understand that: It is recommended to give the answer in the same form as that of the question unless it is instructed differently.

In this question, a student may consider H_2S as the producer of S^{2-} which is oxidised to S by MnO_4^- thus writing overall balanced redox reaction equation as follows;



But in the problem, it is given H_2S and not S^{2-} (which is not necessary to be from H_2S). So in the half oxidation reaction we must consider H_2S as appears in the question.

i.e. $\text{H}_2\text{S} \rightarrow \text{S} + 2\text{H}^+ + 2\text{e}^-$ and not $\text{S}^{2-} \rightarrow \text{S} + 2\text{e}^-$ so as to give correct overall reaction equation.

(b) Molar mass of potassium salt is 254 g mol^{-1}

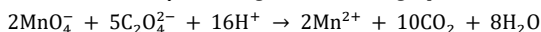
$$\text{Using } n = \frac{m}{M_r};$$

$$\text{Number of moles of the potassium salt} = \frac{0.16 \text{ g}}{254 \text{ g mol}^{-1}} = 6.299 \times 10^{-4} \text{ mol}$$

From the molecular formula of the potassium salt, one mole of the salt produces 2 moles of the oxalate ions ($\text{C}_2\text{O}_4^{2-}$).

Thus number of moles of $\text{C}_2\text{O}_4^{2-}$ was $2 \times 6.299 \times 10^{-4} \text{ mol}$ or $1.2598 \times 10^{-3} \text{ mol}$

$\text{C}_2\text{O}_4^{2-}$ reacts with MnO_4^- according to the following equation:



From which mole ratio of $\text{C}_2\text{O}_4^{2-}$ to MnO_4^- is 5:2

Thus number of moles of MnO_4^- reacted = $\frac{2}{5} \times 1.2598 \times 10^{-3} \text{ mol}$

or $5.0392 \times 10^{-4} \text{ mol}$ in 24.5 cm^3 of its solution

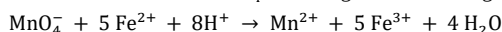
Using $\left[\right] = \frac{n}{v}$;

Molarity of manganate (VII) solution = $\frac{5.0392 \times 10^{-4} \times 10^3}{24.5} \text{ M} = 0.02 \text{ M}$

Molarity of manganate (VII) solution is 0.02M.

Question 2

(a) The given sulphate produced Fe^{2+} which reacts with KMnO_4 according to the following equation:



Where the mole ratio of MnO_4^- to Fe^{2+} is 1:5

But $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}] = \frac{9.85}{392 \times 0.25} \text{ M} = 0.1 \text{ M}$

Number of moles of Fe^{2+} in 25 cm^3 of its solution = $\frac{25}{1000} \times 0.1 \text{ mol} = 2.5 \times 10^{-3} \text{ mol}$

Then from the above mole ratio;

Number of moles of $\text{MnO}_4^- = \frac{1}{5} \times 2.5 \times 10^{-3} \text{ mol} = 5 \times 10^{-4} \text{ mol}$ of KMnO_4 in 24.75 cm^3 of its solution.

Thus $[\text{KMnO}_4] = \frac{5 \times 10^{-4} \times 10^3}{24.75} \text{ M} = 0.0202 \text{ M}$

Hence Molarity of KMnO_4 is 0.0202M

(b) Then mass concentration in $\text{gdm}^{-3} = \text{Molarity} \times \text{molar mass} = 0.0202 \times 158 \text{ gdm}^{-3} = 3.1916 \text{ gdm}^{-3}$

Thus mass concentration of KMnO_4 is 3.1916 gdm^{-3}

(c) Using dilution principle; $M_c V_c = M_d V_d$

Where:

M_c is the molarity of more concentrated KMnO_4 solution = 0.0202M

V_c is the volume of more concentrated KMnO_4 solution = 1800 cm^3

M_d is the molarity of more diluted KMnO_4 solution = 0.02M

V_d is the volume of more diluted KMnO_4 solution

Then $V_d = \frac{M_c V_c}{M_d} = \frac{0.0202 \times 1800}{0.02} \text{ cm}^3 = 1818 \text{ cm}^3$

Thus volume of distilled water to be added = $(1818 - 1800) \text{ cm}^3 = 18 \text{ cm}^3$

Hence 18 cm^3 of distilled water should be added

(d) The simple FeSO_4 is less preferred than $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ due to the following reasons:

Fe^{2+} in FeSO_4 is unstable to oxidation. It oxidised easily by oxygen from the air thus interfering measurement of correct volume of KMnO_4 which is exactly used to oxidize Fe^{2+} into Fe^{3+} .

Having lower molar mass compared to $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, the FeSO_4 does not allow weighing error during preparation of its solution. This makes difficulty to prepare its solution of exactly intended concentration.

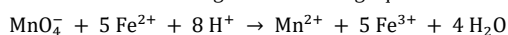
Question 3

(a) High concentration decreases mobility of ions because in the more concentrated solution ions are close to each other, leading to strong ion-ion interactions (inter-ionic forces) and hence the ionic mobility is lowered.

(b) Number of moles of KMnO_4 in 20.7 cm^3 of its solution

$$= \frac{20.7}{1000} \times 0.01 \text{ mol} = 2.07 \times 10^{-4} \text{ mol} = \text{Number of moles of } \text{MnO}_4^-$$

MnO_4^- reacts with Fe^{2+} according to the following equation



From which mole ratio of MnO_4^- to Fe^{2+} is 1:5

Thus number of moles of Fe^{2+} in 20 cm^3 of its solution = $5 \times 2.07 \times 10^{-4} \text{ mol}$

Thus number of moles of Fe^{2+} in 1 dm^3 (1000 cm^3) of its solution

$$= \frac{5 \times 2.07 \times 10^{-4} \times 1000}{20} \text{ mol} = 0.05175 \text{ mol}$$

Equation for reduction of Fe^{2+} by zinc: $2\text{Fe}^{3+} + \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{Fe}^{2+}$

From which mole ratio of Fe^{3+} to Fe^{2+} is 1:1

Thus number of moles of Fe^{3+} in 1000cm^3 of the solution was also 0.05175mol

Mass of iron (III) in 25g of the salt = $0.05175 \times 56\text{g} = 2.898\text{g}$

Then $\% \text{Fe}^{3+} = \frac{2.898}{25} \times 100\% = 11.592\%$

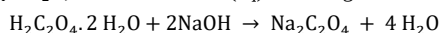
Hence the percentage of iron (III) by mass is 11.592%

(In above calculation, mass of one mole of Fe^{3+} has taken as that of neutral atom of Fe because mass of an electron which removed in the ionisation process is very small and it is negligible compared to total mass of protons and neutrons which are unaltered in the ionisation process).

Question 4

(a) Because its **reduction product, Cr^{3+} , is not colourless**; it is green.

(b) Ethanedioic acid crystals ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) react with NaOH (aq) according to the following equation:



From which mole ratio of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ to NaOH is 1:2

Number of moles of NaOH in 19.8cm^3 of its solution

$$= \frac{19.8}{1000} \times 0.1\text{mol} = 1.98 \times 10^{-3}\text{mol}$$

Then number of moles of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 20cm^3 of the solution

$$= \frac{1.98 \times 10^{-3}}{2}\text{mol} = 9.9 \times 10^{-4}\text{mol}$$

And number of moles of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 100cm^3 of the solution

$$= \frac{9.9 \times 10^{-4} \times 100}{20}\text{mol} = 4.95 \times 10^{-3}\text{mol}$$

Using $m = nM_r$;

Mass of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 100cm^3 of the solution = $4.95 \times 10^{-3} \times 126\text{g} = 0.6237\text{g}$

And mass of $\text{Na}_2\text{C}_2\text{O}_4 = (1.5 - 0.6237)\text{g} = 0.8763\text{g}$

Then number of moles of $\text{Na}_2\text{C}_2\text{O}_4 = \frac{0.8763}{134\text{g mol}^{-1}} = 0.00654\text{mol}$

It follows that:

- Number of moles of $\text{C}_2\text{O}_4^{2-}$ from $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \text{number of moles of } \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 0.00495\text{mol}$
- Number of moles of $\text{C}_2\text{O}_4^{2-}$ from $\text{Na}_2\text{C}_2\text{O}_4 = \text{Number of moles of } \text{Na}_2\text{C}_2\text{O}_4 = 0.00654\text{mol}$

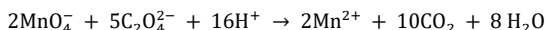
The total number of moles of $\text{C}_2\text{O}_4^{2-}$ in 100cm^3 of the solution

$$= (0.00495 + 0.00654)\text{mol} = 0.01149\text{mol}$$

Thus total number of moles $\text{C}_2\text{O}_4^{2-}$ in 25cm^3 of the solution

$$= \frac{0.01149 \times 25}{100}\text{mol} = 0.0028725\text{mol}$$

$\text{C}_2\text{O}_4^{2-}$ reacts with MnO_4^- according to the following equation:



From which mole ratio of MnO_4^- to $\text{C}_2\text{O}_4^{2-}$ is 2:5

Thus number of moles of MnO_4^- required

$$= \frac{2}{5} \times 0.0028725\text{mol} = 0.001149\text{mol} = \text{number of moles of } \text{KMnO}_4$$

From $[\] = \frac{n}{v}$; $V = \frac{n}{[\]}$

Thus volume of KMnO_4 solution required = $\frac{0.001149}{0.01}\text{dm}^3 = 0.1149\text{dm}^3$ or 114.9cm^3

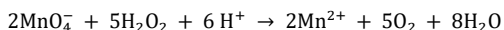
Hence 114.9cm^3 is required to for complete oxidation of the solution.

Question 5

(a) Number of moles of KMnO_4 in 47.8cm^3 of its solution

$$= \frac{47.8}{1000} \times 0.02\text{mol} = 9.56 \times 10^{-4}\text{mol of } \text{MnO}_4^-$$

MnO_4^- reacts with H_2O_2 according to the following equation:



From which mole ratio of MnO_4^- to H_2O_2 is 2:5

Then number of moles of H_2O_2 in 25cm^3 of its diluted solution

$$= \frac{5}{2} \times 9.56 \times 10^{-4} \text{ mol} = 2.39 \times 10^{-3} \text{ mol}$$

$$\text{Thus molarity of diluted solution} = \frac{2.39 \times 10^{-3} \times 10^3}{25} \text{ M} = 0.0956 \text{ M}$$

$$\text{Using dilution principle, } M_c V_c = M_d V_d \text{ or } M_c = \frac{M_d V_d}{V_c}$$

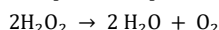
$$\text{Where } M_d = 0.0956 \text{ M, } V_d = 1000 \text{ cm}^3 (1 \text{ dm}^3), V_c = 100 \text{ cm}^3$$

$$\text{Substituting } M_c = \frac{0.0956 \times 1000}{100} = 0.956 \text{ M}$$

$$\text{Using mass concentration in } \text{g dm}^{-3} = [\quad] M_r = 0.956 \times 34 \text{ g dm}^{-3} = 32.504 \text{ g dm}^{-3}$$

Hence mass concentration of original H_2O_2 is 32.504 g dm^{-3}

(b) H_2O_2 undergo decomposition to produce O_2 according to the following equation;



From which mole ratio of H_2O_2 to O_2 is 2: 1

$$\text{Number of moles of } \text{H}_2\text{O}_2 \text{ in } 100 \text{ cm}^3 \text{ of its solution} = \frac{100}{1000} \times 0.956 \text{ mol} = 0.0956 \text{ mol}$$

$$\text{Thus } 0.0956 \text{ mol of } \text{H}_2\text{O}_2 \text{ produces } \frac{0.0956}{2} \text{ or } 0.0478 \text{ mol of } \text{O}_2$$

But 0.0956 mol of H_2O_2 is contained in 100 cm^3 its solution

And 1 mol of O_2 contains 22.4 dm^3 or 22400 cm^3 of its volume

Thus 100 cm^3 of H_2O_2 produces $0.0478 \times 22400 \text{ cm}^3$ or 1070.72 cm^3 of O_2

Whence 1 cm^3 of H_2O_2 produces $\frac{1070.72}{100} \text{ cm}^3$ or 10.7072 cm^3 of O_2

Hence volume rating of H_2O_2 solution is 10.7072 .

Question 6

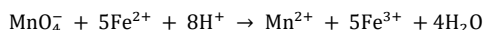
(a) It is due to presence of very small amount of unreacted potassium permanganate after the equivalence point.

(b) **Titration by KMnO_4 only:**

Number of moles of KMnO_4 in 24.2 cm^3 of its solution

$$= \frac{24.2}{1000} \times 0.02 \text{ mol} = 4.84 \times 10^{-4} \text{ mol of } \text{MnO}_4^-$$

Fe^{2+} (from $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) reacts with MnO_4^- according to the equation:



From which mole ratio of MnO_4^- to Fe^{2+} is 1: 5

$$\text{Number of moles of } \text{Fe}^{2+} = 5 \times 4.84 \times 10^{-4} \text{ mol} = 2.42 \times 10^{-3} \text{ mol in } 25 \text{ cm}^3 \text{ of its solution}$$

$$\text{Then } [\text{Fe}^{2+}] = [\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}] = \frac{2.42 \times 10^{-3} \times 10^3}{25} \text{ M} = 0.0968 \text{ M}$$

Titration by KClO_3 followed by KMnO_4 :

Number of moles KMnO_4 in 24.6 cm^3 of its solution

$$= \frac{24.6}{1000} \times 0.02 \text{ mol} = 4.92 \times 10^{-4} \text{ mol of } \text{MnO}_4^-$$

But 1 mol of MnO_4^- reacts with 5 mol of Fe^{2+} (from the mole ratio of equation of the reaction between Fe^{2+} and MnO_4^-)

Then number of moles of an excess $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ which unreacted with KClO_3

$$= 5 \times 4.92 \times 10^{-4} \text{ mol or } 2.46 \times 10^{-3} \text{ mol}$$

But total number of moles of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in 50 cm^3 of its solution

$$= \frac{50}{1000} \times 0.0968 \text{ mol} = 4.84 \times 10^{-3} \text{ mol}$$

Thus number of moles of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ reacted with KClO_3

$$= (4.84 \times 10^{-3} - 2.46 \times 10^{-3}) \text{ mol} = 2.38 \times 10^{-3} \text{ mol of } \text{Fe}^{2+}$$

From the given equation; mole ratio of Fe^{2+} to ClO_3^- is 6: 1

It follows that:

$$\text{Number of moles of } \text{ClO}_3^- \text{ in } 25 \text{ cm}^3 \text{ of its solution} = \frac{1}{6} \times 2.38 \times 10^{-3} \text{ mol}$$

$$\text{Then } [\text{ClO}_3^-] = [\text{KClO}_3] = \frac{2.38 \times 10^{-3} \times 10^3}{6 \times 25} \text{ M} = \frac{2.38}{150} \text{ M}$$

Using mass concentration in $\text{g dm}^{-3} = [\quad] M_r$

$$\text{Then mass concentration of potassium chlorate (V)} = \frac{2.38}{150} \times 122.5 \text{ g dm}^{-3} = 1.94 \text{ g dm}^{-3}$$

Hence the concentration of potassium chlorate (V) solution is 1.94 g dm^{-3} .

Question 7

(a) Assigning oxidation numbers for iodine: $2 \text{Na}_2\text{S}_2\text{O}_3 + \overset{0}{\text{I}_2} \rightarrow \overset{-1}{2\text{NaI}} + \text{Na}_2\text{S}_4\text{O}_6$

Thus iodine molecules are being reduced because their oxidation state has been decreased from 0 to -1 in the reaction.

(b) Number of moles of $\text{Na}_2\text{S}_2\text{O}_3$ in 30cm^3 of its solution

$$= \frac{30}{1000} \times 0.1\text{mol}$$

From the given reaction equation, mole ratio of $\text{Na}_2\text{S}_2\text{O}_3$ to I_2 is 2: 1

$$\text{Then number of moles of } \text{I}_2 = \frac{30 \times 0.1}{1000 \times 2} \text{mol} = 1.5 \times 10^{-3} \text{mol}$$

Using $m = nM_r$;

$$\text{Mass of iodine required} = 1.5 \times 10^{-3} \times 254\text{g} = 0.381\text{g}$$

Hence mass of iodine required is 0.381g

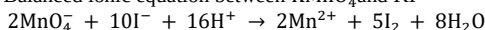
(c) The titration is iodimetry

Reason:

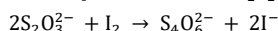
Sodium thiosulphate which is reducing agent is titrated directly with iodine solution which was initially present at the start of the titration.

Question 8

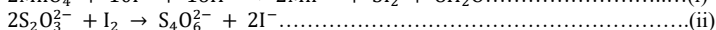
(a)(i) Balanced ionic equation between KMnO_4 and KI



(ii) Balanced ionic equation between $\text{Na}_2\text{S}_2\text{O}_3$ and I_2

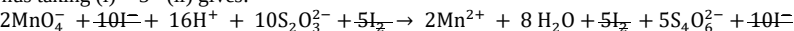


(b) From (a) above

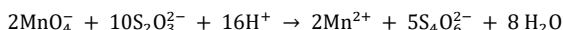


The overall reaction equation is written by eliminating I_2 in the two equations.

Thus taking (i) + $5 \times$ (ii) gives:



Hence the overall reaction equation is:



(c) Number of moles of KMnO_4 in 25cm^3 of its solution

$$= \frac{25}{1000} \times 0.0204\text{mol} = 5.1 \times 10^{-4}\text{mol of MnO}_4^-$$

But from the overall reaction equation, mole ratio of MnO_4^- to $\text{S}_2\text{O}_3^{2-}$ is 2: 10 or 1: 5

Thus number of moles of $\text{S}_2\text{O}_3^{2-}$ in 24.4cm^3 of its solution

$$= 5 \times 5.1 \times 10^{-4}\text{mol} = 2.55 \times 10^{-3}\text{mol of Na}_2\text{S}_2\text{O}_3$$

Then using $\left[\right] = \frac{n}{v}$;

$$[\text{Na}_2\text{S}_2\text{O}_3] = \frac{2.55 \times 10^{-3} \times 10^3}{24.4} \text{M} = 0.1045\text{M}$$

Hence Molarity of sodium thiosulphate solution is 0.1045M

(d) By dilution principle; $M_c V_c = M_d V_d$

$$\text{From which, } V_d = \frac{M_c V_c}{M_d}$$

Where $M_d = 0.1 \text{ M}$ (Decimolar solution)

$$M_c = 0.1045\text{M}, V_c = 1750\text{cm}^3$$

$$\text{Substituting } V_d = \frac{0.1045 \times 1750}{0.1} \text{cm}^3 = 1828.75\text{cm}^3$$

$$\text{Volume of distilled water added} = (1828.75 - 1750)\text{cm}^3 = 78.75\text{cm}^3$$

Hence 78.75cm^3 of distilled water must be added to 1750cm^3 solution in order to convert into a decimolar solution.

(e) The titration is iodometry because iodine used in the titration was firstly produced from oxidation of potassium iodide which is reducing agent by potassium permanganate which is an oxidising agent i.e. there was indirect titration of iodine.

Question 9

(a) Oxidation: acidic medium; reduction: basic medium.

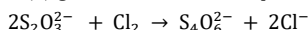
(b) Equations for reactions:



From bleaching power

Then $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \dots\dots\dots(ii)$

Taking (i) + (ii) gives overall reaction equation which is:



From which, mole ratio of $S_2O_3^{2-}$ to Cl_2 is 2: 1

Number of moles of $Na_2S_2O_3$ in $24.2cm^3$ of its solution

$$= \frac{24.2}{1000} \times 0.1mol = 2.42 \times 10^{-3}mol \text{ of } S_2O_3^{2-}$$

Thus number of moles of Cl_2 in $25cm^3$ of the solution

$$= \frac{2.42 \times 10^{-3}}{2} mol = 1.21 \times 10^{-3}mol$$

Then number of moles of Cl_2 in $250cm^3$ of the solution

$$= \frac{1.21 \times 10^{-3} \times 250}{25} = 1.21 \times 10^{-2}mol$$

Using $m = nM_r$;

Mass of chlorine in 2.5g of bleaching powder = $1.21 \times 10^{-2} \times 71g = 0.8591g$

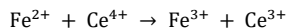
Whence the percentage of chlorine = $\frac{0.8591}{2.5} \times 100\% = 34.364\%$

Therefore, the percentage of the chlorine is 34.364%.

Question 10

(i) Cerium sulphate oxidizes siderite only which is reducing agent as it contains Fe^{2+} (in $FeCO_3$) which can be oxidised according to the following equation of oxidation half reaction: $Fe^{2+} \rightarrow Fe^{3+} + e$

Combining the above equation and the given reduction half reaction equation gives the overall reaction equation which is:



From which, mole ratio of Fe^{2+} to Ce^{4+} is 1:1;

Number of moles of cerium (IV) sulphate in $100cm^3$ of its solution

$$\frac{100}{1000} \times 0.1mol = 0.01mol = \text{number of moles of } Ce^{4+}$$

Thus from the mole ratio, number of moles of Fe^{2+} is also $0.01mol = \text{Number of moles of } FeCO_3$.

Using $m = nM_r$;

Mass of $FeCO_3$ (siderite) = $0.01 \times 116g = 1.16g$

Whence mass of haematite (Fe_2O_3) is $(3.9 - 1.16)g = 2.74g$

$$\text{Then } \%Fe_2O_3 = \frac{2.74}{3.9} \times 100 = 70.3\%$$

$$\text{And } \%FeCO_3 = \frac{1.16}{3.9} \times 100 = 29.7\%$$

Hence:

- The percentage of $FeCO_3$ (siderite) is 29.7%
- The percentage of Fe_2O_3 (haematite) is 70.3%

(ii) Using, $n = \frac{m}{M_r}$;

$$\text{Number of moles of } Fe_2O_3 = \frac{2.74}{160} mol = 0.017125mol$$

But 1 mole of Fe_2O_3 contains 2 moles of Fe^{3+} which in turn gives 2 moles of Fe^{2+} after reduction.

Hence number of moles of Fe^{2+} which are formed after reduction of the haematite = $0.017125 \times 2 \text{ mole} = 0.03425 \text{ mole}$

It follows that; Total number of moles of Fe^{2+} after the reduction = $(0.03425 + 0.01) \text{ mole} = 0.04425 \text{ mole}$

Where 0.01 mole of Fe^{2+} is from siderite (from (i) above)

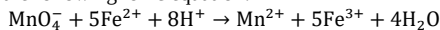
From the mole ratio in (i); number of moles of cerium (IV) sulphate required to react with Fe^{2+} will be also $0.04425mol$

Using $V = \frac{n}{c}$;

$$\text{Substituting } V = \frac{0.04425}{0.1} dm^3 = 0.4425dm^3 \text{ or } 442.5cm^3$$

Hence $442.5 cm^3$ of cerium (IV) sulphate would be required

Fe^{2+} reacts with $KMnO_4$ according to the following ionic equation:



From which mole ratio of MnO_4^- to Fe^{2+} is 1:5

$$\text{Thus number of moles required to react with } 0.04425 \text{ mol of } Fe^{2+} = \frac{0.04425}{5} mol = 8.85 \times 10^{-3}mol$$

$$\text{Using } V = \frac{n}{c}; \text{ then volume of } KMnO_4 = \frac{8.85 \times 10^{-3}}{0.05} dm^3 = 0.177dm^3 = 177cm^3$$

And cell diagram of the Daniel cell is: $\text{Zn(s)} \mid \text{Zn}^{2+}(2\text{M}) \parallel \text{Cu}^{2+}(0.5\text{M}) \mid \text{Cu(s)}$

From which $E_{\text{cell}}^{\theta} = E_{\text{cathode}}^{\theta} - E_{\text{anode}}^{\theta} = 0.34\text{V} - (-0.76\text{V}) = 1.1\text{V}$

Cell reaction: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

From which $n = 2$ and $Q_c = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{2}{0.5} = 4$

From Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{RT}{nF} \ln Q_c$

But $\ln Q_c = 2.303 \log Q_c$; Then $E_{\text{cell}} = E_{\text{cell}}^{\theta} - \frac{2.303RT}{nF} \log Q_c$

Where $E_{\text{cell}}^{\theta} = 1.1\text{V}$, $R = 8.3143$, $T = 35^{\circ}\text{C} = (35 + 273)\text{K} = 308\text{K}$, $n = 2$, $F = 96500$ and $R_Q = 4$

Substituting $E_{\text{cell}} = 1.1 - \frac{2.303 \times 8.3143 \times 308}{2 \times 96500} \log 4 = 1.0816$

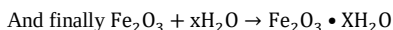
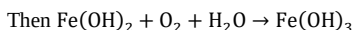
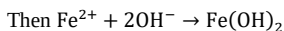
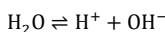
Hence the e.m.f of the cell is 1.0816

Note: In the above question temperature is not standard (25°C) so we cannot use the simplified Nernst equation which assumes the temperature to be 25°C .

Question 16

(a) To enable formation of Fe(OH)_2 , then Fe(OH)_3 and finally to hydrate Fe_2O_3 to form the rust ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$).

That is:



(b) **Reduction half reaction:** $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn(s)}$

From which $n = 2$ and $Q_c = \frac{1}{[\text{Zn}^{2+}]}$

Since ZnSO_4 is 95% dissociated and its mole ratio to Zn^{2+} is 1:1;

It follows that; $[\text{Zn}^{2+}] = \frac{95}{100} \times 0.1\text{M} = 0.095\text{M}$; Whence $Q_c = \frac{1}{0.095} = 10.5263$

From Nernst equation: $E = E^{\theta} - \frac{0.0591}{n} \log Q_c$

Substituting $E = -0.76 - \frac{0.0591}{2} \log 10.5263 = -0.79\text{V}$

Hence the electrode potential is -0.79V

Question 17

(a) (i) Is the degradation of the metal caused by unwanted oxidation over its surface.

(ii) Is the redox reaction whereby both reduction and oxidation occurs in the same element contained in a particular molecule or compound.

(b) Cell diagram corresponding to given redox reaction is: $\text{Fe}^{2+}(\text{aq}) \mid \text{Fe}^{3+}(\text{aq}) \parallel \text{Sn}^{4+}(\text{aq}) \mid \text{Sn}^{2+}(\text{aq})$

Then; $E_{\text{cell}}^{\theta} = E_{\text{cathode}}^{\theta} - E_{\text{anode}}^{\theta} = (0.150 - 0.771)\text{V} = -0.621\text{V}$

Using $E_{\text{cell}}^{\theta} = \frac{0.0591}{n} \log K_c$; Where $n = 2$ (From cell reaction)

Then $-0.621 = \frac{0.0591}{2} \log K_c$; $\log K_c = -21$

$K_c = \log^{-1}(-21) = 1 \times 10^{-21}$

Hence the equilibrium constant of the reaction is 1×10^{-21}

(Very small value of K_c indicates that the position of chemical equilibrium is far backward i.e. reverse reaction is spontaneous while forward reaction is not spontaneous).

Question 18

(a) This is due to its significances which are:

1. It allows the ions to migrate from cathode half-cell into the anode half-cell so as to complete the circuit.
2. It prevents the diffusion of the electrolyte from one half-cell to the other thus maintaining the charge balance in the two half cells.

(b) From Nernst equation; $E = E^{\theta} - \frac{0.0591}{n} \log Q_c$

But reduction half-cell reaction for copper is: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu(s)}$

From which $Q_c = \frac{1}{[\text{Cu}^{2+}]}$ and $n = 2$

Then $E = E^\ominus - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]}$ or $E = -0.02955 \log [\text{Cu}^{2+}]^{-1} + E^\ominus$

Or $E = 0.02955 \log [\text{Cu}^{2+}] + E^\ominus$

Hence (by comparing the bolded equation with general equation of straight line, $y = mx + c$) if the graph of electrode potential, E , is constructed against logarithms of concentrations of copper (II) ions, $[\text{Cu}^{2+}]$, will have the following features:

The graph will be straight line with positive slope amounted to 0.02955

The y – intercept = $E^\ominus$ (standard electrode potential)

TABLE OF DATA ANALYSIS

Electrode potential, E in volts	0.310	0.320	0.324	0.328	0.331
$[\text{Cu}^{2+}]$ in mol dm^{-3}	0.1	0.2	0.3	0.4	0.5
$\log [\text{Cu}^{2+}]$	-1.0	-0.7	-0.5	-0.4	-0.3

Then on your own plot the graph of E (on y – axis) against $\log [\text{Cu}^{2+}]$ (on x – axis); thereafter determine the y – intercept of the graph whose value is equal to standard electrode potential of copper.

Question 19

(a) (i) **Salt** which is **strong electrolyte** like potassium nitrate (KNO_3)

(ii) Salt bridge allows flow of ions while the wire allows flow of electrons and not the required flow of ions.

The cost of electricity will vary directly proportional to electrochemical equivalent of the metal.

So if:

C_1 and C_2 are electricity costs per kg for producing Mg and Al respectively,

Z_1 and Z_2 are electrochemical equivalent for Mg and Al respectively,

And E_1 and E_2 are equivalent weights for Mg and Al respectively.

Then from; $\frac{E_1}{Z_1} = \frac{E_2}{Z_2}$

It follows that; $\frac{E_1}{C_1} = \frac{E_2}{C_2}$

But $E_1 = \frac{\text{Atomic mass of Mg}}{\text{Magnitude of charge in } \text{Mg}^{2+}} = \frac{24}{2} = 12$

$E_2 = \frac{\text{Atomic mass of Al}}{\text{Magnitude of charge in } \text{Al}^{3+}} = \frac{27}{3} = 9$

And $C_1 = x\text{Tsh}$

Substituting $E_1 = \frac{12}{x} = \frac{9}{C_2}$; $C_2 = \frac{12}{9}x$ or $\frac{4}{3}x\text{Tsh}$ per kg of Al

Then for y kg, the cost become $\left(\frac{4}{3}x\right)y = \frac{4}{3}xy\text{Tsh}$

Hence the cost for producing y kg of aluminium $\frac{4}{3}xy\text{Tsh}$

Question 20

(a) Voltaic cell is a device which uses spontaneous chemical reactions to generate electricity while electrolytic cell is a device which uses electric current to produce non-spontaneous chemical reaction.

(b) **For water electrolysis:**

(i) Hydrogen gas is liberated at cathode as per reaction equation: $2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2(\text{g})$

From which $2F = 2 \times 96500\text{C}$ or 193000C liberates 1 mol of H_2

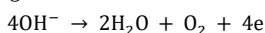
Then by using $Q = It = 0.65 \times 5.5 \times 3600\text{C}$ or 12870C liberates $\frac{12870}{193000} = 0.06668\text{mol}$ of H_2

From ideal gas equation; $V = \frac{nRT}{P}$

Substituting $V = \frac{0.06668 \times 0.082 \times 286 \times 760}{750} \text{ dm}^3 = 1.585 \text{ dm}^3$

Hence volume of hydrogen gas liberated is 1.585 dm^3

(ii) Oxygen gas is liberated at anode according to the following equation:



From which $4F$ liberates one mole of O_2

Then $2F$ liberates 0.5mol of O_2

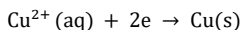
But according Avogadro's law; mole ratio = volume ratio (For gases)

Thus 0.5mol of $\text{O}_2 \equiv$ A half of volume of hydrogen liberated by the same amount of electricity.

Hence volume of oxygen liberated = $\frac{1.585}{2} \text{ dm}^3 = 0.7925 \text{ dm}^3$

(iii) For CuSO_4 electrolysis:

Copper is deposited at cathode according to the following equation:



From which $2F = 2 \times 96500 \text{ C}$ deposit 64g of copper

Then 12870C deposits $\frac{12870}{2 \times 96500} \times 64 \text{ g} = 4.268 \text{ g}$ of Cu

Hence mass of copper precipitated is 4.268g

Question 21

(a) The methods are:

1. Galvanization

In this method, iron is covered with another metal like zinc which form protective layer to prevent iron from rusting. The protective metal must be stronger reducing agent than iron for the method to be more efficient.

2. Cathodic protection

In this method iron is connected to more reactive metal like magnesium and zinc whereby the iron (weaker reductant) acts as cathode while the more reactive metal (stronger reductant) acts as anode of the galvanic cell. In this galvanic cell arrangement, iron behaving as cathode will not get oxidized and hence it is prevented from rusting.

(b) By Kohlrausch's law: $\Lambda_{\infty}(\text{AgCl}) = \Lambda_{\infty}(\text{Ag}^+) + \Lambda_{\infty}(\text{Cl}^-)$

$$= 6.2 \times 10^{-3} + 7.6 \times 10^{-3} = 1.38 \times 10^{-2} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$$

AgCl being sparingly soluble electrolyte;

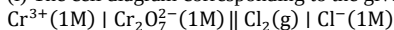
molar conductivity of its saturated solution = molar conductivity at infinite dilution

$$\text{Using } V = \frac{\Lambda_m}{\kappa} = \frac{1.38 \times 10^{-2} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}}{1.5 \times 10^{-4} \text{ m}^{-1} \Omega^{-1}} = 92 \text{ m}^3 \text{ mol}^{-1} = 92000 \text{ dm}^3 \text{ mol}^{-1}$$

$$\text{Then molar solubility of AgCl} = \frac{1}{89610} \text{ mol dm}^{-3} = 1.087 \times 10^{-5} \text{ mol dm}^{-3}$$

Question 22

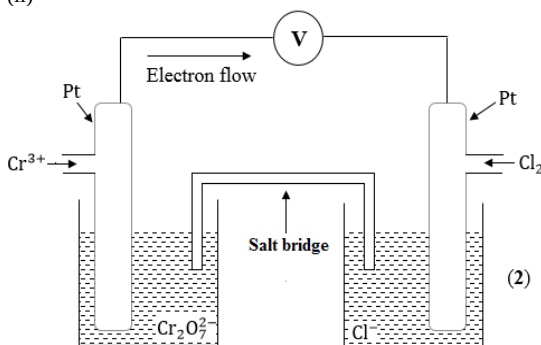
(i) The cell diagram corresponding to the given cell reaction is:



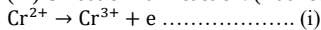
$$\text{Thus } E_{\text{cell}}^{\circ} = E_{\text{R}}^{\circ} - E_{\text{L}}^{\circ} = (1.36 - 1.33)\text{V} = 0.03\text{V}$$

Hence the standard e.m.f is 0.03V

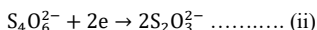
(ii)



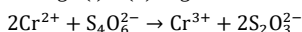
(iii) Oxidation half reaction: (At anode)



Reduction half reaction: (At cathode)



Taking 2(i) + (ii) to get overall reaction equation;



From which, number of electron transferred, $n = 2$

$$\text{Also using } E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

The e.m.f corresponding to given reaction;

$$E_{\text{cell}}^{\circ} = 0.17\text{V} - (-0.5\text{V}) = 0.67\text{V}$$

$$\text{Using } E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log Q_c$$

But at equilibrium; $E_{\text{cell}} = 0$ and $Q_c = K_c$

It follows that: $0 = E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log K_c$ or $E_{\text{cell}}^{\ominus} = \frac{0.0591}{n} \log K_c$

Substituting $0.67 = \frac{0.0591}{n} \log K_c$

$$K_c = 4.71 \times 10^{22}$$

Hence the equilibrium constant is 4.71×10^{22}

(iv) The equilibrium constant is **very large** implying that the **operating time of the cell is large**.

Question 23

(a) The differences are:

1. Electronic conductors, conduct electricity by using moving electrons (delocalised valence electrons) while electrolytic conductors conduct electricity by using moving ions.
2. Electronic conductors, conduct electricity in solid state while electrolytic conductors, conduct electricity in liquid state.
3. Electronic conductors are elements while electrolytic conductors are compounds.

(b) Cell constant = $\frac{1}{A}$

Substituting: Cell constant = $\frac{1 \text{ cm}}{2 \text{ cm}^2} = 0.5 \text{ cm}^{-1}$

The cell constant is 0.5 cm^{-1}

Conductivity = Conductance $\times$ Cell constant

But Conductance = $\frac{1}{\text{Resistance}}$

The conductivity = $\frac{\text{Cell constant}}{\text{Resistance}} = \frac{0.5 \text{ cm}^{-1}}{7.25 \Omega} = 0.069 \Omega^{-1} \text{ cm}^{-1}$

The conductivity is $0.069 \Omega^{-1} \text{ cm}^{-1}$

Resistance, $R = \rho \times \text{Cell constant}$

Where $\rho = 361 \Omega \text{ cm}$

And cell constant = 0.5 cm^{-1} (It is constant for given cell)

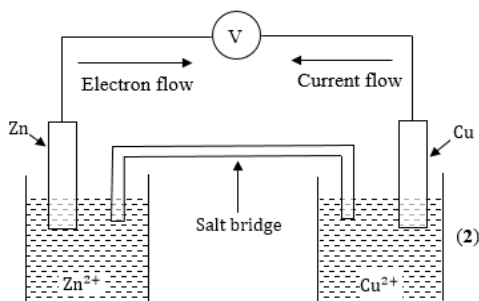
Then **$R = 361 \Omega \text{ cm} \times 0.5 \text{ cm}^{-1} = 180.5 \Omega$**

Question 24

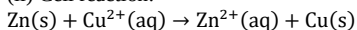
(a)

- (i) Is the electrode at which **reduction** occurs.
- (ii) Is the electrode at which **oxidation** occurs.
- (iii) Is the potential difference between the electric double layers which is formed when an electrode is in contact with solution containing 1M of its ions measured at 25°C and 1 atm (standard conditions).
- (iv) Is the **electrochemical cell** which consists of the same electrodes and the same electrolyte at different concentration which are connected by salt bridge.

(b)(i)



(ii) Cell reaction:



$$E_{\text{Cell}}^{\ominus} = E_{\text{cathode}}^{\ominus} - E_{\text{anode}}^{\ominus} = E_{\text{Cu}^{2+}/\text{Cu}}^{\ominus} - E_{\text{Zn}^{2+}/\text{Zn}}^{\ominus} = +0.34\text{V} - (-0.76\text{V}) = 1.1\text{V}$$

The e.m.f is 1.1V

From the Nernst equation; $E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log Q_c$

But at equilibrium: $E_{\text{cell}} = 0$ and $Q_c = K_c$

$$\text{Thus } 0 = E_{\text{Cell}}^{\ominus} - \frac{0.0591}{n} \log K_c$$

$$\text{An therefore } E_{\text{Cell}}^{\ominus} = \frac{0.0591}{n} \log K_c$$

$$\text{Where } E_{\text{Cell}}^{\ominus} = 1.1\text{V} \text{ and } n = 2$$

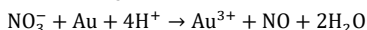
$$\text{Substituting } 1.1 = \frac{0.0591}{n} \log K_c$$

$$\text{From which } K_c = 1.68 \times 10^{37}$$

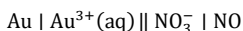
Hence the equilibrium constant is 1.68×10^{37}

Question 25

(a) For HNO_3 to dissolve Au, the following reaction must occur:



The cell diagram corresponding to the above reaction is as follows:



$$\text{From which: } E_{\text{Cell}}^{\ominus} = E_{\text{R}}^{\ominus} - E_{\text{L}}^{\ominus} = E_{\text{NO}_3^-/\text{NO}}^{\ominus} - E_{\text{Au}^{3+}/\text{Au}}^{\ominus} = (0.96 - 1.5)\text{V} = -0.54\text{V}$$

Since $E_{\text{Cell}}^{\ominus}$ is negative, the reaction is not spontaneous and hence the given nitric acid will not dissolve the gold.

(b) Using $n = \text{MV}$;

$$\text{Number of moles of KMnO}_4 \text{ used} = \frac{20}{1000} \times 0.02 \text{ mol} = 4 \times 10^{-4} \text{ mol} = \text{number of moles of MnO}_4^-$$

But from the given balanced reaction equation; mole ratio of MnO_4^- to $\text{C}_2\text{H}_4\text{O}_4 \cdot x\text{H}_2\text{O}$ is 2:5

$$\text{Thus number of moles of } \text{C}_2\text{H}_4\text{O}_4 \cdot x\text{H}_2\text{O} \text{ is } \frac{5}{2} \times 4 \times 10^{-4} \text{ mol} = 1 \times 10^{-3} \text{ mol}$$

$$\text{Using } M_r = \frac{m}{n} \left(\text{From } n = \frac{m}{M_r} \right)$$

Where $m = 0.126\text{g}$ (given)

$$M_r(\text{C}_2\text{H}_4\text{O}_4 \cdot x\text{H}_2\text{O}) = \frac{0.126\text{g}}{1 \times 10^{-3} \text{ mol}} = 126\text{g/mol}$$

$$\text{Thus: } (2 \times 12) + (4 \times 1) + (4 \times 16) + 18x = 126$$

From which $x = 2$

Hence the value of x is 2

PART SEVEN

Question 1

(a)

- (i) Endothermic
- (ii) Exothermic (common electron affinity of iodine is the one which involve the formation of I^- which is first electron affinity).
- (iii) The electron affinity leading to O^- is first electron affinity which is **exothermic**. The electron affinity leading to O^{2-} is second electron affinity which is **endothermic**.

(b) Since the reaction was accompanied with an increase in temperature, it was exothermic.

$$\text{Thus } \Delta H = -mc\Delta T; \text{ where } m = m_{\text{NaOH}} + m_{\text{H}_2\text{O}} = 6.5\text{g} + (1\text{gcm}^{-3} \times 100\text{cm}^3) = 106.5\text{g}$$

$$\text{Then } \Delta H = -106.5\text{g} \times 4.18\text{Jg}^{-1}\text{K}^{-1} \times (37.8 - 21.6)\text{K} = -7211.754\text{J}$$

$$\text{Using: } \Delta H_{\text{soln}} = \frac{\Delta H}{n_{\text{NaOH}}}; \text{ where } n_{\text{NaOH}} = \frac{6.5\text{g}}{40\text{g mol}^{-1}} = 0.1625\text{mol}$$

$$\text{Then } \Delta H_{\text{soln}} = \frac{-7211.754\text{J}}{0.1625\text{mol}} = -44380\text{J/mol or } -44.38\text{kJ/mol}$$

The enthalpy of solution is -44.38kJ/mol .

Question 2

(a) $\text{NO}_2(\text{g})$

Explanation

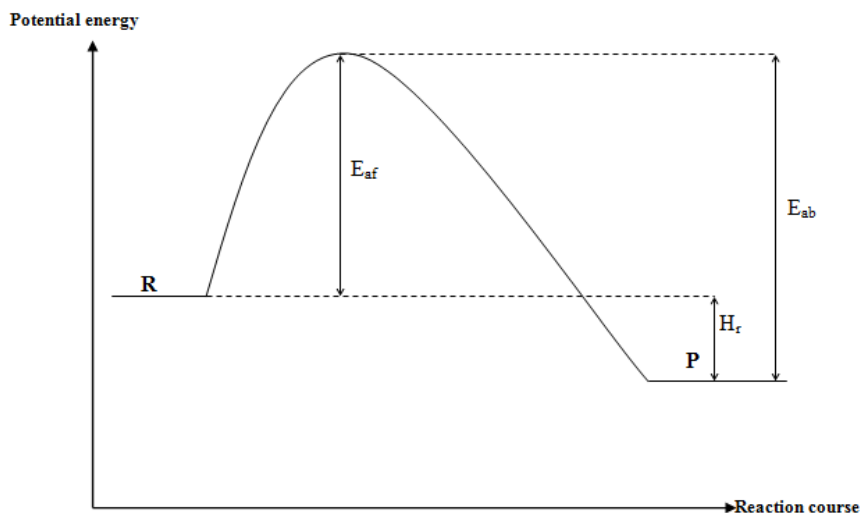
All the substances are in their elemental states, thus their standard heats of formation is zero, with the exception of $\text{NO}_2(\text{g})$, which is a compound.

(b)(i) For reversible reaction

Heat of reaction = Activation energy of forward reaction – Activation energy for backward reaction

$$= (32 - 82.1)\text{kJ/mol} = -50.1\text{kJ/mol}$$

Hence heat reactions -50.1kJ/mol .



(ii)

Where **R** is the reactants ($\text{CO(g)} + \text{NO}_2\text{(g)}$)

P is the products ($\text{CO}_2\text{(g)} + \text{NO(g)}$)

E_{af} is the activation energy for forward reaction.

E_{ab} is the activation energy for backward reaction.

H_r is the heat of reaction

Question 3

(a) MgCl_2 is most stable among given elements as it has most negative heat of formation followed by MgCl which is more stable, than MgCl_3 . MgCl_3 having most positive heat of formation among given compounds is least stable.

(b) Since the reaction was accompanied with a decrease in temperature, it was endothermic.

Thus $\Delta H = \text{Heat capacity} \times \Delta T = 1071\text{J/}^\circ\text{C} \times (25 - 21.56)^\circ\text{C} = 3684.24\text{J}$

Using; $\Delta H_{\text{soln}} = \frac{\Delta H}{n_{\text{NaNO}_3}}$; where $n_{\text{NaNO}_3} = \frac{15.3\text{g}}{85\text{g mol}^{-1}} = 0.18\text{mol}$

Then $\Delta H_{\text{soln}} = \frac{+3684.24\text{J}}{0.18\text{mol}} = +20468\text{J/mol}$ or $+20.468\text{kJ/mol}$

The enthalpy of solution is $+20.468\text{kJ/mol}$.

Question 4

(a) Compound with more negative lattice energy is more stable so the order becomes:

$\text{XO}_2 < \text{X}_2\text{C} < \text{XN} < \text{XS}_3$

↑
Increase of their stabilities

(b) Using $\Delta H = m\Delta T = \rho V\Delta T$ ($m = \rho V$)

$\rho_{\text{water}} = 1\text{kg dm}^{-3}$, $V = 200\text{cm}^3 = 0.2\text{dm}^3$ $C = 4.18\text{kJ kg}^{-1}\text{K}^{-1}$

$\Delta T = (31.24 - 25)^\circ\text{C} = 6.24^\circ\text{C}$

$\Delta H = 1\text{kg dm}^{-3} \times 0.2\text{dm}^3 \times 4.18\text{kJ kg}^{-1}\text{K}^{-1} \times 6.24\text{K} = 5.21664\text{kJ}$

The heat value of ethanol is 5.21664kJ .

Mass of ethanol burnt = $(56.69 - 56.46)\text{g} = 0.23\text{g}$

Number of moles of ethanol burnt = $\frac{0.23\text{g}}{46\text{g mol}^{-1}} = 0.005\text{mol}$ ($n = \frac{M}{M_r}$)

From the given equation of ethanol combustion mole ratio of ethanol to CO_2 is 1:2

Thus number of moles of CO_2 produced = $(2 \times 0.005)\text{mol} = 0.01\text{mol}$

Used $n = \frac{V}{GMV} = \frac{V}{22.4\text{L/mol}}$; $V = n \times 22.4\text{L/mol}$

$V = 0.01\text{mol} \times 22.4\text{L/mol} = 0.224\text{L}$

Volume of CO_2 produced was 0.224L

Question 5

(a) Change in the physical state is always accompanied with an energy change.

(b)

- (i) The solutions involved are all strong acids and strong bases which are essentially full ionised. So in each case the same process: $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ is taking place and hence values become similar.
- (ii) In 5 and 6 the process involved the absorption of energy when weak base (NH_3) and weak acid (CH_3COOH) respectively, are dissolved in their respectively reaction solutions and hence their value become low.
- (iii) The large negative value in 4 indicates that although HF is a relatively weak acid; as it dissociated the small F^- (Fluoride ions) has a large exothermic (negative) enthalpy of hydration which overweighs that factor (of weak acidic strength).

Low value in 7 because both NH_3 and HCN are weak base and weak acid respectively; such that both absorb energy in being dissociated as the neutralisation proceed.

Question 6

(a)

- (i) Heat of vapourisation; endothermic
 (ii) Heat of solution; endothermic
 (iii) Heat of fusion; endothermic
 (iv) **Molar** heat of condensation; exothermic
 (v) **Molar** heat of solidification; exothermic

(b) Number of moles in 1g of anhydrous $\text{CuSO}_4 = \frac{1\text{g}}{159.5\text{g mol}^{-1}} = \frac{2}{319} \text{ mol}$

Thus heat evolved when the anhydrous salt is dissolved in large amount of water in kJ/mol is $\frac{0.418\text{kJ}}{\frac{2}{319}\text{mol}} = \frac{0.418 \times 319}{2} \text{ kJ mol}^{-1}$
 $= 66.671 \text{ kJ mol}^{-1}$

Number of moles in 5g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \frac{5\text{g}}{249.5\text{g mol}^{-1}} = \frac{10}{499} \text{ mol}$

Thus heat absorbed when the hydrated salt is dissolved in large amount of water in kJ/mol

$$= \frac{0.23\text{kJ}}{\frac{10}{499}\text{mol}} = \frac{0.23 \times 499}{10} \text{ kJ mol}^{-1} = 11.477 \text{ kJ mol}^{-1}$$

When anhydrous copper (II) sulphate (CuSO_4) is dissolved in **large amount of water**, the following reactions occur:

Firstly $\text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{l}) \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}); \Delta H = Z \text{ kJ/mol}$.

Then $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) + \text{aq} \rightarrow [\text{Cu}(\text{OH})_4]\text{SO}_4(\text{aq}); \Delta H = +11.477 \text{ kJ/mol}$.

Blue solution

But when the anhydrous salt is dissolved in **large amount of water**, 66.671 kJ/mol is evolved.

Then $-66.671 = Z + 11.477; Z = -78.148$

Hence the heat change for the given reaction is -78.148 kJ/mol .

Question 7

(a) True

Explanation

Since stability implies lower energy; the greater amount of heat released in forming a compound, the more stable is the compound relative to its elements whose heat of formations are always zero.

$$\begin{aligned} \text{Heat rise in calorimeter} &= \text{heat capacity of calorimeter} \times \text{temperature rise} \\ &= 90 \times 5.3 = 477 \text{ J} \end{aligned}$$

(b) Heat rise in the solution $= MC\Delta T = \rho VC\Delta T = 1 \times (100 + 100) \times 4.2 \times 5.3 = 4452 \text{ J}$

Total heat evolved in the neutralisation $= -(477 + 4452) = -4929 \text{ J}$

Equation for the reaction: $\text{NaOH}(\text{aq}) + \text{CH}_3\text{COOH}(\text{aq}) \rightarrow \text{CH}_3\text{COONa}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

From stoichiometric ratio of above equation;

Number of moles of water formed $= \frac{100}{1000} \times 1 \text{ moles} = 0.1 \text{ moles}$

$$\begin{aligned} \text{Enthalpy of neutralisation} &= \frac{\text{Total heat evolved}}{\text{Number of moles of water}} \\ &= \frac{-4929}{0.1} = -49290 \text{ J/mol} = -49.29 \text{ kJ/mol} \end{aligned}$$

Hence the standard enthalpy of neutralisation is -49.29 kJ/mol .

Question 8

(a) Increase

Explanation:

In the equation, heat is produced in the product side as one of the products and thus the process is exothermic. Being exothermic, the process release heat to the surroundings including water causing the temperature of water to increase.

$$(b) \text{ Number of moles of water formed} = \frac{100}{1000} \text{ mol} = 0.1 \text{ mol}$$

$$\text{Heat rise in calorimeter} = \text{Heat capacity} \times \text{temperature rise} = 95 \times 6.25 \text{ J} = 593.75 \text{ J}$$

$$\text{Heat rise in solution} = \rho V \Delta T = 1 \times (100 + 100) \times 4.2 \times 6.25 \text{ J} = 5250 \text{ J}$$

$$\text{Total heat evolved in combustion} = -(593.75 + 5250) \text{ J} = -5843.75 \text{ J}$$

$$\text{Enthalpy of neutralisation} = \frac{\text{Total heat evolved}}{\text{Number of moles of water}} = \frac{-5843.75}{0.1} \text{ J mol}^{-1} \text{ or } 58.4375 \text{ kJ mol}^{-1}$$

Hence the standard enthalpy of neutralisation is -58.4375 kJ/mol

Question 9

(a) Because both strong acid and strong base ionises completely (to give H^+ and OH^- respectively) it easier for neutralisation reaction to take place between them than if one of them would be weak as weak acid and base tend to ionise only partially. Easier for H^+ and OH^- to combine means more heat is evolved and hence greater enthalpy of neutralisation between strong acid and strong base.

$$(b) \text{ Total enthalpy change} = \Delta T(m_v C_v + m_c C_c)$$

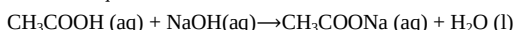
$$\text{But } C_v = 0; \text{ so total enthalpy change} = m_c C_c \Delta T$$

$$\text{But } m_c = \rho_c V_c = 1 \text{ g/cm}^3 \times (100 + 100) \text{ cm}^3 = 200 \text{ g and } \Delta T = (21.45 - 18.2)^\circ\text{C} = 3.25^\circ\text{C}$$

$$\text{Total enthalpy change} = -200 \times 4.2 \times 3.25 \text{ J} = -2730 \text{ J}$$

$$\text{Using enthalpy of neutralisation} = \frac{\text{Total enthalpy change}}{\text{Number of moles of water produced}}$$

From the equation for the reaction:



$$\begin{aligned} \text{Number of moles of water produced} &= \text{Number of moles of CH}_3\text{COOH} \\ &= \frac{100}{1000} \times 0.5 \text{ moles} = 0.05 \text{ moles} \end{aligned}$$

$$\text{Enthalpy of neutralisation} = \frac{-2730 \text{ J}}{0.05 \text{ mol}} = -54600 \text{ J/mol or } -54.6 \text{ kJ/mol}$$

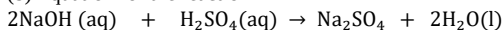
Hence enthalpy of neutralisation is -54.6 kJ/mol .

Question 10

(a)

- (i) Reactants have weaker bonds than products.
- (ii) Reactants have stronger bonds than products.

(b) Equation for the reaction



$$\begin{aligned} \frac{50}{1000} \times 0.4 \text{ mol} \quad \frac{20}{1000} \times 0.5 \text{ mol} \quad \quad \quad 0.02 \text{ mol} \\ = 0.02 \text{ moles} \quad = 0.01 \text{ mol} \end{aligned}$$

Number of moles of water formed in the reaction is 0.02 moles.

$$\text{Heat evolved in neutralisation reaction} = -mC\Delta T = \rho V \Delta T$$

Assuming density of solution = density of water = g cm^{-3}

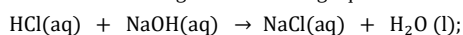
$$\text{Then the heat evolved} = -1 \times (50 + 20) \times 4.2 \times 3.9 \text{ J} = -1146.6 \text{ J}$$

$$\begin{aligned} \text{Standard enthalpy of neutralisation} &= \frac{\text{Heat evolved}}{\text{Number of moles of water formed}} \\ &= \frac{-1146.6}{0.02} = 57330 \text{ J/mol} = 57.33 \text{ kJ/mol} \end{aligned}$$

Hence the standard enthalpy of neutralisation is -57.33 kJ/mol .

Question 11

Hydrochloric acid and sodium hydroxide reacts according to the following equation:

**Initially:**

$$\text{Number of moles of HCl (aq)} \text{ was } \frac{25}{1000} \times 1 \text{ mol} = 0.025 \text{ mol}$$

$$\text{Number of moles of NaOH (aq)} \text{ was } \frac{50}{1000} \times 1 \text{ mol} = 0.05 \text{ mol}$$

From the equation of reaction, moles ratio of HCl to NaOH is 1:1

So NaOH (aq) present in excess and HCl (aq) is the **limited reactant** which predicts amount of water formed in the reaction.

Mole ratio of number of moles of HCl(aq) to water is 1:1

So number of moles of water formed was also 0.025 moles.

Then since the reaction is neutralisation reaction;

It follows that: standard enthalpy change for the reaction = standard enthalpy for neutralisation.

$$\begin{aligned} \text{But Standard enthalpy of neutralisation} &= \frac{\text{Heat evolved}}{\text{Number of moles of water formed}} \\ &= \frac{mC\Delta T}{n_{\text{H}_2\text{O}}} = \frac{\rho VC\Delta T}{n_{\text{H}_2\text{O}}} = \frac{-1 \times (25 + 50) \times 4.2 \times 4.6}{0.025} = -57960 \text{ J/mol or } -57.96 \text{ kJ/mol} \end{aligned}$$

Hence the standard enthalpy for the reaction is -57.96 kJ/mol

Assumptions made are:

- 1) Polystyrene cup calorimeter has negligible heat capacity; that is no heat passes to the cup.
- 2) There is no volume change in mixing two solutions: that is $V_{\text{mixture}} = V_{\text{acid}} + V_{\text{base}}$
- 3) Enthalpy of solution is negligible, i.e. the temperature change results from neutralisation reaction only.

Question 12

(a) Heat evolved in combustion = $-mC\Delta T$

But $m = \rho V$

Then, heat evolved in combustion = $-\rho VC\Delta T$.

But density of water 1 g cm^{-3} , $V = 200 \text{ cm}^3$, $C = 4.2 \text{ J g}^{-1} \text{ K}^{-1}$, $\Delta T = 10^\circ \text{C}$

So heat evolved in combustion = $-1 \times 200 \times 4.2 \times 10 \text{ J} = -8400 \text{ J}$

Heat of combustion of ethanol = $\frac{\text{Heat evolved in combustion}}{\text{Number of moles of ethanol reacted}}$

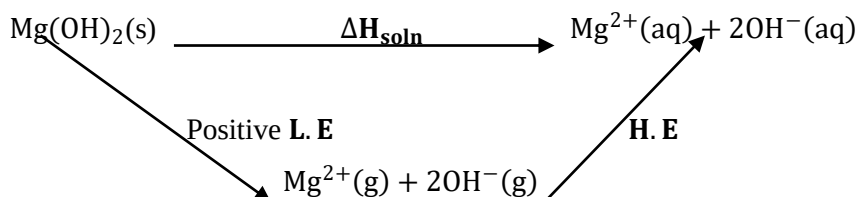
But mass of ethanol reacted = decrease in mass of ethanol = 0.4 g

So number of moles of ethanol reacted = $\frac{0.4}{46} \text{ mol} = \frac{1}{115} \text{ mol}$

Therefore, heat of combustion of ethanol = $-8400 \times 115 \text{ J/mol} = -966000 \text{ J/mol or } -966 \text{ kJ/mol}$

Hence the heat of combustion of ethanol is -966 kJ/mol .

(b)



$$\Delta H_{\text{soln}} = \text{Positive L. E} + \text{H. E}$$

Where L. E = -2842 kJ/mol

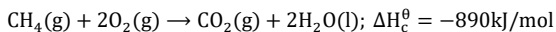
$$\begin{aligned} \text{and H. E} &= \Delta_{\text{hyd}}(\text{Mg}^{2+}(\text{aq})) + 2\Delta_{\text{hyd}}(\text{OH}^{-}(\text{aq})) \\ &= -1920 \text{ kJ/mol} + 2 \times -460 \text{ kJ/mol} = -2840 \text{ kJ/mol} \end{aligned}$$

Thus $\Delta H_{\text{soln}} = 2842 \text{ kJ/mol} - 2840 \text{ kJ/mol} = 2 \text{ kJ/mol}$.

Question 13

(a)

(i) Methane undergoes combustion according to the following equation:



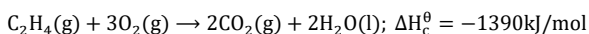
From which; $\Delta H_c^\ominus = 2\Delta H_f^\ominus(\text{H}_2\text{O}) + \Delta H_f^\ominus(\text{CO}_2) - 2\Delta H_f^\ominus(\text{O}_2) - \Delta H_f^\ominus(\text{CH}_4)$

But $\Delta H_f^\ominus(\text{O}_2) = 0$, $\Delta H_f^\ominus(\text{CO}_2) = \Delta H_c^\ominus(\text{C}) = -394 \text{ kJ/mol}$, $\Delta H_f^\ominus(\text{H}_2\text{O}) = \Delta H_c^\ominus(\text{H}_2) = -286 \text{ kJ/mol}$

Then $-890 \text{ kJ/mol} = (2 \times -286 \text{ kJ/mol}) + (-394 \text{ kJ/mol}) - \Delta H_f^\ominus(\text{CH}_4)$

From which $\Delta H_f^\ominus(\text{CH}_4) = -76 \text{ kJ/mol}$

(ii) Ethene undergoes combustion according to the following equation:



From which; $\Delta H_c^\ominus = 2\Delta H_f^\ominus(\text{H}_2\text{O}) + 2\Delta H_f^\ominus(\text{CO}_2) - 3\Delta H_f^\ominus(\text{O}_2) - \Delta H_f^\ominus(\text{C}_2\text{H}_4)$

But $\Delta H_f^\ominus(\text{O}_2) = 0$, $\Delta H_f^\ominus(\text{CO}_2) = \Delta H_c^\ominus(\text{C}) = -394 \text{ kJ/mol}$, $\Delta H_f^\ominus(\text{H}_2\text{O}) = \Delta H_c^\ominus(\text{H}_2) = -286 \text{ kJ/mol}$

Then $-1390 \text{ kJ/mol} = (2 \times -286 \text{ kJ/mol}) + (2 \times -394 \text{ kJ/mol}) - \Delta H_f^\ominus(\text{C}_2\text{H}_4)$

From which $\Delta H_f^\ominus(\text{C}_2\text{H}_4) = +30 \text{ kJ/mol}$

(iii) $\Delta H_f^\ominus = \Delta H_f^\ominus(\text{CH}_3\text{CH}_2\text{OH}) - \Delta H_f^\ominus(\text{H}_2\text{O}) - \Delta H_f^\ominus(\text{C}_2\text{H}_4)$

$$= -276 \text{ kJ/mol} - (-286 \text{ kJ/mol}) - 30 \text{ kJ/mol} = -20 \text{ kJ/mol}$$

(iv) From ideal gas equation; $n = \frac{PV}{RT}$, Where $P = 1 \text{ atm}$ and $T = 298 \text{ K}$ (standard conditions)

$$n_{\text{ethene}} = \frac{1 \text{ atm} \times 4.48 \text{ dm}^3}{0.0821 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 0.183 \text{ mol}$$

Then $\Delta H = n_{\text{ethene}} \times \Delta H_c^\ominus(\text{ethene}) = 0.183 \text{ mol} \times (-1390 \text{ kJ/mol}) = -254.37 \text{ kJ}$

Hence the heat change is approximately -254 kJ

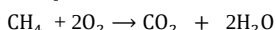
(b) Given that:

$\Delta H_c^\ominus = \Delta H_f^\ominus(\text{CO}_2) = -395.5 \text{ kJ/mol}$ (Heat of Combustion is the heat evolved so it must be negative even if it is deliberately omitted)

$\Delta H_f^\ominus(\text{H}_2\text{O}) = -285.9 \text{ kJ/mol}$ (Here $\Delta H_f^\ominus(\text{H}_2\text{O}) = \Delta H_c^\ominus(\text{H}_2)$, so it must be negative too.

$\Delta H_c^\ominus(\text{CH}_4) = -895.5 \text{ kJ/mol}$ (Again the negative sign must be included)

An equation to show the combustion of CH_4 :



From Hess's law of constant heat summation, it can be shown that:

$$\Delta H_r^\ominus = \sum \Delta H_f^\ominus(\text{Products}) - \sum \Delta H_f^\ominus(\text{Reactants})$$

Thus $\Delta H_c^\ominus(\text{CH}_4) = \Delta H_f^\ominus(\text{CO}_2) + 2\Delta H_f^\ominus(\text{H}_2\text{O}) - \Delta H_f^\ominus(\text{CH}_4) - 2\Delta H_f^\ominus(\text{O}_2)$

But $\Delta H_f^\ominus(\text{O}_2)$ (Heat of formation of an element in its normal state is zero)

So $-895.5 = -395.5 + (2 \times -285.9) - \Delta H_f^\ominus(\text{CH}_4)$; $\Delta H_f^\ominus(\text{CH}_4) = -71.8 \text{ kJ/mol}$

Hence the standard enthalpy of formation of methane is -71.8 kJ/mol .

Question 14

(a)

(i) Endothermic

(ii) $\Delta H = +129 \text{ kJ}$

(iii) From the stoichiometry of the equation;

2 mol of baking soda requires 129 kJ (for its decomposition)

Thus 2.24 mol of it requires $\frac{2.24 \text{ mol}}{2 \text{ mol}} \times 129 \text{ kJ} = 144.48 \text{ kJ}$

The amount of heat required is 144.48 kJ

(b) From (iii)

$\Delta H = 130 = 2H_f(\text{NO}) - H_f(\text{N}_2) - H_f(\text{O}_2)$ (Here exceptionally, heat of combustion of N_2 is positive due to its inert character. So high energy is absorbed in breaking $\text{N} \equiv \text{N}$ of N_2)

But $H_f(\text{N}_2) = 0$ and $H_f(\text{O}_2) = 0$

Then $H_f(\text{NO}) = \frac{130}{2} = 65 \text{ kJ/mol}$

From (i); $\Delta H = -57.05 = H_f(\text{NO}_2) - \frac{1}{2}H_f(\text{O}_2) - H_f(\text{NO})$

But $H_f(\text{O}_2) = 0$

Then $-57.05 = H_f(\text{NO}_2) - 65$; $H_f(\text{NO}_2) = 7.95 \text{ kJ/mol}$

From (ii); $\Delta H = -110.2 = 2H_f(\text{N}_2\text{O}_5) - 4H_f(\text{NO}_2) - H_f(\text{O}_2)$

But $H_f(\text{O}_2) = 0$ and $H_f(\text{NO}_2) = 7.95 \text{ kJ/mol}$

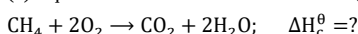
Then $-110.2 = 2H_f(\text{N}_2\text{O}_5) - (4 \times 7.95)$

From which $H_f(\text{N}_2\text{O}_5) = -39.2 \text{ kJ/mol}$

Hence heat of formation of N_2O_5 is -39.2 kJ/mol .

Question 15

(a) Equation for combustion of methane (CH_4)



$$\Delta H_c^\ominus = \Delta H_f^\ominus(\text{CO}_2) + 2\Delta H_f^\ominus(\text{H}_2\text{O}) - \Delta H_f^\ominus(\text{CH}_4) - 2\Delta H_f^\ominus(\text{O}_2)$$

$$\text{But } \Delta H_f^\ominus(\text{O}_2) = 0$$

$$\text{Then } \Delta H_c^\ominus = -394.8 + (2 \times -241.6) + 76.2 = -801.8 \text{ kJ/mol}$$

$$\text{Thus } \Delta H_c^\ominus(\text{CH}_4) = -801.8 \text{ kJ/mol}$$

$$\text{At s.t.p: } T = 273\text{K}, P = 1 \text{ atm}$$

$$\text{And we are given with volume of methane} = 1\text{m}^3 = 10^3\text{dm}^3$$

Assuming methane gas behaves as ideal gas, then;

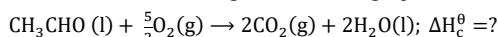
$$PV = nRT \text{ or } n = \frac{PV}{RT} = \frac{1 \times 10^3}{0.082 \times 273} = 44.67 \text{ mol}$$

$$\text{But enthalpy of combustion} = \frac{\text{Heat evolved}}{\text{Number of moles of substance burnt}}$$

$$\begin{aligned} \text{From which, heat evolved in burning methane} &= \Delta H_c^\ominus(\text{CH}_4) \times \text{number of moles of CH}_4 \\ &= -801.8 \text{ kJ/mol} \times 44.67 \text{ mol} = -35816.4 \text{ kJ} \end{aligned}$$

The amount of heat evolved by burning given amount of methane is 35816.4 kJ.

(b) The given compound undergoes the combustion according to the following equation:



$$\text{Using } \Delta H_r^\ominus = \sum \Delta H_f^\ominus(\text{Products}) - \sum \Delta H_f^\ominus(\text{Reactants})$$

$$\text{Then } \Delta H_c^\ominus(\text{CH}_3\text{CHO}) = 2\Delta H_f^\ominus(\text{CO}_2) + 2\Delta H_f^\ominus(\text{H}_2\text{O}) - \Delta H_f^\ominus(\text{CH}_3\text{CHO}) \quad (\Delta H_f^\ominus(\text{O}_2) = 0)$$

$$\text{Substituting } \Delta H_c^\ominus(\text{CH}_3\text{CHO}) = (-395 \text{ kJ/mol} \times 2) + (-284 \text{ kJ/mol} \times 2) - (-166 \text{ kJ/mol}) = -1192 \text{ kJ/mol}$$

$$\text{Then } n_{\text{CH}_3\text{CHO}} = \frac{5.93 \text{ g}}{44 \text{ g mol}^{-1}} = 0.1348 \text{ mol}$$

$$\text{And } n_{\text{O}_2} = \frac{PV}{RT} = \frac{1 \text{ atm} \times 9.29 \text{ L}}{0.082 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 0.38 \text{ mol}$$

From the above equation of combustion, 1 mol of CH_3CHO reacts with $\frac{5}{2}$ mol of O_2 .

Thus 0.1348 mol of CH_3CHO reacts with $\frac{5}{2} \times 0.1348 \text{ mol} = 0.337 \text{ mol}$ of O_2 which is smaller than the given amount of O_2 and hence the oxygen was in excess (as expected) and CH_3CHO was limited reactant.

The limited is the one that determine the amount of heat change (in this case heat released) in the reaction because it is entirely consumed in the reaction.

$$\text{Using } \Delta H_c^\ominus(\text{CH}_3\text{CHO}) = \frac{\Delta H}{n_{\text{CH}_3\text{CHO}}}$$

$$\text{From which; } \Delta H = \Delta H_c^\ominus(\text{CH}_3\text{CHO}) \times n_{\text{CH}_3\text{CHO}} = -1192 \text{ kJ/mol} \times 0.1348 \text{ mol} = -160.7 \text{ kJ}$$

The amount of heat produced is approximately 161 kJ.

Question 16

$$\text{Number of moles in 1g of graphite (carbon)} = \frac{1}{12} \text{ mol}$$

$$\text{Thus enthalpy of combustion of carbon} = -32 \times 12 \text{ kJ/mol} = -384 \text{ kJ/mol} = \Delta H_f^\ominus(\text{CO}_2)$$

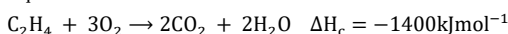
$$\text{Number of moles in 1g of hydrogen} = \frac{1}{2} \text{ mol}$$

$$\text{Thus enthalpy of combustion of hydrogen} = -143 \times 2 = -286 \text{ kJ/mol} = \Delta H_f^\ominus(\text{H}_2\text{O})$$

$$\text{Number of moles in 1g of ethene (C}_2\text{H}_4) = \frac{1}{28} \text{ mol}$$

$$\text{Thus enthalpy of combustion of ethene} = -50 \times 28 = -1400 \text{ kJ/mol}$$

Equation to show combustion of ethene:



$$\text{Using } \Delta H_r^\ominus = \sum \Delta H_f^\ominus(\text{Products}) - \sum \Delta H_f^\ominus(\text{Reactants});$$

$$\Delta H_c(\text{C}_2\text{H}_4) = 2\Delta H_f^\ominus(\text{CO}_2) + 2\Delta H_f^\ominus(\text{H}_2\text{O}) - \Delta H_f^\ominus(\text{C}_2\text{H}_4)$$

$$\text{Substituting } -1400 = (2 \times -384) + (2 \times -286) - \Delta H_f^\ominus(\text{C}_2\text{H}_4);$$

$$\text{From which } \Delta H_f^\ominus(\text{C}_2\text{H}_4) = 60 \text{ kJ/mol}$$

Hence the standard enthalpy of formation of ethene is 60 kJ/mol.

Question 17

Using enthalpy of combustion = $\frac{\text{Enthalpy evolved}}{\text{Number of moles of substance burned}}$

Number of moles in 2g of carbon = $\frac{2}{12} \text{ mol} = \frac{1}{6} \text{ mol}$

Thus enthalpy of combustion of carbon = $-66.1 \times 6 \text{ kJ/mol} = -396.6 \text{ kJ/mol}$

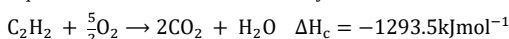
Number of moles in 2g of hydrogen = $\frac{2}{2} \text{ mol} = 1 \text{ mol}$

Thus enthalpy of combustion of hydrogen = $\frac{-284}{1} \text{ kJmol}^{-1} = -284 \text{ kJmol}^{-1}$

Number of moles in 2g of ethyne (C_2H_2) = $\frac{2}{26} \text{ mol} = \frac{1}{13} \text{ mol}$

Thus enthalpy of combustion of ethyne = $-99.5 \times 13 \text{ kJ/mol} = -1293.5 \text{ kJ/mol}$

Equation to show combustion of ethyne:



$$\Delta H_c = -1293.5 = 2\Delta H_f(\text{CO}_2) + \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_2\text{H}_2)$$

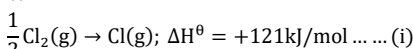
$$\text{Then } -1293.5 = (2 \times -396.6) + -284 - \Delta H_f(\text{C}_2\text{H}_2); \Delta H_f(\text{C}_2\text{H}_2) = 216.3 \text{ kJ/mol}$$

Hence heat of formation of ethyne is 216.3 kJ/mol

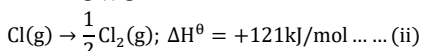
Question 18

(a)

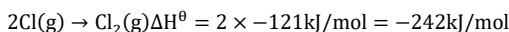
(i) Given:



Reversing (i) gives;

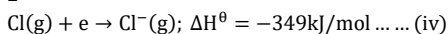
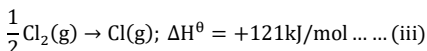
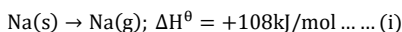


Taking $2 \times$ (ii) gives;

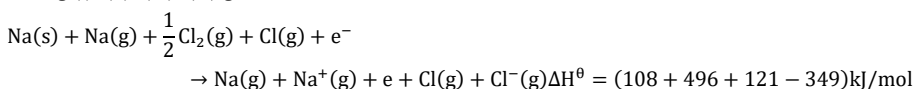


The standard enthalpy change for the given process is -242 kJ/mol

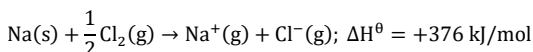
(ii) Given;



Taking (i)+(ii)+(iii)+(iv) gives;



Cancelling like terms which appear as both reactants and products gives;



The enthalpy change for the given process is $+376 \text{ kJ/mol}$.

Comparison:

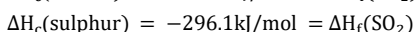
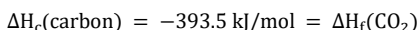
(iii) The enthalpy change of the process, $\text{NaCl}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

is **less endothermic** than that of the process $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$

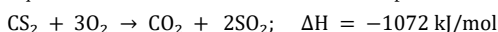
Comment:

The process, $\text{NaCl}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ involves hydration of ions which is exothermic and hence the overall process becomes less endothermic with the hydration energy amounted to -783 kJ/mol ($4 \text{ kJ/mol} - 787 \text{ kJ/mol}$) accounting for the difference in enthalpy change of the two processes.

(b) Given that:



Equation to show combustion of carbon disulphide



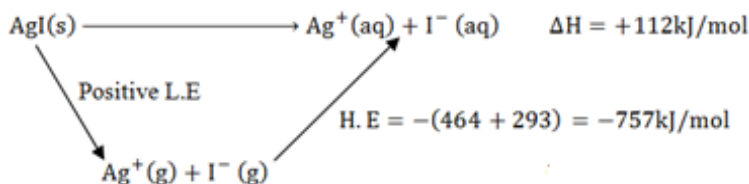
$$\Delta H = -1072 = \Delta H_f(\text{CO}_2) + 2\Delta H_f(\text{SO}_2) - \Delta H_f(\text{CS}_2) = -393.5 + (2 \times -296.1) - \Delta H_f(\text{CS}_2)$$

$$\Delta H_f(\text{CS}_2) = 86.3 \text{ kJ/mol}$$

Hence the enthalpy of formation of carbon disulphide is 86.3 kJ/mol.

Question 19

(a)



By Hess's law:

$$\Delta H = \text{Positive L.E} + \text{H.E}$$

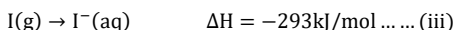
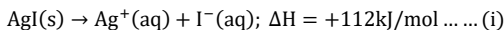
$$\text{Substituting } +112 \text{ kJ/mol} = \text{Positive L.E} + (-757 \text{ kJ/mol})$$

$$\text{From which positive L.E} = +869 \text{ kJ/mol}$$

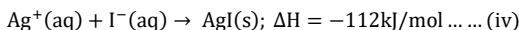
The lattice energy of silver iodide is -869 kJ/mol

Alternative solution:

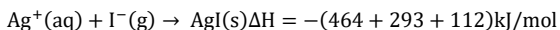
Given that:



Reversing (i) gives;

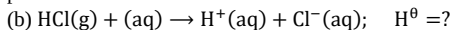


Taking (ii)+(iii)+(iv) and cancelling like terms which appear as both reactants and products gives;



Hence the lattice of silver iodide is -869 kJ/mol

Having high degree of polarisation, AgI is highly covalent in character and therefore practically bonds are stronger than predicted.



$$H^\theta = \Delta H_f^\theta(\text{H}^+) + \Delta H_f^\theta(\text{Cl}^-) - \Delta H_f^\theta(\text{HCl}); \quad \Delta H^\theta = 0 - 167.2 + 92.3 = -74.9 \text{ kJ/mol}$$

Hence ΔH^θ for this reaction is -74.9 kJ/mol.

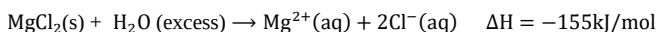
Question 20

(a)

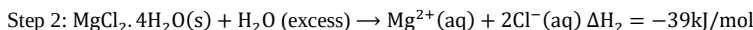
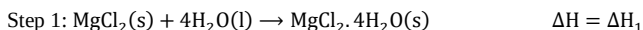
(i) Practically it is impossible to prevent dissolving of the crystals in water thus the obtained enthalpy change will always accompany enthalpy of solution of the dissolved part of the crystals.

(ii) Consider the formation of $\text{Mg}^{2+}(\text{aq})$ and $\text{Cl}^-(\text{aq})$ from anhydrous $\text{MgCl}_2(\text{s})$ and H_2O by the following possible routes:

Route 1: Direct route.



Route 2: Indirect route under the following steps:



Then from Hess's law:

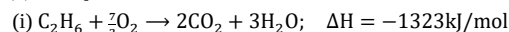
$$\text{Enthalpy change in route 1} = \text{Enthalpy change in route 2}$$

$$\Delta H = \Delta H_1 + \Delta H_2$$

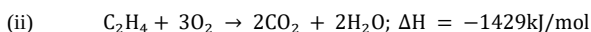
$$\text{Substituting } -155 \text{ kJ/mol} = \Delta H_1 + -39 \text{ kJ/mol}; \quad \Delta H_1 = -116 \text{ kJ/mol}$$

The enthalpy change is -116 kJ/mol

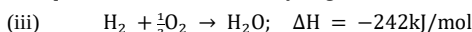
(b) An equation for combustion of ethane is;



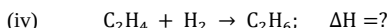
An equation for combustion of ethene is;



An equation for combustion of hydrogen is:



An equation for hydrogenation of ethene is:



From (iii) $\Delta H = \Delta H_f(\text{H}_2\text{O}) = -242\text{kJ/mol}$

From (i) $\Delta H = -1323 = 3\Delta H_f(\text{H}_2\text{O}) + 2\Delta H_f(\text{CO}_2) - \Delta H_f(\text{C}_2\text{H}_6) - \frac{7}{2}\Delta H_f(\text{O}_2)$

Where $\Delta H_f(\text{O}_2) = 0$ and $\Delta H_f(\text{H}_2\text{O}) = -242\text{kJ/mol}$.

So $2\Delta H_f(\text{CO}_2) = \Delta H_f(\text{C}_2\text{H}_6) - 597 \dots \dots \dots (1)$

From (ii) $\Delta H = -1429 = 2\Delta H_f(\text{CO}_2) + 2\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_2\text{H}_4) - 3\Delta H_f(\text{H}_2\text{O})$

Where $\Delta H_f(\text{O}_2) = 0$ and $\Delta H_f(\text{H}_2\text{O}) = -242\text{kJ/mol}$

So $2\Delta H_f(\text{CO}_2) = \Delta H_f(\text{C}_2\text{H}_4) - 945 \dots \dots \dots (2)$

Equating (1) and (2) gives;

$$\Delta H_f(\text{C}_2\text{H}_6) - 597 = \Delta H_f(\text{C}_2\text{H}_4) - 945$$

$$\Delta H_f(\text{C}_2\text{H}_6) - \Delta H_f(\text{C}_2\text{H}_4) = -348 \text{ kJ/mol}$$

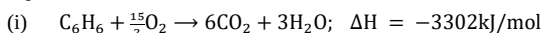
But from (iv);

$$\Delta H_f(\text{C}_2\text{H}_6) - \Delta H_f(\text{C}_2\text{H}_4) = \text{Heat of hydrogenation of ethene; where } \Delta H_f(\text{H}_2) = 0.$$

Hence heat of hydrogenation of ethene is -348 kJ/mol .

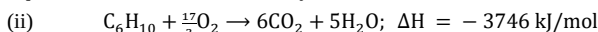
Question 21

Equation to show combustion of benzene:



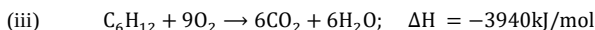
Benzene

Equation to show combustion of cyclohexene



Cyclohexene

Equation to show combustion of cyclohexane



Cyclohexane

From (i)

$$\Delta H = -3302 = 6\Delta H_f(\text{CO}_2) + 3\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_6\text{H}_6) \dots \dots \dots (1)$$

$$\text{From (iii)} \quad \Delta H = -3940 = 6\Delta H_f(\text{CO}_2) + 6\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_6\text{H}_{12}) \dots \dots \dots (2)$$

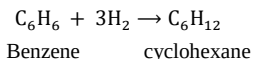
$$(1) - (2) \text{ gives: } 638 = \Delta H_f(\text{C}_6\text{H}_{12}) - \Delta H_f(\text{C}_6\text{H}_6) - 3\Delta H_f(\text{H}_2\text{O})$$

But it is given that: $\Delta H_c(\text{hydrogen}) = -242\text{kJ/mol} = \Delta H_f(\text{H}_2\text{O})$

$$\text{Then } 638 = \Delta H_f(\text{C}_6\text{H}_{12}) - \Delta H_f(\text{C}_6\text{H}_6) - (3 \times -242)$$

$$\text{From which } \Delta H_f(\text{C}_6\text{H}_{12}) - \Delta H_f(\text{C}_6\text{H}_6) = -88\text{kJ/mol}$$

But from the equation of hydrogenation of benzene:



From which, heat of hydrogenation of benzene $= \Delta H_f(\text{C}_6\text{H}_{12}) - \Delta H_f(\text{C}_6\text{H}_6)$.

Hence heat of hydrogenation of benzene is -88kJ/mol .

From (ii)

$$\Delta H = -3746 = 6\Delta H_f(\text{CO}_2) + 5\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_6\text{H}_{10}) \dots \dots \dots (3)$$

Taking (3) – (2) gives;

$$194 = \Delta H_f(\text{C}_6\text{H}_{12}) - \Delta H_f(\text{C}_6\text{H}_{10}) - \Delta H_f(\text{H}_2\text{O})$$

$$\text{But } \Delta H_f(\text{H}_2\text{O}) = -242 \text{ kJ/mol}$$

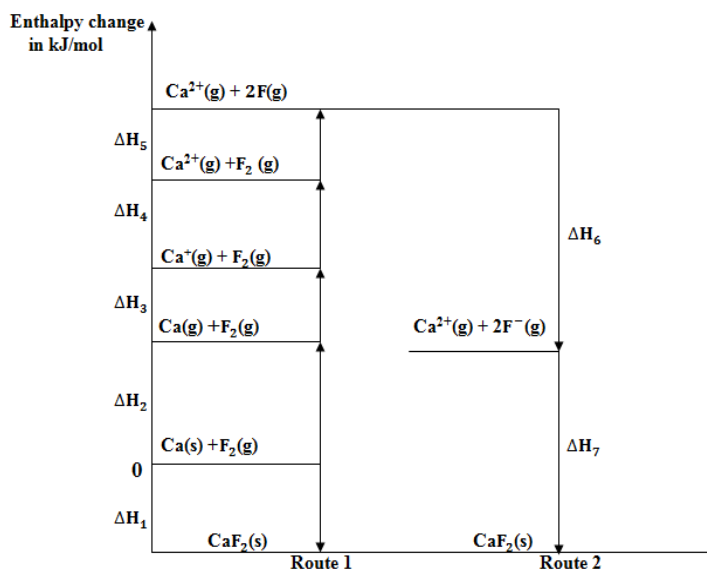
$$\text{Then } \Delta H_f(\text{C}_6\text{H}_{12}) - \Delta H_f(\text{C}_6\text{H}_{10}) = -48\text{kJ/mol.}$$

But from equation of hydrogenation of cyclohexene, $\text{C}_6\text{H}_{10} + \text{H}_2 \rightarrow \text{C}_6\text{H}_{12}$

From which; enthalpy of hydrogenation of cyclohexene $= \Delta H_f(\text{C}_6\text{H}_{12}) - \Delta H_f(\text{C}_6\text{H}_{10})$

Hence enthalpy of hydrogenation of cyclohexene is -48 kJ/mol .

Question 22



Where:

ΔH_1 is the heat of formation of calcium fluoride = -860 kJ/mol

ΔH_2 is the atomisation energy of calcium = $+174 \text{ kJ/mol}$

ΔH_3 is the first ionisation energy of calcium = $+550 \text{ kJ/mol}$

ΔH_4 is the second ionisation energy of calcium = $+1000 \text{ kJ/mol}$

ΔH_5 is the dissociation energy of fluorine gas

ΔH_6 is the twice electron affinity of fluorine = $2 \times -363 = -726 \text{ kJ/mol}$

ΔH_7 is the lattice energy of calcium fluoride = -2100 kJ/mol

By Hess's law of constant heat summation: $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7$

$-860 = 174 + 550 + 1000 + \Delta H_5 - 726 - 2100$; $\Delta H_5 = 242 \text{ kJ/mol}$

Thus dissociation energy of fluorine gas is 242 kJ/mol .

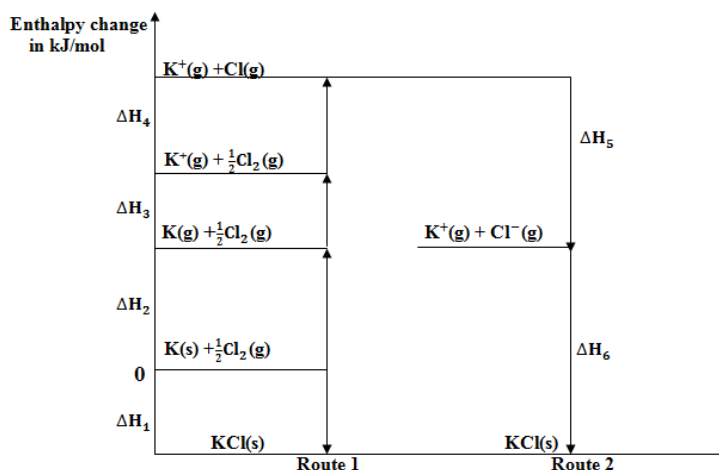
But atomisation energy = $\frac{\text{Dissociation energy}}{2} = \frac{242}{2} = 121 \text{ kJ/mol}$

Hence the atomisation energy of fluorine is 121 kJ/mol .

Question 23

Enthalpy	Amount
Enthalpy of atomisation of potassium	$+353.2 \text{ kJ/mol}$
Dissociation of enthalpy of chlorine gas	$+507.5 \text{ kJ/mol}$
Ionisation enthalpy of potassium atom	$+748 \text{ kJ/mol}$
Electron affinity of chlorine atom	-1488.1 kJ/mol
Lattice energy of potassium chloride	-2900.9 kJ/mol

Born-Haber cycle for KCl



Where:

ΔH_1 is enthalpy of formation of KCl(s)

ΔH_2 is the enthalpy of atomisation of potassium = +353.2 kJ/mol

ΔH_3 is the ionisation enthalpy of potassium atom = +748 kJ/mol

ΔH_4 is the atomisation enthalpy of chlorine = $\frac{1}{2} \times 507.5$ kJ/mol = 253.75 kJ/mol

ΔH_5 is the electron affinity of chlorine atom = -1488.1 kJ/mol

ΔH_6 is the lattice energy of potassium chloride = -2900.9 kJ/mol.

By Hess's law of constant Heat Summation

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$$

$$\Delta H_1 = (353.2 + 748 + 253.75 - 1488.1 - 2900.9) \text{ kJ/mol}$$

$$\Delta H_1 = -3034.05 \text{ kJ/mol}$$

Hence the enthalpy of formation of KCl(s) is -3034.05 kJ/mol.

Question 24

Enthalpy for the reaction = total bond energy of reactants - total bond energy of products

$$= 6(\text{C}-\text{H}) + 2(\text{C}-\text{C}) + (\text{C}=\text{O}) + (\text{C}-\text{H}) + (\text{C}\equiv\text{N}) - 6(\text{C}-\text{H}) - 3(\text{C}-\text{C}) - (\text{C}-\text{O}) - (\text{O}-\text{H}) - (\text{C}\equiv\text{N})$$

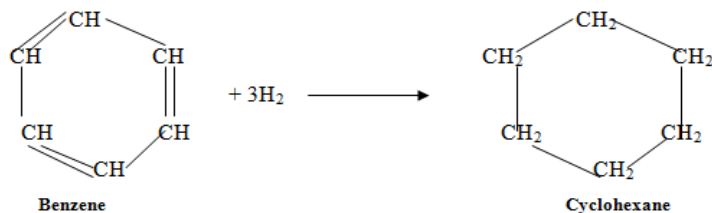
$$= (\text{C}=\text{O}) + (\text{C}-\text{H}) - (\text{C}-\text{O}) - (\text{O}-\text{H}) - (\text{C}-\text{C})$$

$$= 743 + 412 - 360 - 463 - 348 = -16 \text{ kJ/mol}$$

Hence the standard enthalpy change for the reaction is -80 kJ/mol.

Question 25

Equation to show hydrogenation of benzene



$$\text{Using } \Delta H_r = \sum \text{B.E}(\text{reactants}) - \sum \text{B.E}(\text{products})$$

$$= 3(\text{C}-\text{C}) + 3(\text{C}=\text{C}) + 6(\text{C}-\text{H}) + 3(\text{H}-\text{H}) - 6(\text{C}-\text{C}) - 12(\text{C}-\text{H})$$

$$= 3(\text{C}=\text{C}) + 3(\text{H}-\text{H}) - 3(\text{C}-\text{C}) - 6(\text{C}-\text{H})$$

$$= (3 \times 610) + (3 \times 435) - (3 \times 345) - (6 \times 415) = -390 \text{ kJ/mol}$$

Hence standard enthalpy of hydrogenation of benzene is -390 kJ/mol.

Comment:

Experimentally determined value is lower (less negative) than the calculated heat of hydrogenation because π electrons (electron in pi bond) are delocalized throughout the benzene ring in mesomerism. So extra energy amounted to 180 kJ/mol (**resonance energy**) is required to break the resonance of electrons before adding hydrogen atoms.

Question 26

Equation to show formation of benzene: $6\text{C} + 3\text{H}_2 \rightarrow \text{C}_6\text{H}_6$

Energy absorbed in vapourising 6 carbon atoms = $6 \times 715 = 4290 \text{ kJ/mol}$

Energy absorbed in atomizing 6 hydrogen atoms = $6 \times 217.5 = 1305 \text{ kJ/mol}$

Total energy absorbed in the reactant side = $(4290 + 1305) \text{ kJ/mol} = 5595 \text{ kJ/mol}$.

Total energy evolved in the product side

$$= 3(\text{C}-\text{C}) + 3(\text{C}=\text{C}) + 6(\text{C}-\text{H}) \\ = (3 \times 348) + 3 \times 615 + (6 \times 412) = 5361 \text{ kJ/mol}.$$

Enthalpy of reaction (formation of benzene from its elements)

= Total energy absorbed in the reactant side – total energy evolved in product side

$$= (5595 - 5361) \text{ kJ/mol} = 234 \text{ kJ/mol}$$

The standard enthalpy of formation of benzene from the given data is 234 kJ/mol.

The experimental value is lower (less positive) than the theoretical one because practically structure of benzene is stabilized by mesomerism (resonance of electrons) and the energy difference between experimental and theoretical value amounted to 151 kJ/mol is the resonance energy in benzene.

Question 27

(a) The factors are:

- 1) Amount of reactants and products.
- 2) Physical state of reactants and products.
- 3) Temperature of the reaction.
- 4) Specific heat capacity of the container and substances involved in the transformation.

(b) An equation to show formation of methane: $\text{C(s)} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$

Total energy absorbed in the reactant side = $716 + 872.8 = 1588.8 \text{ kJ/mol}$

Total energy evolved in the product side = $4(\text{C}-\text{H}) = 4 \times 414 = 1656 \text{ kJ/mol}$

Heat of reaction = total energy absorbed in reactant side – total energy evolved in the product side
 $= (1588.8 - 1656) \text{ kJ/mol} = -67.2 \text{ kJ/mol}$

Hence heat of formation of methane is -67.2 kJ/mol .

Question 28

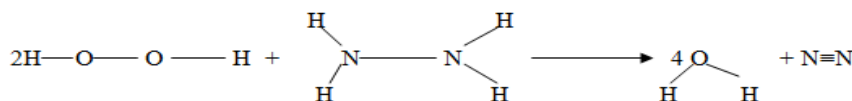
(a) (i) Heat of solution is the **heat change** when **one mole of solute** is added to so much water that further addition of **water produces no further heat change under given conditions of temperature and pressure**.

(ii) Heat of solution is the **heat change** when **one mole of a solute** dissolves in **specified amount of water** to give a solution under **given conditions of temperature and pressure**.

Relation:

When the solution is diluted to infinite dilution, heat of solution becomes equal to heat of dilution.

(b) Rewriting the given chemical reaction in structural formulae;



$$\Delta H_r = \sum \text{B.E}(\text{reactants}) - \sum \text{B.E}(\text{products})$$

$$= 4(\text{O}-\text{H}) + 2(\text{O}-\text{O}) + 4(\text{N}-\text{H}) + \text{N}-\text{N} - 8(\text{O}-\text{H}) - (\text{N} \equiv \text{N})$$

$$= 2(\text{O}-\text{O}) + 4(\text{N}-\text{H}) + (\text{N}-\text{N}) - 4(\text{O}-\text{H}) - (\text{N} \equiv \text{N}).$$

$$= 2 \times 143 + (4 \times 391) + 159 - (4 \times 463) - 945 = -788 \text{ kJ/mol}$$

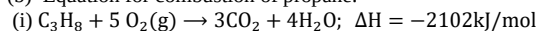
Hence the enthalpy for the reaction is -788 kJ/mol .

Question 29

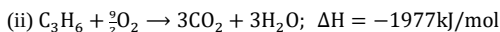
(a)

- (i) Enthalpy of solution
- (ii) Atomisation energy
- (iii) First electron affinity
- (iv) Enthalpy of neutralisation

(b) Equation for combustion of propane:



Equation for combustion of propene



From (i)

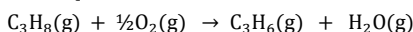
$$\Delta H = -2102 = 4\Delta H_f(\text{H}_2\text{O}) + 3\Delta H_f(\text{CO}_2) - \Delta H_f(\text{C}_3\text{H}_8) \dots \dots \dots (1)$$

From (ii)

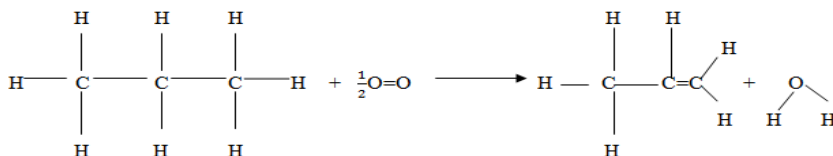
$$\Delta H = -1977 = 3\Delta H_f(\text{H}_2\text{O}) + 3\Delta H_f(\text{CO}_2) - \Delta H_f(\text{C}_3\text{H}_6) \dots \dots \dots (2)$$

$$- (2) \text{ gives: } \Delta H_f(\text{C}_3\text{H}_6) - \Delta H_f(\text{C}_3\text{H}_8) + \Delta H_f(\text{H}_2\text{O}) = 125 \text{ kJ/mol}$$

But $\Delta H_f(\text{C}_3\text{H}_6) + \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_3\text{H}_8) =$ Enthalpy change for the oxidation of propane to propene and steam according to the equation:

Hence the enthalpy change for the oxidation is -125 kJ/mol .

An equation for oxidation of propane into propene:

Then using $\Delta H_r = \sum \text{B.E.}(\text{reactants}) - \sum \text{B.E.}(\text{products})$

$$\begin{aligned} &= 8(\text{C}-\text{H}) + 2(\text{C}-\text{C}) + \frac{1}{2}(\text{O}=\text{O}) - 6(\text{C}-\text{H}) - (\text{C}-\text{C}) - (\text{C}=\text{C}) - 2(\text{O}-\text{H}) \\ &= 2(\text{C}-\text{H}) + (\text{C}-\text{C}) + \frac{1}{2}(\text{O}=\text{O}) - (\text{C}=\text{C}) - 2(\text{O}-\text{H}) \end{aligned}$$

Thus;

$$-125 = (2 \times 413) + 348 + \frac{1}{2}(\text{O}=\text{O}) - 612 - (2 \times 463)$$

From which: $(\text{O}=\text{O}) = 478 \text{ kJ/mol}$.**Question 30**

(a)

- (i) It is wrong to use the phrase "heat change" instead of "heat evolved".

Explanation

Using the word "change" which actually may be positive or negative change, implies that the combustion may be either endothermic or exothermic which is not correct because combustions are commonly exothermic.

- (ii) It is wrong to exclude the phrase "one mole" (of water) in the definition.

Explanation

The amount of heat evolved in the neutralisation reaction depends on the amount of acid and base reacted and hence the amount of water produced. To make the data uniform enthalpy of neutralisation is always given per one mole of water.

- (iii) It is wrong to state "one mole of hydrogen" instead of "one mole of unsaturated compound".

Explanation

Enthalpy of hydrogenation is always given per one mole of the compound that has undergone complete hydrogenation. One mole of compound like alkyne need two moles of H_2 for its complete combustion, so defining the enthalpy of hydrogenation in terms of one mole of H_2 will correspond to 0.5 mole of the alkyne which is not correct.

- (iv) It is wrong to give a definition with an idea that "any valence electron" is removed during ionisation instead of the idea of an electron which is least tightly (most loosely) held by nuclear attractive force.

(b) Given that:

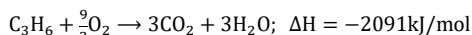
$$\Delta H_c(\text{carbon}) = -393.5 \text{ kJ/mol} = \Delta H_f(\text{CO}_2)$$

$$\Delta H_c(\text{hydrogen}) = -286 \text{ kJ/mol} = \Delta H_f(\text{H}_2\text{O})$$

$$\Delta H_c(\text{C}_3\text{H}_6) = -2091 \text{ kJ/mol.}$$

(Heat of combustion is the heat evolved, so the negative sign must be included in calculations although they are given as positive values).

Equation for combustion for cyclopropane:



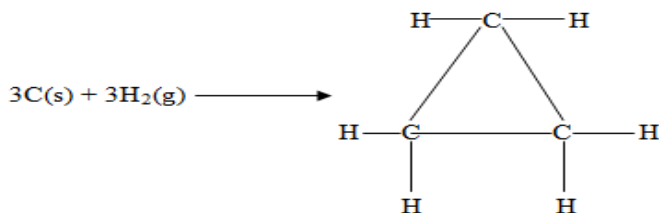
Cyclopropane

$$\Delta H_c(\text{C}_3\text{H}_6) = 3\Delta H_f(\text{CO}_2) + 3\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_3\text{H}_6) - \frac{9}{2}\Delta H_f(\text{O}_2)$$

But $\Delta H_f(\text{O}_2) = 0$

$$\text{So } -2091 = (3 \times -393.5) + (3 \times -286) - \Delta H_f(\text{C}_3\text{H}_6); \Delta H_f(\text{C}_3\text{H}_6) = 52.5 \text{ kJ. mol}$$

Equation to show formation of cyclopropane from its elements:



Total energy absorbed in reactants side

= energy of sublimating three carbon atoms + energy for dissociating three H_2

$$= (3 \times 720) + (3 \times 432) = 3456 \text{ kJ/mol}$$

Total energy evolved in product side = $-6(\text{C}-\text{H}) - 3(\text{C}-\text{C})$

Thus heat of formation of cyclopropane = $3456 - 6(\text{C}-\text{H}) - 3(\text{C}-\text{C})$

$$\text{So } 52.5 = 3456 - (6 \times 414) - 3(\text{C}-\text{C})$$

From which the mean $\text{C}-\text{C}$ bond energy is 306.5 kJ/mol .

APPENDIX A

PERIODIC TABLE OF ELEMENTS

IA H 2.1 IIA Li 1.0 Be 1.5 IIIA B 2.0 Al 1.5 Ga 1.6 In 1.7 Tl 1.8 IVA C 2.5 Si 1.8 Ge 1.8 Sn 1.8 Pb 1.9 VA N 3.0 P 2.1 As 2.0 Sb 1.9 Bi 1.9 VIA O 3.5 S 2.5 Se 2.4 Te 2.1 Po 2.0 VIIA F 4.0 Cl 3.0 Br 2.8 I 2.5 At 2.2																		Electronegativity ← Values		18 VII IA	
1 IA	2 IIA	13 III A	14 IV A	15 VA	16 VIA	17 VII A	18 He 4.00 26														
1 H 1.007 97	2 He	13 B 10.81 1	14 C 12.01 12	15 N 14.00 67	16 O 15.99 94	17 F 18.99 84	2 Ne 20.17 9														
3 Li 6.939 98	4 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
5 Na 22.98 98	6 Mg 24.30 5	13 B 10.81 1	14 C 12.01 12	15 N 14.00 67	16 O 15.99 94	17 F 18.99 84	18 Ne 20.17 9														
7 Li 6.939 98	8 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
9 Li 6.939 98	10 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
11 Na 22.98 98	12 Mg 24.30 5	13 B 10.81 1	14 C 12.01 12	15 N 14.00 67	16 O 15.99 94	17 F 18.99 84	18 Ne 20.17 9														
13 Li 6.939 98	14 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
15 Li 6.939 98	16 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
17 Li 6.939 98	18 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
19 Li 6.939 98	20 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
21 Li 6.939 98	22 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
23 Li 6.939 98	24 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
25 Li 6.939 98	26 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
27 Li 6.939 98	28 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
29 Li 6.939 98	30 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
31 Li 6.939 98	32 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
33 Li 6.939 98	34 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
35 Li 6.939 98	36 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
37 Li 6.939 98	38 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
39 Li 6.939 98	40 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
41 Li 6.939 98	42 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
43 Li 6.939 98	44 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
45 Li 6.939 98	46 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
47 Li 6.939 98	48 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
49 Li 6.939 98	50 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
51 Li 6.939 98	52 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
53 Li 6.939 98	54 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
55 Li 6.939 98	56 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
57 Li 6.939 98	58 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
59 Li 6.939 98	60 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
61 Li 6.939 98	62 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
63 Li 6.939 98	64 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
65 Li 6.939 98	66 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
67 Li 6.939 98	68 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
69 Li 6.939 98	70 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
71 Li 6.939 98	72 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
73 Li 6.939 98	74 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
75 Li 6.939 98	76 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
77 Li 6.939 98	78 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
79 Li 6.939 98	80 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
81 Li 6.939 98	82 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
83 Li 6.939 98	84 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
85 Li 6.939 98	86 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
87 Li 6.939 98	88 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
89 Li 6.939 98	90 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
91 Li 6.939 98	92 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
93 Li 6.939 98	94 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
95 Li 6.939 98	96 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
97 Li 6.939 98	98 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
99 Li 6.939 98	100 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
101 Li 6.939 98	102 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
103 Li 6.939 98	104 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
105 Li 6.939 98	106 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
107 Li 6.939 98	108 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
109 Li 6.939 98	110 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
111 Li 6.939 98	112 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
113 Li 6.939 98	114 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
115 Li 6.939 98	116 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
117 Li 6.939 98	118 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
119 Li 6.939 98	120 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
121 Li 6.939 98	122 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
123 Li 6.939 98	124 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
125 Li 6.939 98	126 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
127 Li 6.939 98	128 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
129 Li 6.939 98	130 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
131 Li 6.939 98	132 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
133 Li 6.939 98	134 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
135 Li 6.939 98	136 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
137 Li 6.939 98	138 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
139 Li 6.939 98	140 Be 9.012 2	13 Na 22.98 98	14 Mg 24.30 5	15 Al 26.9 815	16 Si 28.0 86	17 P 30.97 38	18 S 32.0 64														
141																					

* Lanthanide Series	57 La 138.91	58 Ce 140.115	59 Pr 140.90 77	60 Nd 144.24	61 Pm (145)	62 Sm 150.36 8	63 Eu 151.96 5	64 Gd 157.2 5	65 Tb 158.92 54	66 Dy 162.5 0	67 Ho 164.93 03	68 Er 167.2 6	69 Tm 168.93 42	70 Yb 173.0 4
	89 Ac [227.03]	90 Th 232.03 81	91 Pa 231.03 59	92 U 238.02 89	93 Np 237.0 48	94 Pu [244]	95 Am [260]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]

APPENDIX B

ELECTROCHEMICAL SERIES

Elements	Electrode Reaction	E_{red}° (volts)
Increase Oxidised Form + ne^- $\longrightarrow$ Reduced Form Decrease		
Li	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.05
K	$K^+(aq) + e^- \longrightarrow K(s)$	-2.93
Ba	$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	-2.90
Ca	$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	-2.87
Na	$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71
Mg	$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	-2.37
Al	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	-1.66
Zn	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.76
Cr	$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	-0.74
Fe	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.44
	$H_2O(l) + e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-(aq)$	-0.41
Cd	$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	-0.40
Pb	$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	-0.31
Co	$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	-0.28
Ni	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	-0.25
Sn	$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	-0.14
Pb	$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.13
H_2	$2H^+ + 2e^- \longrightarrow H_2(g)$ (standard electrode)	0.00
Cu	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
I_2	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.54
Fe	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
Hg	$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.79
Ag	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
Hg	$Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$	+0.85
N_2	$NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.97
Br_2	$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+1.08
O_2	$O_2(g) + 2H_3O^+(aq) + 2e^- \longrightarrow 3H_2O$	+1.23
Cr	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33
Cl_2	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
Au	$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.42
Mn	$MnO_4^- + 8H_3O^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 12H_2O(l)$	+1.51
F_2	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87

APPENDIX C**VAPOUR PRESSURE OF PURE WATER AT DIFFERENT TEMPERATURES**

Water vapour pressure table					
Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)
0.0	4.6	19.5	17.0	27.0	26.7
5.0	6.5	20.0	17.5	28.0	28.3
10.0	9.2	20.5	18.1	29.0	30.0
12.5	10.9	21.0	18.6	30.0	31.8
15.0	12.8	21.5	19.2	35.0	42.2
15.5	13.2	22.0	19.8	40.0	55.3
16.0	13.6	22.5	20.4	50.0	92.5
16.5	14.1	23.0	21.1	60.0	149.4
17.0	14.5	23.5	21.7	70.0	233.7
17.5	15.0	24.0	22.4	80.0	355.1
18.0	15.5	24.5	23.1	90.0	525.8
18.5	16.0	25.0	23.8	95.0	633.9
19.9	16.5	26.0	25.2	100.0	760.0

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