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 be 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.

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

By definition: Density of solution = $\frac{\text{Mass of solution}}{\text{Volume of solution}}$

But mass of solution = mass of solute + mass of solvent

Then: Density of solution $= \frac{\text{mass of solute+mass of solvent}}{\text{volume of solution}} = \frac{\text{Mass of solute}}{\text{volume of solution}} + \frac{\text{Mass of solvent}}{\text{Volume of solution}}$

But $\frac{\text{mass of solute}}{\text{volume of solution}}$ = mass concentration of solute

And $\frac{\text{mass of solvent}}{\text{volume of solution}}$ = 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.

Thus Molarity $= \frac{\text{number of moles of solute}}{\text{volume of solution in litres (or dm}^3)}$

It is denoted by two square brackets, [ ]

Its unit is mol/L (or mol/dm^3) or M where $1M = 1mol/dm^3$

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: $1dm^3$ = 1Litre = $1000cm^3$

Relationship between molarity and mass concentration

From Molarity $= \frac{\text{number of moles of solute}}{\text{volume of solution in dm}^3}$

But number of moles of solute $= \frac{\text{mass of solute}}{\text{molar mass of solute}}$

Then: Molarity $= \frac{\text{mass of solute}}{\text{volume of solution in dm}^3 \times \text{molar mass of solute}}$

$\frac{\text{mass of solute}}{\text{volume of solution in dm}^3}$ = Mass of concentration in g/dm^3

Hence: Molarity $= \frac{\text{mass concentration in g/dm}^3}{\text{molar mass of solute in g/mol}}$

Or mass concentration in g/dm^3 = molarity × 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/dm^3.That is 1kg of solvent is contained in 1dm^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 $= \frac{\text{number of moles of solute}}{\text{volume of solution in dm}^3}$

But volume of solution $=$ volume of solvent $+$ volume of solute

So it is clearly understood that: volume of sloution $>$ 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;

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, $\frac{\text{number of moles of solute}}{\text{volume of solvent in dm}^3}$ 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; $\text{volume of solution} = \text{volume of solvent.}$

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: $\text{Normality} = \frac{\text{number of euivalents of solute}}{\text{volume of solution in litres (or dm}^3)}$

Its unit is N

Relationship between normality and molarity

From $\text{Normality} = \frac{\text{number of equivalents of solute}}{\text{volume of solution dm}^3}$

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 = $\frac{\text{mass concentration in g/dm}^3 \times \text{Basicity or Acidity}}{\text{molar mas of solute}}$

But $\frac{\text{mas concentration in g/dm}^3}{\text{molar mass of solute}}$ = molarity

Hence for acid – base reaction

Normality = Molarity × Basicity (or Acidity)

For redox reactions:

Equivalent weight = $\frac{\text{molar mass}}{\text{number of electrons transfered}}$

Then from $\text{Normality} = \frac{\text{mass concentration in g/dm}^3}{\text{equivalent weight of solute}}$

It becomes:

Normality = $\frac{\text{mass concentration in g/dm}^3 \times \text{number of electrons transfered}}{\text{Molar mass of solute}}$

But $\frac{\text{mass concentration in g/dm}^3}{\text{molar mass of solute}}$ = Molarity

Hence for redox reactions: $\text{Normality} = \text{Molarity} \times \text{Number of electrons transferred}$

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

$\frac{M_aV_a}{M_bV_b} = \frac{n_a}{n_b}$……………………………………(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 stochiometric coefficient of acid in a balanced chemical equation for the reaction

n_b is the stochiometric coefficient of base in a balanced chemical equation for the reaction

Then:

$M_an_bV_a \;=\; M_bn_aV_a$ (By rearranging equation (i) above)

But $n_b \;=\;$ Basicity of acid

And $n_{a=}$ Acidity of acid

So $M_an_b \;=\; N_a$ (Normality for acid)

And $M_bn_a \;=\; N_b$ (Normality for base)

Hence: $N_aV_a \;=\; N_bV_b$

Similarly, for redox reaction;

$N_oV_o = N_rV_r$

Where N_0 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:

$$\textbf{Normality} = \textbf{molarity} \times \textbf{equivalent factor}$$

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.

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

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 × volume of solution

(From Density = $\frac{\text{mass}}{\text{volume}}$; mass = Density × volume).

Then:

$\%\left(\frac{m}{m}\right) = \frac{\text{mass of solute in g}}{\text{volume of solution} \times \text{Density of solution}}$

But $\frac{\text{mass of solute in g}}{\text{volume of solution}}$ = mass concentration

Then $\% \frac{m}{m} = \frac{\text{mass concentration}}{\text{Density of solution}}$

Hence: Mass concentration = 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

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 $10^6 cm^3$.

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 $\frac{m}{v}$ = ppm in $\frac{m}{m}$ (or $^{w}/_{w}$) 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 $100cm^3$ of the solution

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

Thus $X_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$

Where $X_{\text{solute}} + X_{\text{solvent}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} + \frac{n_{\text{solvent}}}{n_{\text{solvent}} + n_{\text{solute}}} = \frac{n_{\text{solvent}} + n_{\text{solute}}}{n_{\text{solvent}} + n_{\text{solute}}} = 1$

Hence: $X_{\text{solute}} + X_{\text{solvent}} = 1$

Also with mixture of two components, say A and B;

$X_A = \frac{n_A}{n_A + n_B}$ And $X_B = \frac{n_B}{n_A + n_B}$

Then $\frac{X_A}{X_B} = \frac{n_A}{n_A + n_B} \times \frac{n_A + n_B}{n_B} = \frac{n_A}{n_B}$

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.*

Thus Dilution = $\frac{\text{Volume of solute in litres } (dm^3)}{\text{Number of moles of solute}}$

Or Dilution = $\frac{1}{\text{Molarity}}$

Its unit is dm^3mol^{-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 = constant (n is constant)

From which $M_1V_1 = M_2V_2 = M_3V_3 = \ldots\ldots = M_nV_n$

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 $\left(V_c + V_{H_2O}\right)$

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 $100cm^3$ of the solution. What is:

(i) Mass concentration of the salt
(ii) Molarity

Solution

(i) Mass concentration = $\frac{\text{mass of solute in g}}{\text{volume of solution in dm}^3} = \frac{10g}{0.1dm^3} = 100g/dm^3$

So mass concentration is $100g/dm^3$

(ii) A common salt is NaCl whose molar mass is $58.5g/mol$

Using Molarity = $\frac{\text{mass concentration in g/dm}^3}{\text{molar mass of solute in g/mol}} = 100/58.5\ M = 1.71M$

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 = $(100 - 36)g = 64g$

$n_{HCl} = \frac{m_{HCl}}{M_{HCl}} = 36/36.5\ \text{moles} = 0.986\ \text{moles}$

$n_w = \frac{m_W}{M_W} = \frac{64}{18}\ \text{moles} = 3.556\ \text{moles}$

Then $X_{HCl} = \frac{n_{HCl}}{n_{HCl}+n_W} = \frac{0.986}{0.986+3.556} = 0.22$

Hence mole fraction of HCl is 0.22

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 $\mathbf{15.4mol/kg}$

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

$\text{Mass of solution} = \text{mass of water} + \text{mass of common salt} = (100 + 10)\text{g} = 110\text{g}$

Using $\%\left(\frac{m}{m}\right) = \frac{\text{mas of solute}}{\text{mass of solute}} \times 100\% = \frac{10}{110} \times 100\% = 9.09\%$

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 $100cm^3$ of its solution is 0.9g

So mass of NaCl in $1000cm^3$(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 H_2SO_4 per dm^3 of solution at 20℃ has density of 1.3294g/ml. calculate

(i) Molarity of sulphuric acid
(ii) Percentage of mass of H_2SO_4
(iii) Mole fraction of the solution components
(iv) Normality of the acid solution
(v) Molality of hydrochloric acid

Solution

(i) Molarity $= \frac{\text{mass concentration in g/dm}^3}{\text{molar mass of the } H_2SO_4\text{(solute)}} = \frac{571.6}{98} = 5.83\text{M}$

Molarity of sulphuric acid is 5.83M

(ii) Using: Mass concentration $=$ Density $\times \%\left(\frac{\text{m}}{\text{m}}\right)$

Then$\%\left(\frac{\text{m}}{\text{m}}\right) = \frac{\text{mass concentration}}{\text{Density}} \times 100\%$

But density $= 1.3294\text{g/ml} = 1329.4\text{g/L}$

Then mass percentage $= \frac{571.6}{1329.4} \times 100\% = 43\%$

So mass percentage of H_2SO_4 is $43\%\left(\frac{\text{m}}{\text{m}}\right)$

(iii) Mass of solution in 1L of solution is 1329.4g

Mass of H_2SO_4 in 1L of the solution $= 571.6\text{g}$

Thus mass of water in 1l of the solution $= (1329.4 - 571.6)\text{g} = 757.8\text{g}$

Number of moles of $H_2SO_4 = \frac{571.6}{98}$ mol $= 5.83$moles

Number of moles of water $= \frac{757.8}{18}$mole $= 42.1$ moles

Moles fraction of $H_2SO_4 = \frac{\text{number of moles of } H_2SO_4}{\text{Total number of moles of solution}} = \frac{5.83}{5.83+42.1} = 0.12$

Mole fraction of H_2SO_4 is 0.12

Mole fraction of water $= 1 -$ mole fraction of $H_2SO_4 = 1 - 0.12 = 0.88$

(iv) Normality of acid $=$ Molarity $\times$ Basicity

But Basicity of $H_2SO_4 = 2$

Then Normality of the acid solution $= 2 \times 5.83\text{N} = 11.66\text{N}$

(v) Molality $= \frac{\text{number of moles of solute } (H_2SO_4)}{\text{mass of solvent(water)in kg}}$

But number of moles of H_2SO_4 in 757.8g or 0.7578kg of water is 5.83moles

Then Molality of $H_2SO_4 = \frac{5.83}{0.7578}$ mol/kg $= 7.69$mol/kg

Hence Molality of the acid is 7.69mol/kg

Example 6

You want to prepare 100cm^3 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 100cm^3?

Solution

By dilution law: $M_cV_c = M_dV_d$ or $V_c = \frac{M_d V_d}{M_c}$

Where: $M_d = 2\text{M}$, $V_d = 100\text{cm}^3$ $M_c = 18\text{M}$

Then $V_c = \frac{2\times100}{18}\text{cm}^3 = 11.11\text{cm}^3$

Hence volume of concentrated acid required is 11.11cm^3. (In the example, 11.11cm^3 of concentrated solution must be mixed with (100 – 11.11) cm^3 or 88.89cm^3 of distilled water)

Example 7

Find the concentration of the mixture obtained by mixing 100mL of 0.2MHCl and $150cm^3$ of 0.1MHCl.

Solution

Concentration of the mixture $= \frac{M_1V_1 + M_2V_2}{V_1 + V_2} = \frac{(100\times0.2) + (150\times0.1)}{(100+250)} = 0.14M$

Thus the concentration of the solution mixture is 0.14M

Example 8

450g of 30% $\left(\frac{m}{m}\right)$ hydrochloric acid are being mixed with 150g of 20% $\left(\frac{m}{m}\right)$ hydrochloric acid. Which concentration will the mixture have?

Solution

Mass of HCl in 450g of 30% $\left(\frac{m}{m}\right)$ HCl = $\frac{30}{100} \times 450g = 135g$

Mass of HCl in 150g of 20%$\left(\frac{m}{m}\right)$ HCl = $\left(\frac{20}{100}\right) \times 150g = 30g$

Total mass of HCl = $(135 + 30)g = 165g$

Total mass of solution = $(450 + 150)g = 600g$

% ${}^{m}/_{m}$ 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% $\left(\frac{m}{m}\right)$

Example 9

Dilute 10g of 65% mass – percentage of nitric acid so that a 12% mass – percentage of the acid will be formed.

Solution

Mass of HNO_3 in 10g of 65% $({}^{m}/_{m})HNO_3 = \frac{65}{100} \times 10g = 6.5g$

Let mass of water to be added = xg

So total mass of solution after dilution = $(10 + x)g$

Then using: $\%({}^{m}/_{m})$ $= \frac{\text{mass of } HNO_3 \text{ (solute)}}{\text{mass of solution}} \times 100\% = \frac{6.5}{10+x} \times 100 = 12$

$= \frac{650}{10+x} = 12$ Then $650 = 120 + 12x$

$12x = 530$ or $x = 44.17g$

Hence 44.17g of water is required for dilution

Example 10

Dilute 65% $({}^{m}/_{m})$ nitric acid to 12%

Solution

Let mass of 65% $({}^{m}/_{m})$ HNO_3 taken be xg

And mass of water used for dilution be yg

Then mass of 65%$({}^{m}/_{m})$ HNO_3 taken will be $\frac{65x}{100} = 0.65x$

And total mass of solution after dilution will be $(x + y)g$

Using $\%(^{m}/_{m}) = \frac{\text{mass of HNO}_3\text{(solute)}}{\text{mass of solution}} \times 100\% = \frac{0.65x}{x+y} = \frac{12}{100}$

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 $= \frac{\text{Partial volume}}{\text{Molar volume}}$

Then $n_p = \frac{V_p}{74.166}$

And $n_t = \frac{V_t}{80.235}$

It follows that: $\frac{n_p}{n_t} = \frac{80.235V_p}{74.166V_t}$

But $\frac{n_p}{n_t} = \frac{X_p}{X_t} = \frac{1-0.4693}{0.4693} = 1.13083$

Thus $1.13083 = \frac{80.235V_p}{74.166V_t}$ or $V_p = 1.04529V_t$ … … … … … … … … … (i)

Also using $m = nM_r$:

$m_p = n_p \times \text{molar mass of } CH_3COCH_3$

$m_p = \frac{V_P}{74.166} \times 58 = 0.78203V_P$

$m_t = n_t \times \text{molar mass of } CHCl_3$

$m_t = \frac{V_t}{80.235} \times 119.5 = 1.48937V_t$

But $m_p + m_t = 1000\text{g}$

Thus $0.78203V_P + 1.48937V_t = 1000 \rightarrow$ (ii)

Solving (i) and (ii) simultaneously gives;

$V_t = 433.4972\text{cm}^3$

$V_P = 453.13029\text{cm}^3$

Therefore $V_{Soln} = V_t + V_P = (433.4972 + 453.13029)\text{cm}^3 = 886.62749\text{cm}^3$

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

$0.05\mathrm{M}$ NaoH Solution in water has density of $1.112\mathrm{g/mL}$. 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 $1.072\mathrm{g/mL}$, 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 $1.25\mathrm{g/mL}$ 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 1.5×10^{-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 $= 342.2948$g/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 morality 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($^{m}/_{v}$). How many moles of O_2 per litre of water, does this correspond to?

Question 16

Calculate the molarity of a 60% ($^{w}/_{w}$) 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, liquid $\rightleftharpoons$ 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).

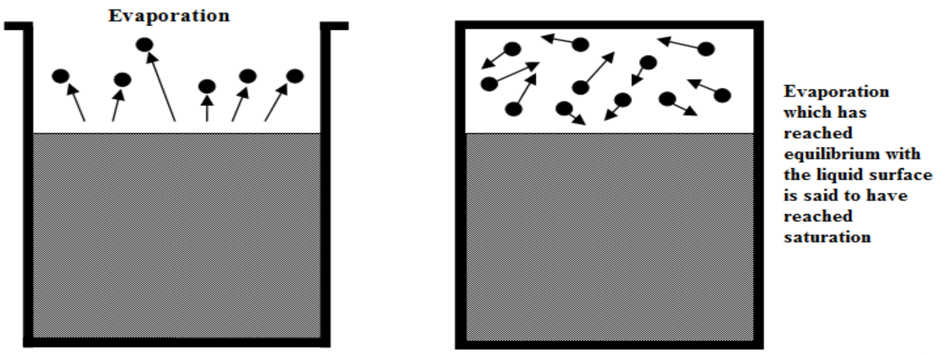


Figure 6.1 Saturated vapour pressure

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 deference 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^o and P_B^o respectively

Hence:

$$\mathbf{P_A = X_A P_A^o} \text{ and } \mathbf{P_B = X_B P_B^o}$$

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^o and P_b^o 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;

$$P_A = X_A P_A^o \text{ and } P_B = X_B P_B^o$$

But by Dalton's law of partial pressures:

$P_{soln} = P_A + P_B$; where $P_{soln} =$ vapour pressure of the solution

Hence $\mathbf{P_{soln} = X_A P_A^o + X_B P_B^o}$

Recall: $X_A + X_B = 1$

So if A is less volatile than B i.e. $P_A^o < P_B^o$

Then $P_A^o < P_{soln} < P_B^o$

(Vapour pressure of solution must be between P_A^o and P_B^o)

It should be understood that:

The vapour composition of the solution can be obtained by using the fact that:

$X_A^V = \frac{P_A}{P_{soln}}$ and $X_B^V = \frac{P_B}{P_{soln}}$

Where X_A^V and X_A^V are mole fractions in vapour phase for liquids A and B respectively.

But $P_A = X_A^L P_A^o$ and $P_B = X_B^L P_B^o$

Then $\mathbf{X_A^V = \frac{X_A^L P_A^o}{P_{soln}}}$ and $\mathbf{X_B^V = \frac{X_B^L P_B^o}{P_{soln}}}$

Since A is less volatile, $P_B^o > P_A^o$

And $P_B^o > P_{soln}$ while $P_A^o < P_{soln}$

So from $X_A^V = \frac{X_A^L P_A^o}{P_{soln}}$, it becomes $\frac{P_A^o}{P_{soln}} < 1$ and hence $X_A^V < X_A^L$

While from $X_B^V = \frac{X_B^L P_B^o}{P_{soln}}$, $\frac{P_B^o}{P_{soln}} > 1$ 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 1.5×10^4Pa and 3.5×10^4Pa respectively. If a mixture of A and B obeys Raoult's law, calculate the mole fraction o f A and B if the solution has a total vapour pressure of 2.9×10^4Pa at 20°C.

Solution

By Dalton's law of vapour pressure, total vapour pressure of solution is given by,

$P_{soln=} P_A + P_B$

But from Raoult's law: $P_A = X_A P_A^0$; and $P_B = X_B P_B^0$

Then $P_{soln} = X_A P_A^0 + X_B P_B^0$

But $X_A + X_B = 1$ or $X_B = 1 - X_A$

So $P_{soln} = X_A P_A^0 + (1 - X_A) P_B^0$

$P_{soln} = X_A P_A^0 - X_A P_B^0 + P_B^0$

Or $X_A = \frac{P_{soln} - P_B^0}{P_A^0 - P_B^0} = \frac{(2.9-3.5)\times 10^4}{(1.5-3.5)\times 10^4} = 0.3$

$X_B = 1 - X_A = 1 - 0.3 = 0.7$

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: $P_{soln} = X_H P_H^o + X_O P_O^o$

$$P_{soln} = (0.6 \times 473) + (0.4 \times 140) = 339.8\text{Pa}$$

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 o f A and B)

Then $X_A = X_B = {}^1/_2$

So $X_A P_A^o = {}^1/_2 \times 17000Nm^{-2} = 8500Nm^{-2}$

And $X_B P_B^o = {}^1/_2 \times 35000Nm^{-2} = 17500Nm^{-2}$

Then $X_A P_A^o + X_B P_B^o = (8500 + 17500)Nm^{-2} = 26000Nm^{-2}$

That is; $P_{soln} = X_A P_A^o + X_B P_B^o$ 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:

$P_{soln} = X_A P_A^o + X_B P_B^o = (0.8 \times 17000) + (0.2 \times 35000)$

= $(13600+7000)Nm^{-2}$ = $20600Nm^{-2}$

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:

(a) The total vapour pressure
(b) 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.

Then $P_{soln} = X_{hexane} P_{hexane}^o + X_{heptane} P_{heptane}^o$

But as $n_{hexane} = n_{heptane}$ (equimolar mixture of hexane and heptane)

It follows that $X_{hexane} = X_{heptane} = {}^1/_2$

So $P_{soln} = {}^1/_2 \times 56000Nm^{-2} + {}^1/_2 \times 24000Nm^{-2}$

$P_{soln} = 40000Nm^{-2}$

(a) Thus the vapour pressure of the solution is $40000Nm^{-2}$

From (a) above;
$P_{heptane} = X_{heptane} P_{heptane}^o = {}^1/_2 \times 24000Nm^{-2} = 12000Nm^{-2}$

And $P_{soln} = 40000Nm^{-2}$

Then $X^{V}_{heptane} = \frac{P_{heptane}}{P_{soln}} = \frac{12000}{40000} = 0.3$

(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 (C_2H_5OH). If the vapour pressure of methanol and ethanol at the same temperature are 6265Pa and 2933Pa respectively. Calculate the:

(i) Partial pressure exerted by each component in the mixture.
(ii) The composition of the vapour.

Solution

$$n_{methanol} = \frac{m_{methanol}}{M_{methanol}} = \frac{10}{32}\text{moles} = 0.3125\text{mol}$$

$$n_{ethanol} = \frac{m_{ethanol}}{M_{ethanol}} = \frac{50}{46}\text{moles} = 1.1\text{mol}$$

$$X_{methanol} = \frac{n_{methanol}}{n_{methanol} + n_{ethanol}} = \frac{0.3125}{0.3125 + 1.1} = 0.22$$

$X_{ethanol} = 1 - X_{methanol} = 1 - 0.22 = 0.78$

Since the solution is ideal, then it obeys Raoult's law.

Then $P_{soln} = X_{methanol}P^{o}_{methanol} + X_{ethanol}P^{o}_{ethanol}$

$P_{soln} = (0.22 \times 6265) + (0.78 \times 2933)$

$= 1378.3Pa + 2287.74Pa = 3666.04Pa$

Then $X^{V}_{methanol} = \frac{P_{methanol}}{P_{soln}}$

But $P_{methanol} = X_{methanol}P^{o}_{methanol}$ = 1378.3Pa

So$X^{V}_{methanol} = \frac{1378.3}{3666.04}$ = 0.376 or 37.6%

And $X^{V}_{ethanol} = 1 - X^{V}_{methanol} = 1 - 0.376 = 0.624$ 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× 10^5Nm^{-2} . If the vapour pressure of Y at this temperature is 1.15× 10^5Nm^{-2} and that of Z is 6.04× 10^5Nm^{-2}. Calculate the mole fraction of Y:

(i) In the liquid mixture
(ii) In the vapour mixture

Solution

Since the solution is completely miscible, it obeys Raoult's law:

Then $P_{soln} = X_YP^{o}_{Y} + X_ZP^{o}_{Z}$

But $X_Y + X_Z = 1$

Or $X_Z = 1 - X_Y$

So $P_{soln} = X_YP^{o}_{Y} + (1 - X_Y)P^{o}_{Z}$

$P_{soln} = X_Y(P_Y^o - P_Z^o) + P_Z^o$

Or $X_Y = \frac{P_{soln} - P_Z^0}{P_Y^0 - P_Z^0} = \frac{(1.63 - 6.04)\times 10^5}{(1.15 - 6.04)\times 10^5} = 0.9$

Hence mole fraction of Y in the liquid mixture is 0.9

Then $P_y = X_Y p_Y^o = 0.9 \times 1.15 \times 10^5 Nm^{-2} = 1.035 \times 10^5 Nm^{-2}$

$P_Z = X_Z p_Z^o = (1 - X_Y)P_Z^o = 0.1 \times 6.04 \times 10^5 Nm^{-2} = 6.04 \times 10^4 Nm^{-2}$

$P_{soln} = P_y + P_z = 1.035 \times 10^5 Nm^{-2} + 6.04 \times 10^4 Nm^{-2}$

$= 1.639 \times 10^5 Nm^{-2}$

It follows that: $X_Y^V = \frac{P_Y}{P_{soln}} = \frac{1.035\times 10^5}{1.639\times 10^5} = 0.63$

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℃ (the saturated vapour pressure of A and B at 88℃ 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;

$$\textbf{Vapour pressure of the solution} = \textbf{Atmospheric pressure}$$

But the atmospheric pressure is 760mmHg (Given)

So the vapour pressure of solution, $P_{soln} = 760mmHg$

As the solution Obey Raoult's law:

$P_{soln} = X_A P_A^o + X_B P_B^o$

But $X_B = 1 - X_A$

Then $P_{soln} = X_A P_A^o + (1 - X_A)P_B^o$

$P_{soln} = X_A(P_A^o - P_B^o) + P_B^o$

Therefore: $X_A = \frac{P_{soln} - P_B^0}{P_A^0 - P_B^0} = \frac{760 - 378}{957 - 378} = 0.66$ 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

$P_A = X_A P_A^o = 0.66 \times 957mmHg$

$= 631.62mmHg$

Then $X_A^V = \frac{P_A}{P_{soln}} = \frac{631.62}{760} = 0.831$ or 83.1%

And $X_B^V = 1 - X_A^V = 1 - 0.831 = 0.169$ 0r 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.

(i) Calculate the partial pressure of each component that would be in equilibrium with the solution at 80°C.
(ii) At what atmospheric pressure will this solution boil at 80°C?
(iii) What will be the composition of the liquid that condenses when this vapour is cooled?

Solution

(i) 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: $P_t = P_t^o X_t = \frac{290 \times 39}{45}\text{torr} = 133\text{torr}$

And $P_b = P_b^o X_t = \frac{753 \times 46}{85}\text{ torr} = 407.5\text{torr}$

Hence:

Partial pressure of toluene is 133torr

Partial pressure of benzene is 407.5torr

(ii) 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: $P_{soln} = P_t + P_b = (133 + 407.5)\text{torr} = 540.5\text{torr}$
Hence the atmospheric pressure required to boil the solution is 540.5torr

(iii) Mole fraction of toluene in the vapour phase, $X_t^v = \frac{P_t}{P_{soln}} = \frac{133\text{ torr}}{540.5\text{ torr}} = 0.246$

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.

(i) Is this an ideal solution?
(ii) Rationalise the answer stated in (i) above.

Solution

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

$$n_{Acetone} = \frac{5.81g}{58.1gmol^{-1}} = 0.1mol$$

$$n_{Chloroform} = \frac{11.9g}{119.4gmol^{-1}} = 0.1mol$$

Using; Mole fraction, $X = \frac{n}{n_T}$

$$X_{Acetone} = \frac{0.1mol}{(0.1 + 0.1)mol} = 0.5$$

And $X_{Chloroform} = 1 - X_{Acetone} = 1 - 0.5 = 0.5$

According to Raoult's law;

Ideal $P_{soln} = X_{Acetone}P^o_{Acetone} + X_{Chloroform}P^o_{Chloroform}$

$= 0.5 \times 345Pa + 0.5 \times 293Pa$ =319Pa

But the real $P_{soln} = 260Pa$ which is less than the ideal P_{soln} $(319Pa)$.

(i) Since the given real pressure is not equal to ideal pressure determined by Raoult's law, the solution is not ideal.

(ii) 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:

$A \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots A = B \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots B = A \ldots\ldots\ldots\ldots\ldots\ldots\ldots B$

(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 $P_{soln} = X_A P_A^o + X_B P_B^o$ as $P_A = X_A P_A^o$ and $P_B = X_B P_B^o$ 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.
$$P_A^o < P_{soln} < P_B^o \text{ (if A is less volatile than B)}$$
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 $V_{soln} = V_A + V_B$ 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.
$$T_B < T_{soln} < T_A \text{ if A is less volatile than B}$$
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:

$$A \ldots\ldots\ldots\ldots.. A \neq B \ldots\ldots\ldots\ldots B \neq A \ldots\ldots\ldots\ldots B$$

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 $P_{soln} \neq X_A P_A^o + X_B P_B^o$ as $P_A \neq X_A P_A^o$ and $P_B \neq X_B P_B^o$
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 $V_{soln} \neq V_A + V_B$
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.

CLASSIFICTAION OF NON-IDEAL SOLUTIONS

Depending or 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 decrease with an increase in intermolecular forces of attraction;

Non – ideal solution with positive deviation has intermolecular forces of attraction which is 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 weakens 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 become 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 $V_{soln} > V_A + V_B$.

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 $P_{soln} > X_A P_A^o + X_B P_B^o$ as $P_A > X_A P_A^o$ and $P_B > X_B P_B^o$

3. Its formation is endothermic, that is heat is absorbed during formation of non-ideal solution with positive deviation.
4. The volume of the solution is greater than the summation of volume.
   That is, $V_{soln} > V_A + V_B$
5. The boiling point of the solution is less than the ideal boiling point.
6. Its components cannot be separated by fractional distillation.

Non- ideal solution of negative deviation

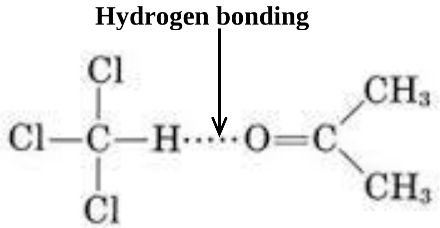
This is the solution whose vapour pressure is less than that predicted by Raoult's law.

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:

$A \ldots \ldots \ldots \ldots \ldots . B > A \ldots \ldots \ldots \ldots \ldots \ldots \ldots A$ and $A \ldots \ldots \ldots \ldots \ldots . B > B \ldots \ldots \ldots . \ldots \ldots B$

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 $V_{soln} < V_A + V_B$.

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, $P_{soln} < X_A P_A^o + X_B P_B^o$ as $P_A < X_A P_A^o$ and $P_B < X_B P_B^o$
3. It 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 $V_{soln} < V_A + V_B$
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 $\left(P_A^\circ > P_B^\circ\right)$ 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_A°).

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: $P_{soln} = P_A + P_B$

Substituting $P_{soln} = X_A P_A^\circ + X_B P_B^\circ$

But $X_B = 1 - X_A$

It follows that: $P_{soln} = X_A P_A^\circ + (1 - X_A) P_B^\circ$

Or $P_{soln} = X_A P_A^\circ + P_B^\circ - X_A P_B^\circ$

Or $P_{soln} = X_A\left(P_A^\circ - P_B^\circ\right) + P_B^\circ$

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 $= \mathbf{P_A^\circ - P_B^\circ}$

This can easily be deduced by equating terms of the equation, $P_{soln} = X_A\left(P_A^\circ - P_B^\circ\right) + P_B^\circ$ with the general equation of straight line which is $y = mx + c$ where $y = P_{soln}, x =, X_A$,
$m = P_A^\circ - P_B^\circ$ 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;
$P_{soln} = X_B\left(P_B^\circ - P_A^\circ\right) + P_A^\circ$ and $c = P_A^\circ$

2) $\mathbf{y - intercept = P_B^\circ}$.

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;

$$P_{soln} = X_A\left(P_A^\circ - P_B^\circ\right) + P_B^\circ$$

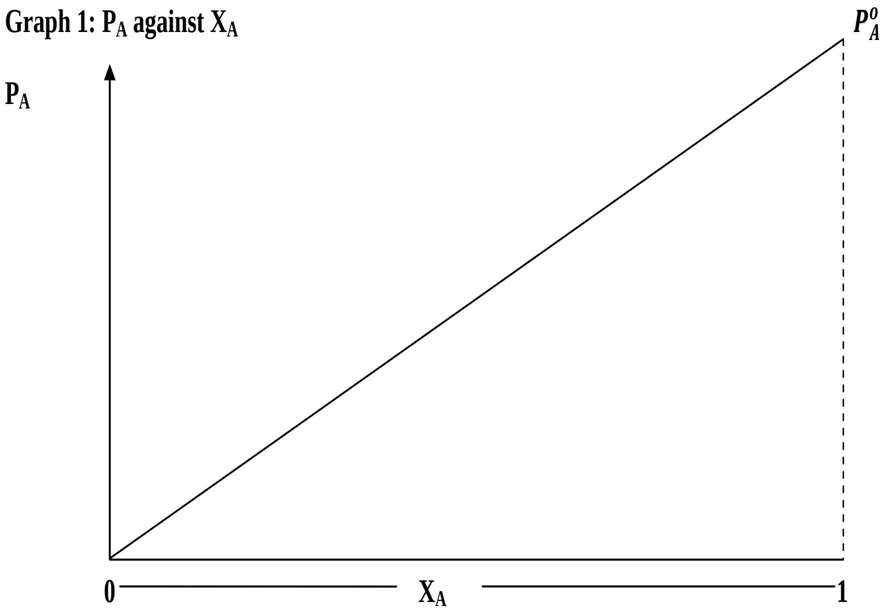
When $X_A = 0$; $P_{soln} = P_B^\circ$(when there is no A in the solution, the vapour pressure of the 'solution' is the pressure of pure B).
By similar argument, vapour pressure of pure A can be found if $X_A = 1$(there is only A in the 'solution').

That is from;

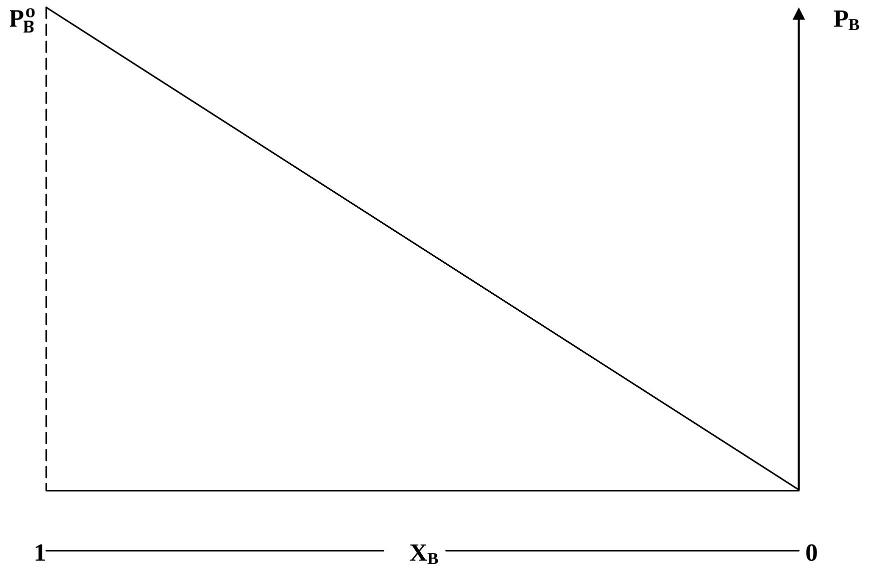
$$P_{soln} = X_A\left(P_A^\circ - P_B^\circ\right) + P_B^\circ$$

When $X_A = 1$; $P_{soln} = P_A^\circ - P_B^\circ + P_B^\circ = P_A^\circ$

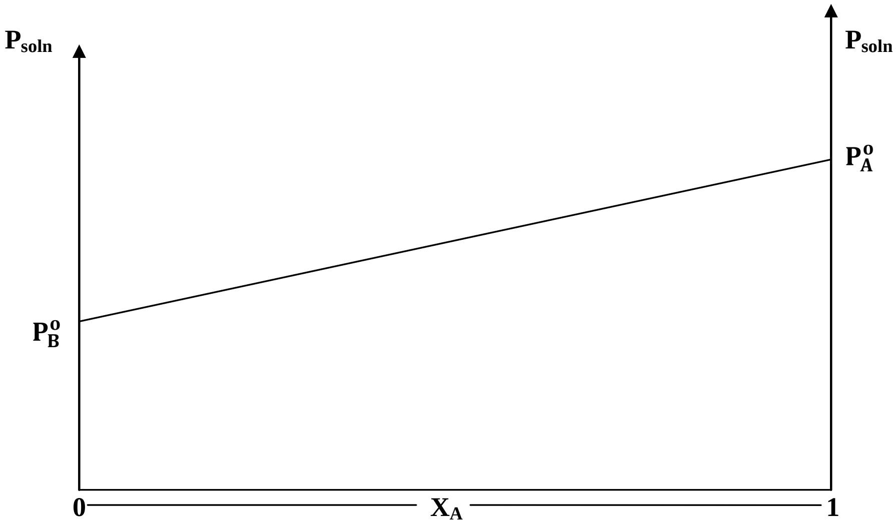
Graph 1: P_A against X_A



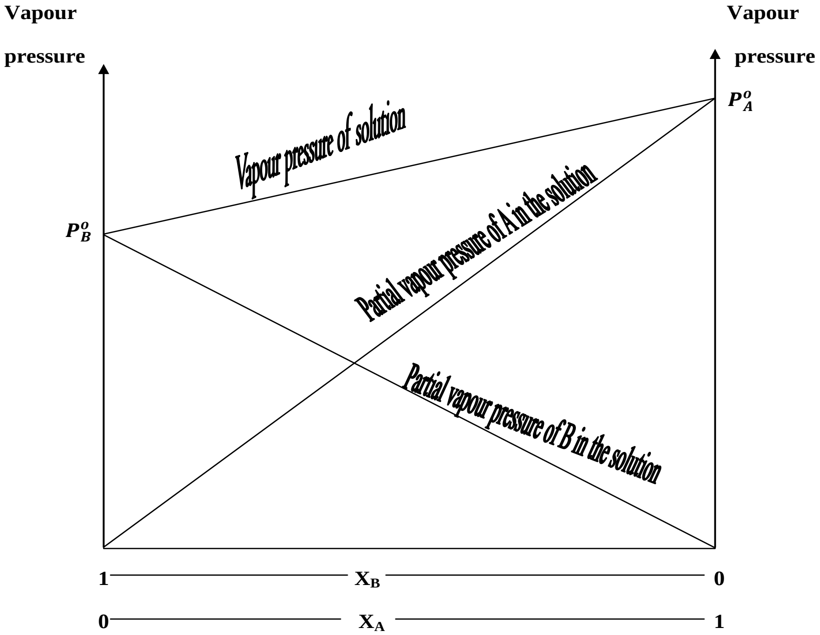
Graph 2: P_B against X_B



Graph 3: P_{soln} against X_A



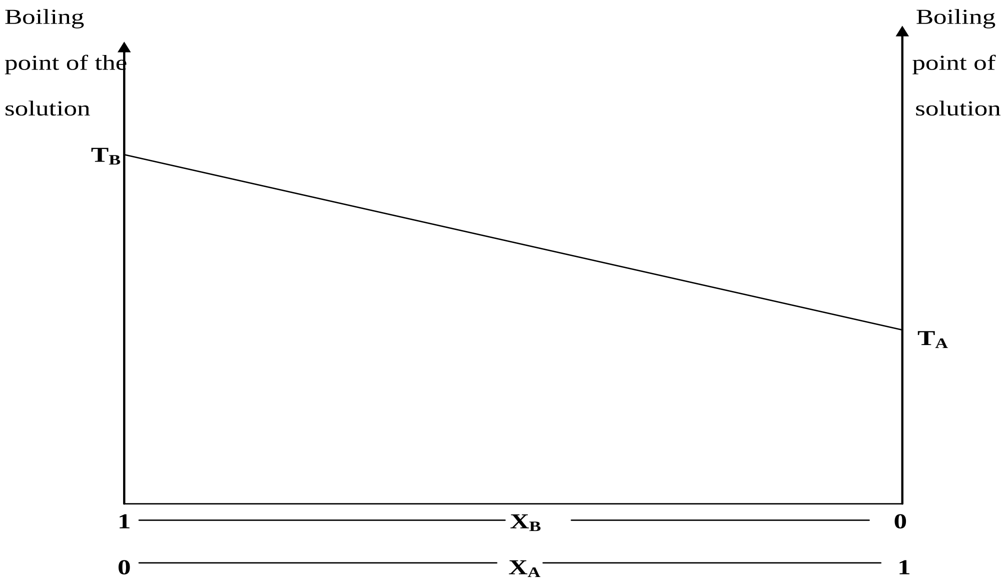
Combining **graph 1,2**and **3** gives more detailed of graph vapour pressure of solution against mole fraction of its components which show variation of partial pressure of each component in the solution as follows:



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 A.

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.

$$\mathbf{P = 200X + 400}$$

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) $\mathrm{X} + \text{mole fraction of another component} = 1$

$\mathrm{X} = 1 - \text{mole fraction of another component} = 1 - 0.2$ or $\mathrm{X} = 0.8$
Substituting $\mathrm{P} = (200 \times 0.8 + 400)\mathrm{mmHg} = 560\mathrm{mmHg}$

Hence the vapour pressure of the solution is $560\mathrm{mmHg}$

(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 $\mathrm{X} = 0$
So substituting $\mathrm{X} = 0$ in $\mathrm{P} = 200\mathrm{X} + 200$, gives;

$\mathrm{P} = 200 \times 0 + 400$ or $400\mathrm{mmHg}$

Hence vapour pressure of the pure component which is less volatile is $400\mathrm{mmHg}$

(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 $\mathrm{X} = 1$ in $\mathrm{P} = 200\mathrm{X} + 200$ gives;
$\mathrm{P} = 200 \times 1 + 400$ or $600\mathrm{mmHg}$

Hence vapour pressure of the pure component which is more volatile is $600\mathrm{mmHg}$

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:

$$\mathbf{P = -150X + 600} \qquad \text{(At 10°C)}$$

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 $\mathrm{P} = 495$;

$495 = -150X + 600$; from which $X = 0.7 = X_M$
But $X_M + X_N = 1$

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'.
Substituting $X = 1$ in $P = -150X + 600$ gives; $P = -150 \times 1 + 600$ or 450mmHg
Hence the vapour pressure of the pure component which is less volatile is 450mmHg

(iii) When $X = 0$,there is pure N(more volatile) in the 'solution'.

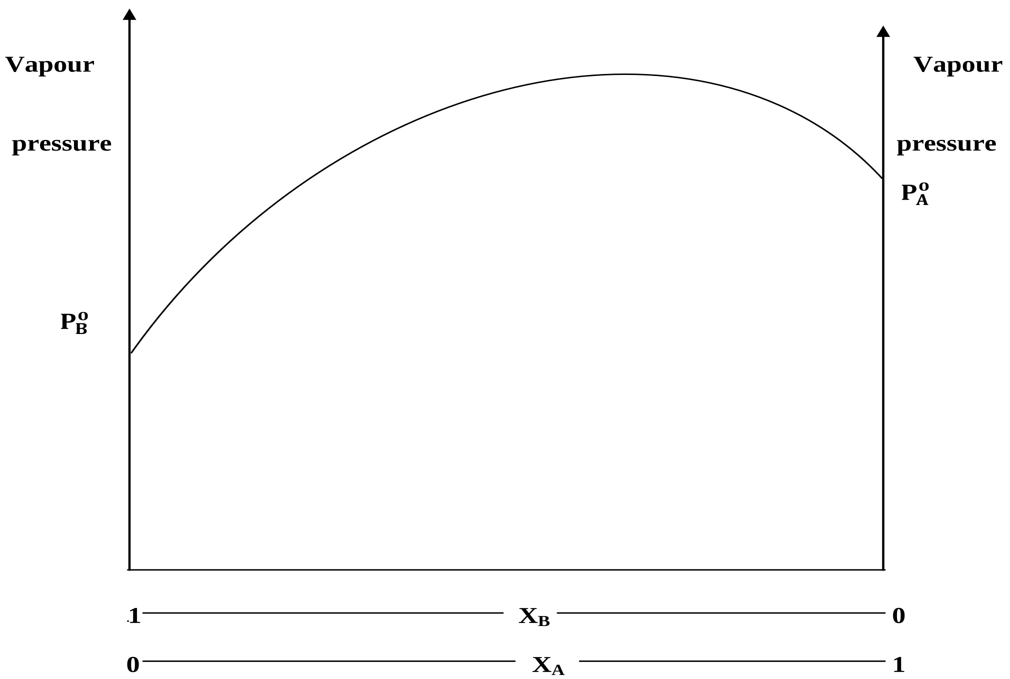
Then $P = -150 \times 0 + 600$ or 600mmHg
Hence the vapour pressure of the pure component which is more volatile is 600mmHg

(iv) The solution is said to boil, if the vapour pressure of the solution is equal to the atmospheric pressure

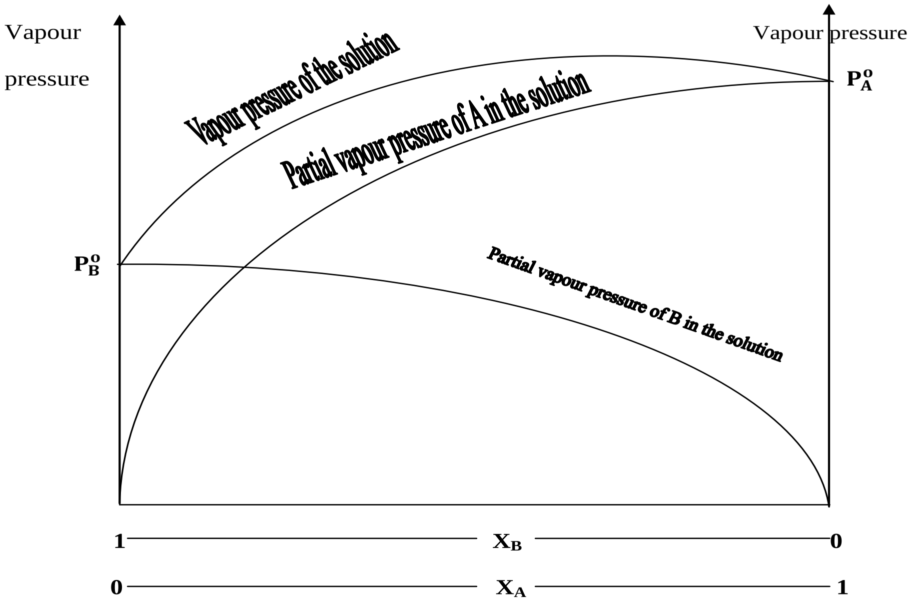
When mole fraction of $M = 0.01$; $X = 0.01$ and $P = -150 \times 0.1 + 600$ or 585 mmHg
So if the atmospheric pressure $= 585$ mmHg, the solution will boil at $10°C$.
Hence the amount of atmospheric pressure required is 585 mmHg.

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.

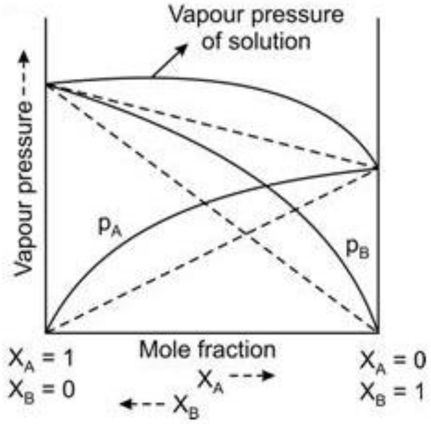


Graph II: Showing how partial vapour pressure of each component constitute to the vapour pressure of the solution



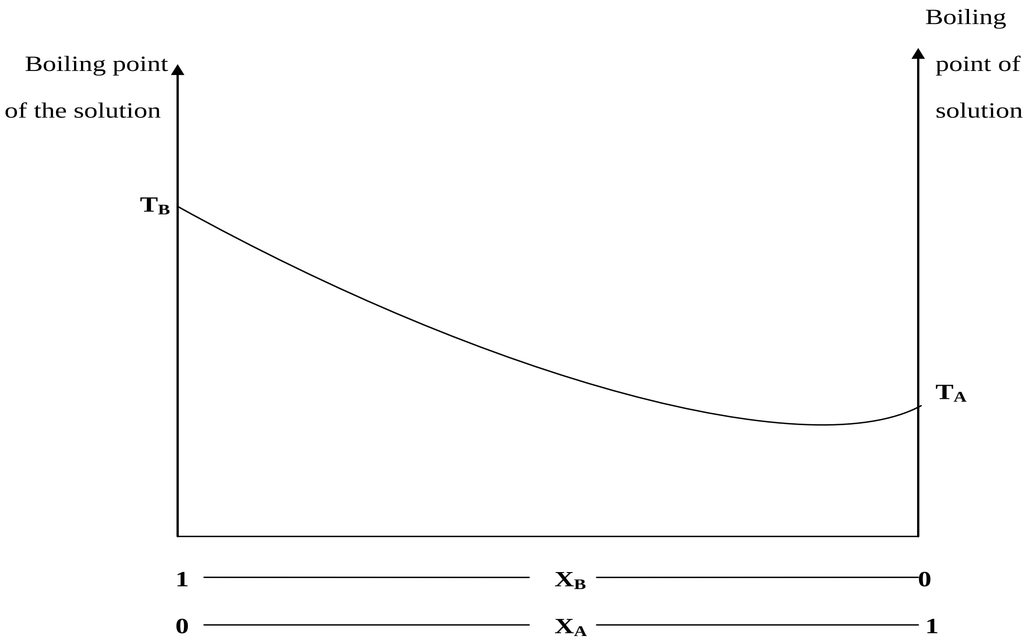
It should be noted that:

- Above graphs (see **graph I**) for non-ideal solution with positive deviation shows the maximum, hence the name **maximum vapour pressure mixture** for non- solution with positive deviation.
- If straight lines are drawn between (**0** and $\mathbf{P_B^o}$**)** 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 $\mathbf{P_B^o}$ and $\mathbf{P_A^o}$ 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:

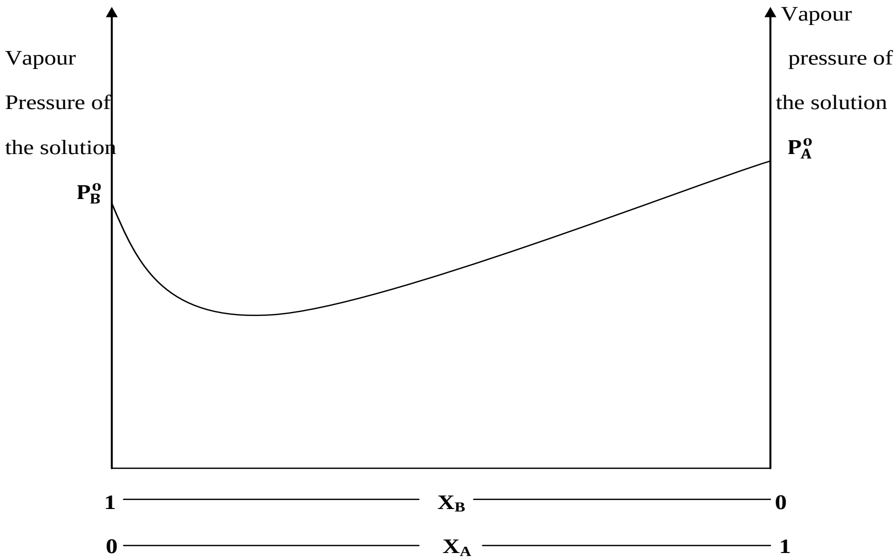
A graph of boiling point of non- ideal solution with positive deviation against mole fraction of its components



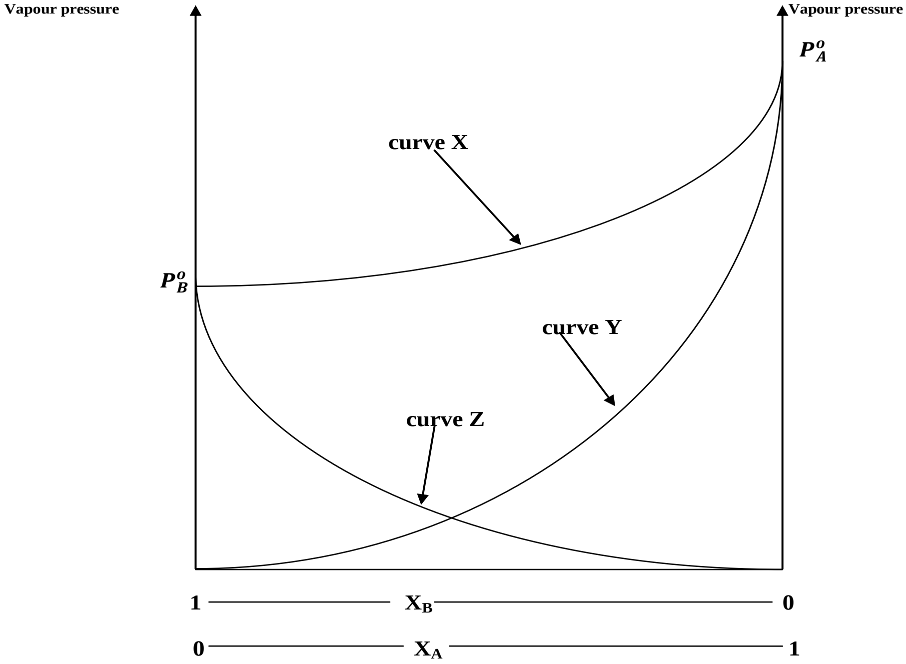
Where T_A and T_B are boiling points of pure A and B respectively, so from the above graph of boiling point of the non-ideal solution with positive deviations versus mole fraction of its components, it is clearly understood that; while the graph of the vapour pressure shows maximum, the graph of boiling 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



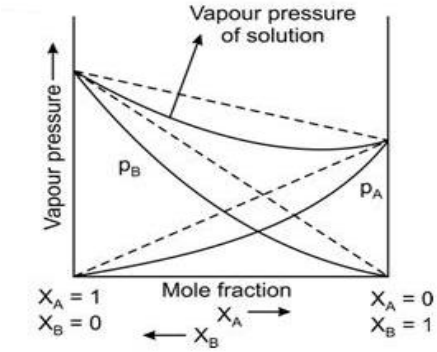
Where curve **X** represent vapour pressure of the solution

curve Y represent partial vapour pressure of A in the solution

curve Z represent partial vapour pressure of B in the solution

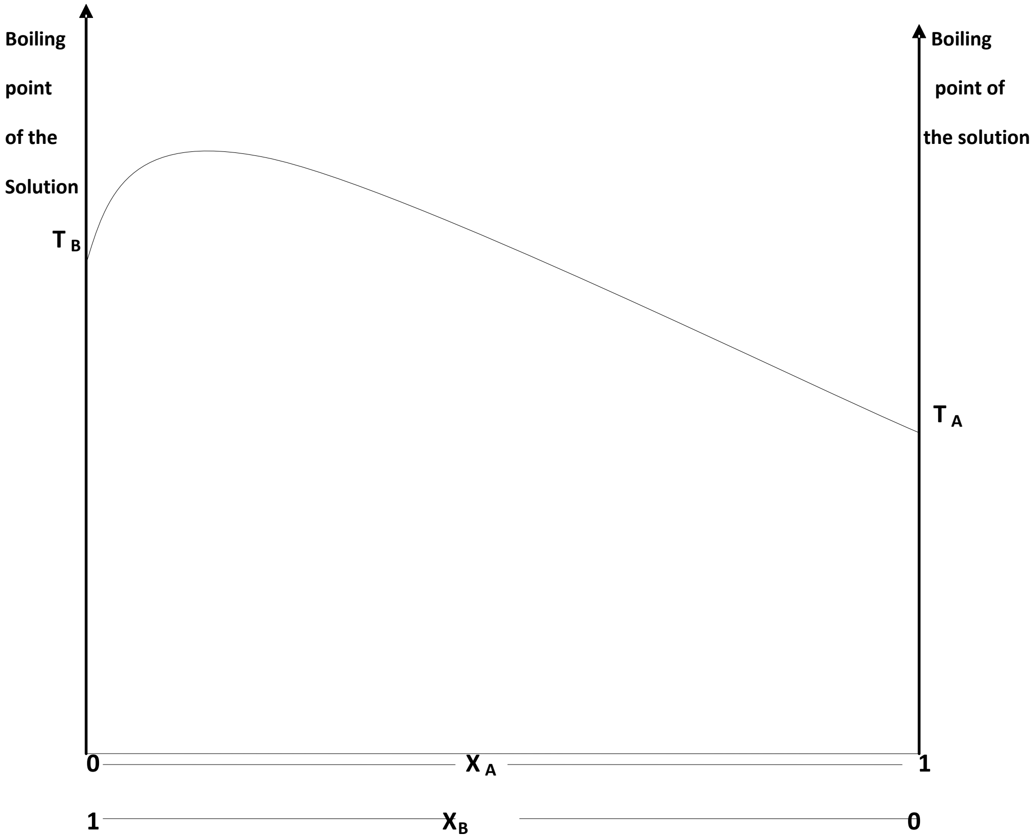
The reader should note that:

- 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 $\mathbf{P_B^o}$**)** 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 $\mathbf{P_B^o}$ and $\mathbf{P_A^o}$ 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 $\mathbf{T_A}$ and $\mathbf{T_B}$ 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

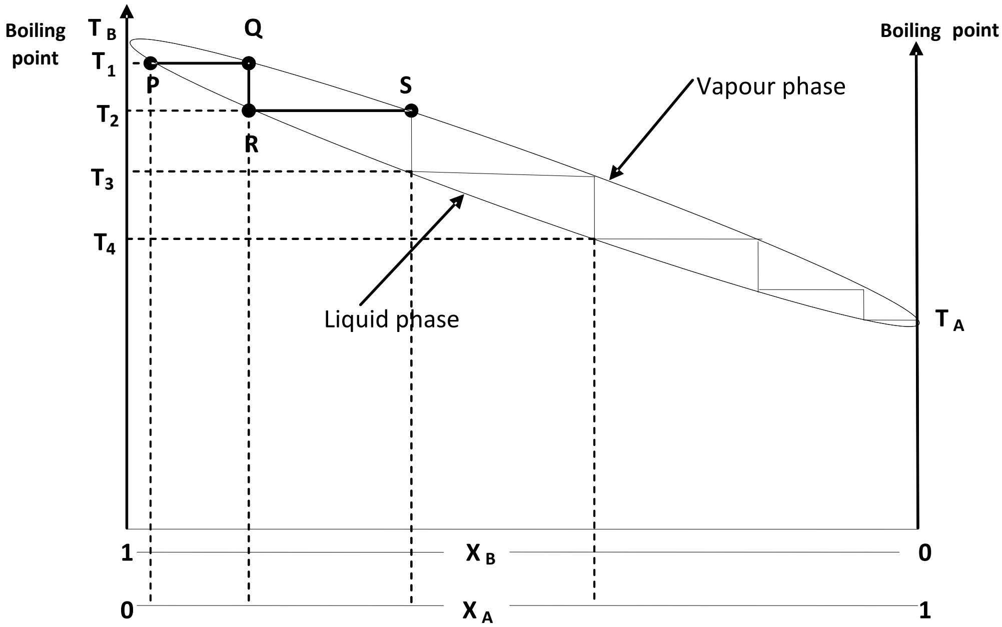
The important character about ideal solution in distillation is that; the vapour composition of the solution is continuously changing compared to its liquid composition on successive distillation and condensation. This make possible to separate components of ideal solution by **fractional distillation.**

Ideal solution boils in such a way that, the vapour formed is richer in one component which 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%

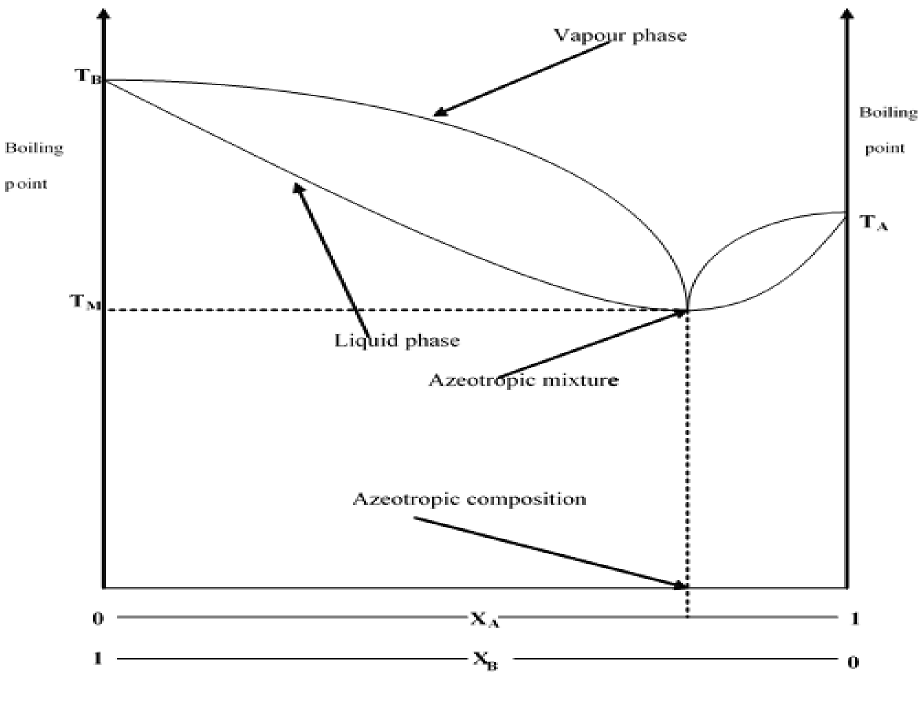
What happens when the solution containing greater than 96%(e.g. 98%) of ethanol is distilled?

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)**

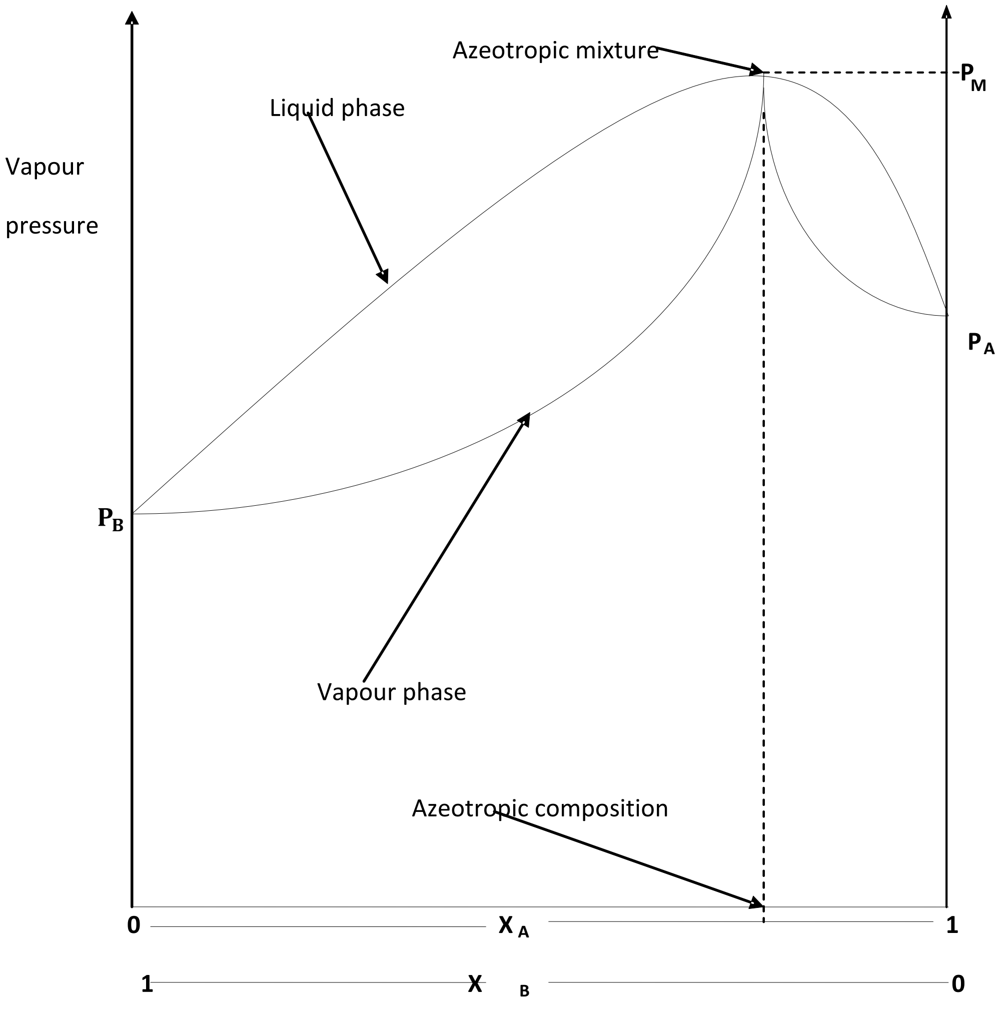
The boiling point of azeotropic mixture is known as **azeotropic point**.

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 90ºC) and B (Boiling point is 60ºC) form the solution whose azeotropic mixture is obtained when A is 60% and the mixture boils at 55ºC

(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℃ and B has boiling point of 60℃.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℃.Explain how the solution will behave on distillation if the solution contain:

(i) 40% of A
(ii) 80% of A

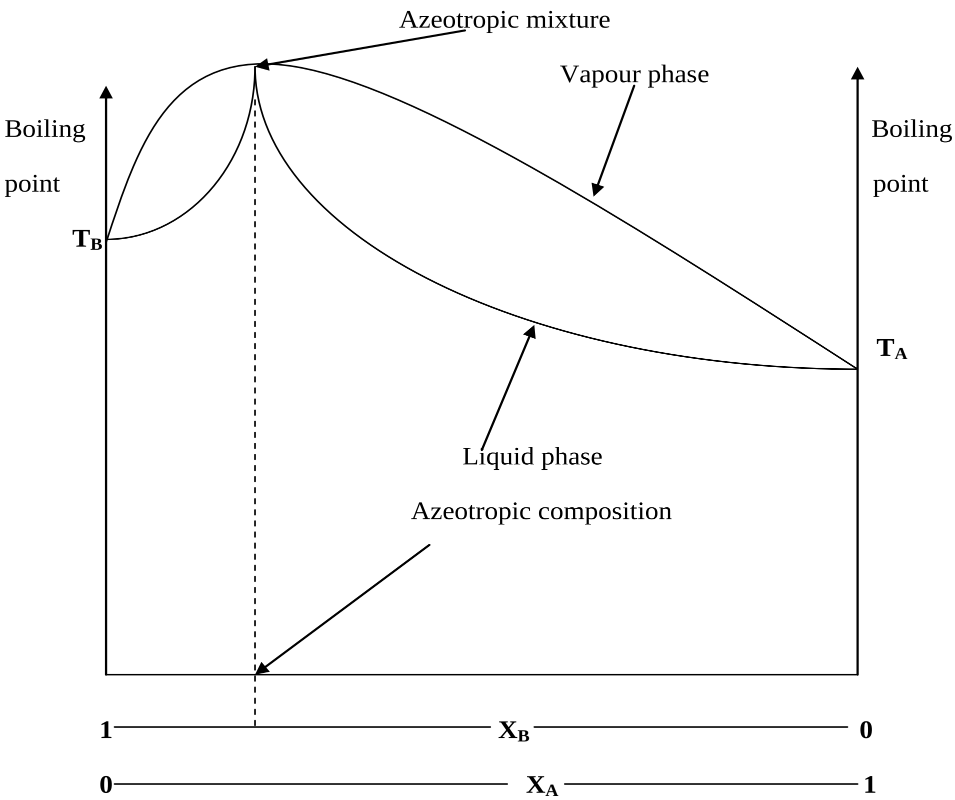
Solution

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.

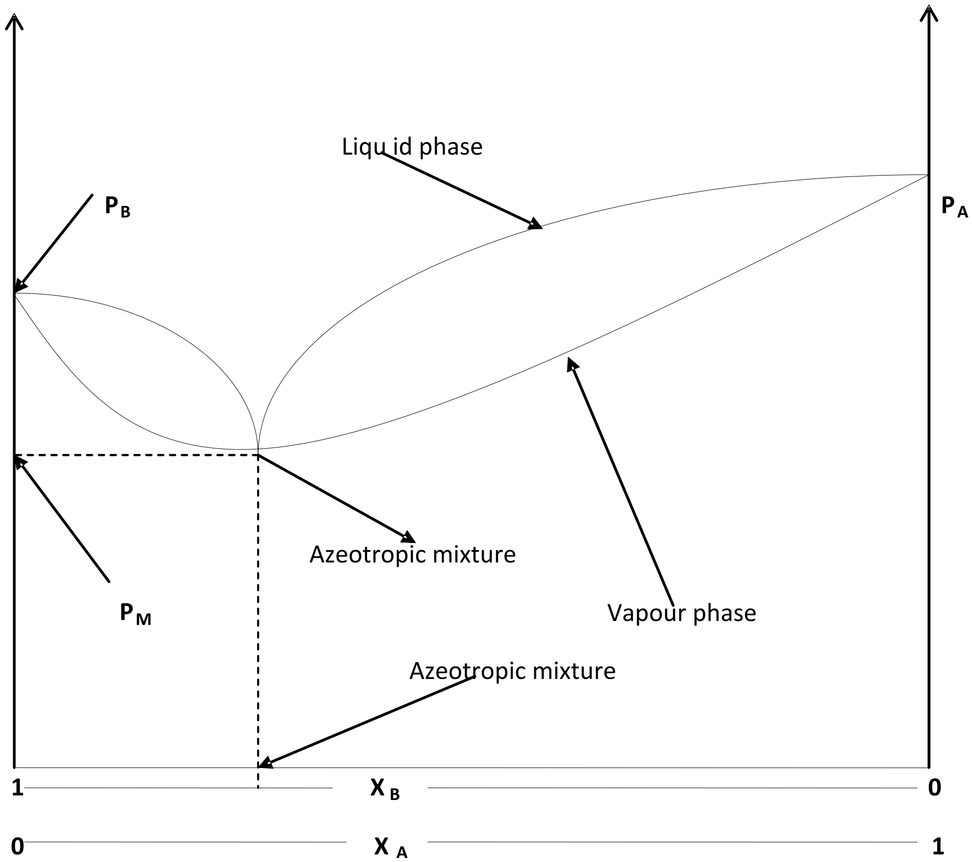
Graph(ii): To illustrate boiling point –composition relation of non ideal solution with negative deviation



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; $\Delta H_{mix} = 0$	02	Heat is absorbed during dissolution; $\Delta H_{mix} > 0$	02	Heat is evolved during dissolution; $\Delta H_{mix} < 0$
03	Total volume of solution is equal to the sum of individual volumes of components; $\Delta V_{mix} = 0$	03	Volume is increased after dissolution; $\Delta V_{mix} > 0$	03	Volume is decreased after dissolution; $\Delta V_{mix} < 0$
04	$P_{soln} = X_A P_A^o + X_B P_B^o$	04	$P_{soln} > X_A P_A^o + X_B P_B^o$	04	$P_{soln} < X_A P_A^o + X_B P_B^o$
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℃, new ternary azeotrope (ethanol-water-benzene azeotrope) with boiling point of about 65℃ (much lower than the original 78℃) 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:

$$\mathrm{CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)}$$

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 $\mathrm{P_A^o}$ and $\mathrm{P_B^o}$. Then their respective partial pressures in the mixture (solution) remain unchanged.

That is partial pressures of A and B in the solution remains $\mathrm{P_A^o}$ and $\mathrm{P_B^o}$ respectively and hence according to Dalton's law of partial pressures: $\mathrm{P_{soln} = P_A^o + P_B^o}$

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℃
- Its decomposition temperature is lower than its boiling temperature, say 140℃
- 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℃ (boiling temperature of **A**) for **A** to be distilled.

- However this temperature is above the decomposition temperature (140℃); 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.

$$P_{mixture} = P_A^o + P_{H_2O}^o$$

- 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℃, say 95℃, 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℃) 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**.

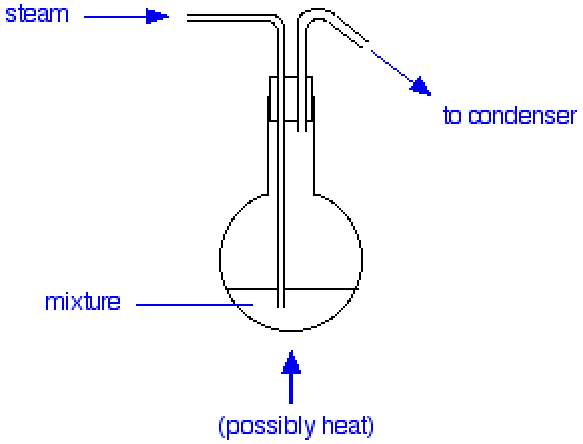


Figure 6.2 Simplified diagram for steam distillation apparatus

Generally, steam distillation is done in preference to ordinary distillation in the following cases:

1) For purification of an organic liquid when the imparities 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 $P_B$respetively in the solution.

Then $P_AV = n_ART$ ………………………………………… (i)

And $P_AV = n_BRT$ ……………………………………….. (ii)

Then taking $\frac{(i)}{(ii)}$ gives

$\frac{P_A}{P_B} = \frac{n_A}{n_B}$ (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: $\mathbf{\frac{m_A}{M_{H_2O}} = \frac{P_A M_A}{P_{H_2O} M_{H_2O}}}$

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 ether 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 (C_6H_5 Br)is 157g/mol.

Let mass percentage of bromobenzene be y

Then mass of water in 100g of the distillate will be $(100-y)$

So using: $\frac{m_b}{m_{H_2O}} = \frac{P_bM_b}{P_{H_2O}M_{H_2O}}$

$$\frac{y}{100-y} = \frac{1.59\times10^4\times157}{8.5\times10^4\times18} = 1.63$$

$y = 163 - 1.63y$ 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℃ 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℃ is 720mmHg. Calculate the relative molecular mass of the aromatic compound.

Solution

Using: $\frac{m_Z}{m_{H_2O}} = \frac{P_ZM_Z}{P_{H_2O}M_{H_2O}}$ or $M_Z = \frac{m_Z\times P_{H_2O}\times M_{H_2O}}{m_{H_2O}\times P_Z}$

But 1 atmosphere = 760mmHg

And at boiling point; total vapour pressure of solution = atmospheric pressure

Then $P_Z + P_{H_2O} = 760$

or $P_Z = 760 - P_{H_2O}$ = (760 – 720) mmHg = 40mmHg

Then $M_Z = \frac{7.4\times720\times18}{25.5\times40}$ g/mol = 94g/mol.

Hence molecular weight of the aromatic compound is 94g/mol.

Example 17

Chlorobenzene which is soluble in water, steam distilled at 91℃ 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

Using $\frac{m_C}{m_{H_2O}} = \frac{P_C M_C}{P_{H_2O} M_{H_2O}}$

But $P_C + P_{H_2O} = 101300$Pa

P_{H_2O} = 101300 - P_C

Then = $\frac{m_c}{m_{H_2O}} = \frac{P_C M_C}{(101300 - P_C) M_{H_2O}}$

Molar mass of chlorobenzene (C_6H_5Cl) is 112.5g/mol

Molar mass of water (H_2O) is 18g/mol.

And it is given that:

Mass of chlorobenzene (m_c) = 23.7g

Mass of water (m_{H_2O}) = 10g

Then $\frac{23.7}{10} = \frac{112.5P_C}{18(101300 - P_C)}$

$$2.37 = \frac{6.25P_C}{(101300 - P_C)}$$

$240081 - 2.37P_C = 6.25P_C$

$P_C = 27851.6P_a$ and $P_{H_2O} = (101300 - 27851.6)P_a = 73448.4P_a$.

Hence the vapour pressure of water is $73448.4P_a$

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

Using $\frac{m_w}{m_c} = \frac{P_w M_w}{P_c M_c}$

Where $P_w = 100 - P_c = (100 - 29)\text{kPa} = 71\text{kPa}$

Substituting $\frac{m_w}{100g} = \frac{71kPa\times18gmol^{-1}}{29kPa\times112.5gmol^{-1}}$

From which $m_w = 39.17g$

Mass of distillate $= m_w + m_c = (39.17 + 100)g = 139.17g$

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℃, 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 Boyles; 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 bottle 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℃ 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.

(i) What will happen to the boiling point of the mixture? Explain.
(ii) 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℃, 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 (℃)	**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℃, 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

(a) Calculate the partial pressure of each component that would be in equilibrium with the solution at 80℃
(b) 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℃. It is virtually insoluble in water

(a) The vapour pressures of water and ethyl benzoate at 50℃ are

Ethylbenzoate	0.2kPa
Water	12.25kPa

(i) What would be the total vapour pressure of an equimolar mixture of the two liquids at 50℃?
(ii) 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℃ 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 ($CH_3CH_2COCH_3$) 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; $0.1MH_2SO_4$ is acidic while $0.1MKOH$ is basic or $0.1MHCl$ is more acidic than $0.1MCH_3COOH$. 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 are 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

	$\mathrm{NaCl(s)}$	$\longrightarrow \mathrm{Na^+(aq)}$	$+\ \mathrm{Cl^-(aq)}$
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 $= (0.1 + 0.1)\mathrm{mol} = 0.2\mathrm{mol}$

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 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:

- $0.1\text{M } Ca(NO_3)_2$ has greater amount of solute in the solution than $0.1\text{M } NaNO_3$ because the former has three ions per formula unit while the latter has two ions per formula unit.
- $0.1\text{M } Ca(NO_3)_2$ 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: $P_{sv} = X_{sv}P^o_{sv}$ (We are applying Raoult's law because the solution is very dilute)

and $P_{su} = X_{su}P^o_{su}$

Where:

P_{sv} and P_{su} are partial vapour pressures exerted in solution by solvent and non-volatile solute respectively.

P^o_{sv} and P^o_{su} 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: $P_{soln} = X_{sv}P^o_{sv} + X_{su}P^o_{su}$

But for non-volatile solute, $P^o_{su} = 0$ (We are using this condition because the solute is non-volatile).

Then $P_{soln} = X_{sv}P^o_{sv}$

But $X_{sv} = 1 - X_{su}$ $(X_{sv} + X_{su} = 1)$

The $P_{soln} = (1 - X_{su})P^o_{sv}$ or $P_{soln} = P^o_{sv} - X_{su}P^o_{sv}$ Or $X_{su}P^o_{sv} = P^o_{sv} - P_{soln}$

But $P^o_{sv} - P_{soln}$ = Lowering in the vapour pressure of the solvent, ΔP

It follows that: $\Delta P = X_{su}P^o_{sv}$

But P^o_{sv} 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: $\Delta P = X_{su}P^o_{sv}$ or $X_{su} = \frac{\Delta P}{P^o_{sv}}$

Where $\frac{\Delta P}{P^o_{sv}}$ 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; $X_{su} = \frac{\Delta P}{P^0_{sv}}$, 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):** $n_{sv} >> n_{su}$

Such that: $n_{sv} + n_{su} \approx n_{sv}$

And it becomes: $X_{su} = \frac{n_{su}}{n_{sv}}$

Thus from: $X_{su} = \frac{\Delta P}{P^0_{sv}}$

It follows that: $\frac{n_{su}}{n_{sv}} = \frac{\Delta P}{P^0_{sv}}$

But $n_{su} = \frac{m_{su}}{M_{su}}$ and $n_{sv} = \frac{m_{sv}}{M_{sv}}$

Then $\frac{n_{su}}{n_{sv}} = \frac{m_{su}M_{sv}}{m_{sv}\times M_{su}} = \frac{\Delta P}{P^0_{sv}}$

Hence: $M_{su} = \frac{m_{su}\times M_{sv}\times P^0_{sv}}{m_{sv}\times \Delta P}$

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^0_{sv} is the vapour pressure of pure solvent

ΔP is the lowering in vapour pressure of solvent in the solution i.e. $\Delta P = P^o_{sv} - P_{soln}$

Example 1

The vapour pressure of 1% urea solution at 38°Cis 49.85mmHg. If the vapour pressure of pure water is 50mmHg and 250mmHg 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} = 49.85mmHg

P^0_{sv} = 50mmHg

So $\Delta P = P^0_{sv} - P_{soln} = (50 - 49.85)mmHg = 0.15mmHg$

Using: $M_{su} = \frac{m_{su}\times M_{sv}\times P^0_{sv}}{m_{sv}\times \Delta P}$

$$M_{su} = \frac{1 \times 18 \times 50}{99 \times 0.15} g/mol = 60.6 g/mol$$

Hence molar mass of urea is 60.6g/mol

At 72°C; $P^0_{sv} = 250\text{mmHg}$

Then: $60.6 = \frac{1\times18\times250}{99\times\Delta P}$

But $\Delta P = P^0_{sv} - P_{soln}$

Or $P_{soln} = P^0_{sv} - \Delta P = (250 - 0.75)\text{mmHg} = 249.25\text{mmHg}$

Therefore, the vapour pressure of 1% urea at 72°C is 249.25mmHg.

Alternative solution

Using: $\frac{\Delta P}{P^0_{sv}} = X_{urea}$

At 38°C: $P^0_{sv} = 50\text{mmHg}$, $P_{soln} = 49.85\text{mmHg}$

So $\Delta P = P^0_{sv} - P_{soln} = (50 - 49.85)\text{mmHg} = 0.15\text{mmHg}$

Then $X_{urea} = \frac{0.15}{50} = 0.003$

At 72˚C: $\Delta P = P^o_{sv}X_{urea}$

Where $P^0_{sv} = 250\text{mmHg}$

Then $\Delta P = 250 \times 0.003\text{mmHg} = 0.75\text{mmHg}$

Using $P_{soln} = P^0_{sv} - \Delta P = (250 - 0.75)\text{mmHg} = 249.25\text{mmHg}$

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 $CO(NH_2)_2$ B: 0.001M AgCl

C: 0.001M$BeCl_2$ D: 0.001M $AlCl_3$

Solution

$\xrightarrow{D < C < B < A}$

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

(a) Compare effect of calcium carbonate and sodium carbonate on vapour pressure of water.
(b) 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

(a) 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.

(b) Using: $\frac{\Delta P}{P^0_{sv}} = X_{su}$

Where $\Delta P = P^o_{sv} - P_{soln}$

And $X_{su} = \frac{n_{su}}{n_{su}+n_{sv}} = \frac{1mol}{(1+3)mol} = \frac{1}{4}$

Then $\frac{P^o_{sv} - P_{soln}}{P^o_{sv}} = \frac{1}{4}$

$4P^o_{sv} - 4P_{soln} = P^o_{sv}$

From which; $3P^o_{sv} = 4P_{soln}$ or $\frac{3}{4} = \frac{P_{soln}}{P^o_{sv}}$

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.

Then: $\Delta T = K_b m$

Where: ΔT is the boiling point elevation in ˚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 $°Ckgmol^{-1}$ or $Kkgmol^{-1}$

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 time the K_b value i.e $10K_b$ or $\mathbf{K_b = \frac{K_{100}}{10}}$

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 °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 $°C\,kg\,mol^{-1}$ or $Kkgmol^{-1}$

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 $\mathbf{K_f = \frac{K_{100}}{10}}$ 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, $C_6H_{12}O_6$ 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 $\Delta T = K_f m$

Where $m = \frac{n_{glucose}}{m_{sv}\ in Kg} = \frac{15}{180 \times 0.05}$ mol/kg

But $\Delta T = 8°C$

Then $8°C = K_f \times \frac{15}{180 \times 0.05}$ mol/Kg

or $K_f = 4.8°Ckgmol^{-1}$

Hence the freezing point depression constant is $4.8°Ckgmol^{-1}$

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 ($K_f = 1.86°Ckgmol^{-1}$)

Solution

Using: $\Delta T = K_f m$

But m = $\frac{n_{su}}{m_{sv}\text{ in kg}} = \frac{n_{su}}{M_{su} \times M_{sv}\text{in kg}}$

Then $\Delta T = \frac{K_f \times m_{su}}{M_{su} \times m_{sv}\text{ in Kg}}$ where $\Delta T = 0^\circ C - (-0.186^\circ C) = 0.186^\circ C$

From which $M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv}\text{ in Kg}} = \frac{1.86 \times 1.125}{0.186 \times 0.125}\text{g/mol} = 90\text{g/mol}$

So molar mass of the organic compound is 90g/mol

Let molecular formula of the compound be $(CHO_2)_n = C_nH_nO_{2n}$

Then $12n + n + 32n = M_r = 90;\ 45n = 90$ or $n = 2$

Hence the molecular formula of the compound is $C_2H_2O_4$

Example 6

Pure ethanol, C_2H_5OH boils at 78.3℃ at pressure of 760mmHg, when 2.51g of methol, $C_{10}H_9OH$ is dissolved in 100g of ethanol, the solution boils at 85.9℃at 760mmHg

(i) Explain why the boiling point of ethanol is raised?
(ii) 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.

$\Delta T = K_b m$ or $K_b = \frac{\Delta T}{m}$

But $\Delta T = (85.9 - 78.3)^\circ C = 7.6^\circ C$

And m = $\frac{m_{methol}}{M_{methol} \times m_{ethanol}\text{ in kg}} = \frac{2.51}{146 \times 0.1}\text{mol/Kg}$

Then $\Delta T = \frac{7.6 \times 146 \times 0.1}{2.51}\ ^\circ C\ mol^{-1}kg = 44.2^\circ C kgmol^{-1}$

Hence the molal boiling point, K_b is $44.2^\circ CKgmol^{-1}$

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 (℃)
Cane sugar $C_{12}H_{22}O_{11}$	0.03	-0.054
Glycerol $C_3H_8O_2$	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: $KBr \rightarrow K^+ + Br^-$ 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 (Mwt $= 62g/mol$, density = 1.11g/cm^3) with two volumes of water.

Given that: K_f of water = $1.86K\ kg^{-1}mol^{-1}$)

Solution

If V is the volume of the glycol in cm^3. The volume of water will be $2Vcm^3$ (one volume of the glycol was mixed with two volume of water).

Using, $m = \rho V$

Mass of the glycol = $1.11g/cm^3 \times Vcm^3 = 1.11Vg$

Mass water = $1g/cm^3 \times 2Vcm^3 = 2Vg$

Number of moles of g the glycol = $\frac{1.11Vg}{62g/mol} = 0.0179Vmol$

Mass of water (solvent) in kg = $\frac{2Vg}{1000g/kg} = 0.002Vkg$

Molality = $\frac{\text{number of moles of solute}}{\text{mass of solvent in kg}} = \frac{0.0179Vmol}{0.002Vkg}$ = 8.95mol/kg

Then $\Delta T = K_f m = 1.86Kkg^{-1}mol^{-1} \times 8.95mol/kg = 16.647K$

Thus the freezing point depression is 16.647K (or °C)

But pure water freezes of 0°C

Hence the freezing point of the antifreeze mixture is $0°C - 16.647°C = -16.647°C$

Example 9

A bottle of wine is $11\% C_2H_5OH$ 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 C_2H_5OH in 100g of solution is 11g

Thus;

Mass of solute (C_2H_5OH)= $11g$

Mass of solvent (Water) = $(100 - 11)g = 89g$

Freezing point depression, $\Delta T = K_f m = \frac{K_f m_{su}}{m_{su} \times m_{sv} \text{in kg}}$

$$\Delta T = \frac{1.86°Ckgmol^{-1} \times 11g}{46gmol^{-1} \times 0.089kg} = 5°C$$

Freezing point of the solution, $T_f = 0°C - \Delta T = 0°C - 5°C = -5°C$

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, $P = \rho hg$).
- **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).

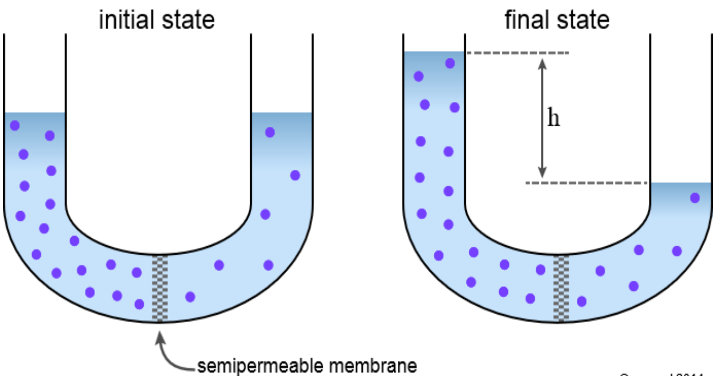


Figure 7.1 Osmosis

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.*

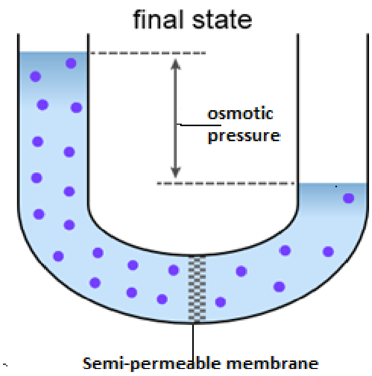


Figure 7.2 Osmotic pressure in terms of hydrostatic pressure

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		**DIFFUSSION**
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 $\pi_1 V_1 = \pi_1 V_2$

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 $\frac{\pi}{T}$ = 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) n gives: $\pi \propto \frac{T}{V}$ Or $\frac{\pi V}{T}$ = constant

And hence $\boldsymbol{\frac{\pi_1 V_1}{T_1} = \frac{\pi_2 V_2}{T_2}}$ (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:

$\frac{\pi_1}{C_1 T_1} = \frac{\pi_2}{C_2 T_2}$ as the concentration, $C \propto \frac{1}{V}$

Also as for gases; it can be shown that: $\boldsymbol{\pi V = nRT}$ or $\boldsymbol{\pi = CRT}$ 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 $\frac{\pi V_1}{\pi V_2} = \frac{n_1 RT}{n_2 RT}$ or $\frac{V_1}{V_2} = \frac{n_1}{n_2}$ ($V \propto n$)

And if $V_1 = V_2 = V$

$\frac{V}{V} = \frac{n_1}{n_2}$ 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	$P \propto \frac{I}{V}$ (Boyle's law)	1	$\pi \propto \frac{I}{V}$ (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	$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ (general equation for gases)	3	$\frac{\pi_1V_1}{T_1} = \frac{\pi_2V_2}{T_2}$ (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 $1dm^3$ of water have an osmotic pressure of $5.15\times 10^5Nm^{-2}$ 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: $m = 35g, R = 8.314, T = 20°C = 293K$

$\pi = 5.15 \times 10^5Nm^{-2}$ and $V = 1dm^3 = 10^{-3}m^3$

$M_r = \frac{35\times8.314\times293}{5.15\times10^5\times10^{-3}}$ g/mol $= 165.56$g/mol.

Hence molar mass of the solute is 165.56g/mol

Example 11

A polysaccharide has the formula $(C_{12}H_{22}O_{11})n$. A solution contains $5g/dm^3$ of the sugar has an osmotic pressure of $7.12\times 10^2Nm^{-2}$ 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: $m = 5g$, $V = 1dm^3 = 1 \times 10^{-3}m^3$ (a concentration of $5g/dm^3$ means the volume of $1dm^3$ contain mass of 5g)

$R = 8.314, T = 20°C = 293K$ and $\pi = 7.12\times 10^2Nm^{-2}$

So: $M_r = \frac{5\times8.314\times293}{7.12\times10^2\times10^{-3}}$ g/mol = 17107g/mol

But the molecular formula of the sugar is $(C_{12}H_{22}O_{11})n$

Then $144n + 22n + 176n = M_r = 17107$ Or $342n = 17107$

$n = 50$

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

From $\pi V = nRT$

$$\pi = \frac{nRT}{V} = \frac{mRT}{M_rV} = \frac{25 \times 8.314 \times 300}{5 \times 10^4 \times 10^{-3}} = 1247.1Pa$$

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

From $\pi V = \frac{m}{M_r}RT$

$M_r = \frac{mRT}{\pi V} = \frac{19.15\times8.314\times293}{136300\times10^{-3}}$ g/mol = 342g/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 PROPERTIESS

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.

$$M_{su} = \frac{m_{su}\times M_{sv}\times P^o_{sv}}{m_{sv}\times\Delta P} \text{ (From lowering of vapour pressure)}$$

$$M_{su} = \frac{K_b\times m_{su}}{\Delta T \times m_{sv} \text{ in Kg}} \text{ (From boiling point elevation)}$$

$$M_{su} = \frac{K_f\times m_{su}}{\Delta T \times m_{sv} \text{ in Kg}} \text{ (From freezing point depression)}$$

$$M_{su} = \frac{m_{su}RT}{\pi V} \text{ (From measured osmotic pressure)}$$

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 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**).

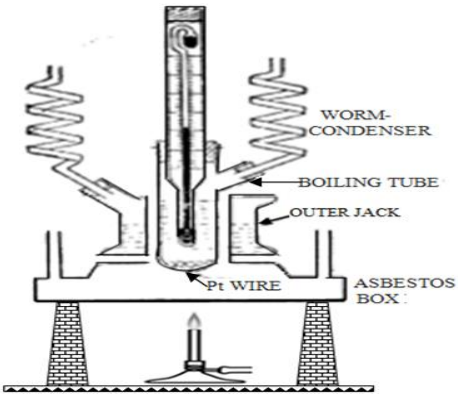


Figure 7.3 Beckmann's boiling point apparatus

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 $\Delta T = \text{Boling point of the solution} - \text{Boiling point of the pure solvent}$

And $M_{su} = \frac{K_b \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}}$

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.

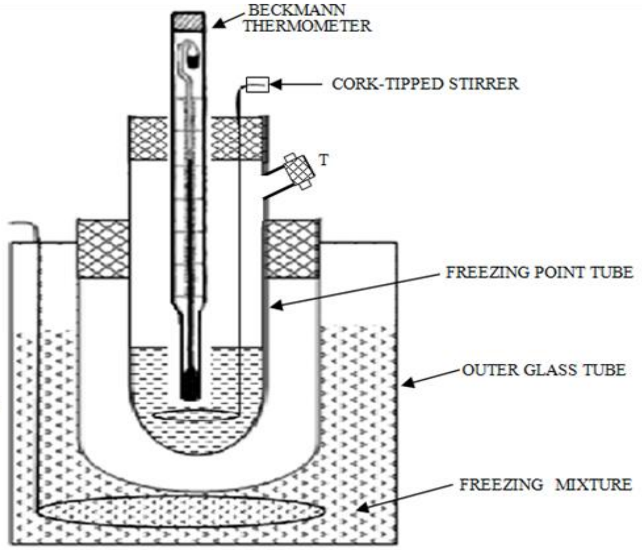


Figure 7.4 Beckmann's freezing point apparatus

Procedures for the determination:

- In an actual determination, weighed quantity($15\text{g} - 20\text{g}$) 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℃ 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:

$$M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}}$$

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℃) 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.

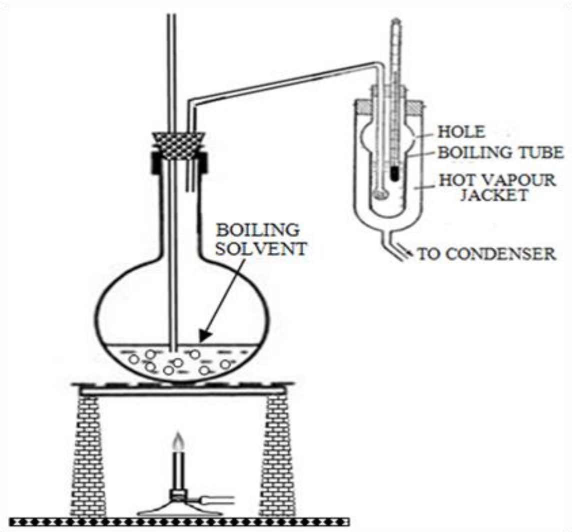


Figure 7.5 Landsberger's boiling point apparatus

Procedure of the determination:

- $5cm^3$ to $7cm^3$ 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:

$$M_{su} = \frac{K_b \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}}$$

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) a 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 is 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:

Van't Hoff factor, $\mathrm{i} = \frac{\text{Observed number of particles}}{\text{Expected number of particles}}$

Thus when a non-volatile solute is dissolved in solution

$\mathrm{i} = \frac{\text{observed number of moles of the solute}}{\text{Expected number of moles of the solute}}$

Since colligative properties varies directly proportional to the number of moles of solute, it follows that: $\mathrm{i} = \frac{\text{observed colligative property}}{\text{Expected colligative property}}$

For lowering in vapour pressure: $\mathrm{i} = \frac{\text{Observed lowering in vapour pressure}}{\text{Expected lowering in vapour pressure}}$

Thus: **Observed lowering in vapour pressure, $\Delta P = i \times$ expected lowering in vapour pressure**

But expected lowering in vapour pressure = $X_{solute}P^{o}_{sv}$

Hence $\Delta P = iX_{solute}\,P^{o}_{sv}$ (In case there is either dissociation or association)

Or $\frac{\Delta P}{P^{o}_{sv}} = \mathrm{i}\,X_{solute}$

Where ΔP the experimental is (observed) lowering in vapour pressure

For boiling point elevation: $\mathrm{i} = \frac{\text{Observed boiling point elevation}}{\text{Expected boiling point elevation}}$

Then: **Observed boiling point elevation, $\Delta T = i \times$ Expected boiling point elevation**

But the expected boiling point elevation = $K_b m$

Hence $\Delta T = \mathrm{i}\,K_b m$

Where ΔT is the observed (experimental) boiling point elevation.

For freezing point depression: $\mathrm{i} = \frac{\text{Observed freezing point depression}}{\text{Expected freezing point depression}}$

Then: **Observed freezing point depression, $\Delta T = i \times$ Excepted freezing point depression**

But excepted freezing point depression = $K_f m$

Hence $\Delta T = \mathrm{i}\,K_f m$

Where ΔT is measured (observed) freezing point depression

For osmotic pressure: $\mathrm{i} = \frac{\text{observed osmotic pressure}}{\text{Expected osmotic pressure}}$

So observed osmotic pressure, $\pi = i \times$ Expected osmotic pressure

But the expected osmotic pressure $= \frac{nRT}{V}$

Hence $\pi = \frac{inRT}{V}$ or $\pi V = inRT$

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,** $\mathbf{g} = \frac{\textbf{observed } \pi}{\textbf{expected } \pi}$

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 iron 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 no 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 $-4.218°C$.

(a) Determine the effective number of particles arising from each Na_2SO_4 formula unit in this solution.
(b) What is the theoretical value of Van't Hoff's factor of the sulphate?
(c) 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) $\Delta T = 0°C - (-4.218°C) = 4.218°C$

Using $\Delta T = iK_f m$;

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.

(b) 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;

$$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}; N = 3$$

Hence theoretical value of Van't Hoff's factor is 3.

(c) 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

From $\pi V = inRT$ or $\pi = \frac{inRT}{V} = iCRT$

$= 3 \times 0.148 \times 0.082 \times 298 = 10.85\text{atm}$

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°C per 1000g of water). Given that: Atomic mass of Sr $= 88$, Cl $= 35.5$

Solution

Observed freezing point depression = $0°C - -0.982°C = 0.982°C$

If $SrCl_2$ was undissociated:

Molar mass of $SrCl_2$ would be 88+71 = 159g/mol

Expected freezing point depression = $K_f m = \frac{k_f \times m_{su}}{M_{su} \times m_{sv} \text{ in Kg}}$

Substituting given values.

Expected freezing point depression

$= \frac{1.86 \times 5.4}{159 \times 0.17}°C = 0.3716°C$

Using: $i = \frac{\text{observed freezing point depression}}{\text{Expected freezing poinht depression}} = \frac{0.982}{0.3716} = 2.64$

One mole of $SrCl_2$ dissociates to give three moles of ions according to the following equation.

$SrCl_2 \rightleftharpoons Sr^{2+} + 2Cl^-; N = 3$

Degree of dissociation is given by: $\alpha = \frac{i-1}{N-1} = \frac{2.64-1}{3-1} = 0.82$ 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

$$n_{Nacl} = \frac{m_{Nacl}}{M_{Nacl}} = \frac{8.5}{58.5} \text{ moles} = 0.1453\text{moles}$$

$$n_{H_2O} = \frac{m_{H_2O}}{M_{H_2O}} = \frac{125}{18} \text{ moles} = 6.9444\text{moles}$$

$$X_{Nacl} = \frac{n_{Nacl}}{n_{Nacl}+n_{H_2O}} = \frac{0.1453}{(0.1453+6.9444)} = 0.02$$

Expected lowering in vapour pressure = $X_{solute}\, P^o_{sv} = X_{Nacl}P_{H_2O}$

$= 0.02 \times 2666Nm^{-2} = 53.32Nm^{-2}$

But observed lowering in vapour pressure = $(2666 - 2567)Nm^{-2} = 99Nm^{-2}$

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:

$$NaCl \rightleftharpoons Na^+ + Cl^-; \; N = 2$$

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?

($K = 5$˚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.

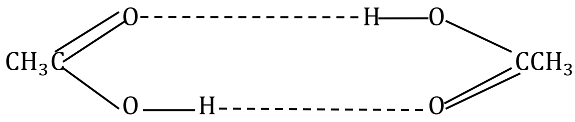
Expected molecular mass of CH_3COOH is $60g/mol$

Using $\Delta T = K_f m = \frac{K_f \times m_{su}}{M_{su} \times m_{sv} \text{ inkg}}$

$$M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}} = \frac{5 \times 0.75}{0.255 \times 0.125} \text{ g/mol} = 118\text{g/mol}$$

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 28350Nm^{-2} at 25°C. Calculate the degree ionisation of methanoic acid at this dilution and temperature.

Solution

Expected osmotic pressure = $\frac{\text{nRT}}{\text{V}}$ but $\frac{\text{n}}{\text{V}} = [\quad]$

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 = 28350Nm^{-2}

$$\text{i} = \frac{\text{observed osmotic presure}}{\text{Exoected osmotic pressure}} = \frac{28350}{24775.72} = 1.144$$

One mole of methanoic acid ionises (dissociates) to produce two moles of ions according to the following equation.

$$\text{HCOOH} \rightleftharpoons \text{HCOO}^- + \text{H}^+;\ \text{N} = 2$$

Then $\alpha = \frac{\text{i}-1}{\text{N}-1} = \frac{1.144-1}{2-1} = 0.144$ 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; $\text{i} = 2$

Using $\pi\text{V} = \text{inRT}$ but n = $\frac{\text{m}}{\text{M}_\text{r}}$

Then $\pi\text{V} = \text{i}\frac{\text{m}}{\text{M}_\text{r}}\text{RT}$ or $\text{M}_\text{r} = \frac{\text{imRT}}{\pi\text{V}}$

Where: $\text{m} = 5\text{g}, \text{R} = 0.082, \text{T} = 25°\text{C} = 298\text{K}$

$\pi = 25\text{torr} = \frac{25}{760}\text{atm}$ and $\text{V} = 100\text{mL} = 0.1\text{dm}^3$

$$\text{M}_\text{r} = \frac{2\times5\times0.082\times298}{\frac{25}{760}\times0.1}\text{g/mol} = 74285\text{g/mol}$$

Hence molar mass of the solute is 74285g/mol.

Example 21

2g of benzoic acid (C_6H_5COOH) 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: $\Delta T = iK_f m$

But m = $\frac{n_{su}}{m_{sv}\text{ in kg}} = \frac{m_{su}}{M_{su}\times m_{sv}\text{in kg}}$

Then $\Delta T = \frac{i\times K_f\times m_{su}}{M_{su}\times m_{sv}\text{ in kg}}$

From which i = $\frac{\Delta T\times M_{su}\times m_{sv}\text{ in kg}}{K_f\times m_{su}} = \frac{1.62\times 122\times 0.025}{4.9\times 2} = 0.5042$

Benzoic acid ionises according to the following equation:

$$C_6H_5COOH \rightarrow C_6H_5COO^- + H^+; N = 2$$

Then $\alpha = \frac{i-1}{\frac{1}{N}-1} = \frac{0.5042-1}{\frac{1}{2}-1} = 0.9916$ 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)

And number of moles of water $= \frac{1000g}{18gmol^{-1}} = 55.5556mol$

$$M_r = \frac{1mol}{(1 + 55.5556)mol} = 0.01768$$

Using $\Delta P = X_{su}P^o_{sv} = 0.01768 \times 12.3kPa = 0.22kPa$

Then $P^o_{soln} = P^o_{sv} - \Delta P = (12.3 - 0.22)kPa = 12.08kPa$

Hence the vapour pressure of the solution is 12.08kPa

Example 23

A 5% solution (by mass) of cane sugar ($M_r = 342g/mol$) in water has freezing point of 271K. What will be the freezing point of 5% glucose ($M_r = 192g/mol$) in water if freezing point of pure water is 273.15K?

Solution

$\Delta T = (273.15 - 271)K = 2.15K$

$m_{su} = 5g, m_{sv} = (100 - 5)g = 95g = 0.095kg$

Using $\Delta T = K_f m = K_f \times \frac{m_{su}}{M_{su}\times m_{sv}\text{in kg}}$

From which $K_f = \frac{\Delta T\times M_{su}\times m_{sv}\text{in kg}}{m_{su}}$

Then $\frac{\Delta T_s\times M_s\times m_{sv}\text{in kg}}{m_s} = \frac{\Delta T_g\times M_g\times m_{sv}\text{in kg}}{m_g}$

Substituting $\frac{2.15K\times 342gmol^{-1}\times 0.095kg}{5g} = \frac{\Delta T_g\times 192g/mol\times 0.095kg}{5g}$

From which; $\Delta T_g = 3.83K$

Hence the freezing point will be $(273.15 - 3.83)K = 269.32K$

Example 24

The boiling point of an aqueous solution is 101.21 °C. What is the freezing point? ($K_f = 1.86°Ckgmol^{-1}, K_b = 0.52°Ckgmol^{-1}$)

Solution

Using $\Delta T = K_b m$ or $m = \frac{\Delta T}{K_b}$

But boiling point of pure water is $100°C$.

And thus $\Delta T = (101.21 - 100)°C = 1.21°C$

Then $m = \frac{1.21°C}{0.52°Ckgmol^{-1}} = 2.33mol/kg$

Then using $\Delta T = K_f m = 1.86°Ckgmol^{-1} \times 2.33mol/kg = 4.33°C$

But freezing point of pure water is $0°C$.

Thus freezing point of the solution= $0°C - 4.33°C = -4.33°C$

Hence the freezing point is $-4.33°C$.

Example 25

At 286 K, 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 1.12 g/mL and $K_f = 1.86°Ckgmol^{-1}$)?

Solution

Using $\pi V = nRT$ or $\pi = \frac{nRT}{V} = CRT$

From which $C = \frac{\pi}{RT} = \frac{9.97}{0.082 \times 286} mol/L = 0.4251mol/L$

Using $m = \rho V$;

Mass of the solution in 1L (1000mL) $= 1.12\ g/mL \times 1000mL = 1120g$

Using $m = nM_r$;

Mass of the solute (glucose) in 1L of the solution

$$= 0.4251mol \times 180g/mol = 76.518g$$

Thus mass of solvent (water) in 1L of the solution

$$= (1120 - 76.518)g = 1043.482g = 1.043482kg$$

Then molality of the solution= $\frac{0.4251mol}{1.043482kg} = 0.4074mol/kg$

It follows that; $\Delta T = K_f m$

$$= 1.86°Ckgmol^{-1} \times 0.4074mol/kg = 0.76°C$$

But freezing point of pure water is $0°C$

Hence freezing point of the solution= $0°C - 0.76°C = -0.76°C$

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.

(a) Calculate molality of benzoic acid.
(b) What is the molal freezing point constant (K_f) of the solvent?
(c) What will be the K_f value if the molality found in (a) above is doubled?

Solution

(a) Molality $= \frac{n_{su}}{m_{sv}\text{ in kg}} = \frac{m_{su}}{M_{su}\times m_{sv}\text{in kg}}$

$$= \frac{0.235\text{g}}{122\text{g/mol} \times 0.01245\text{kg}} = 0.1547\text{mol/kg}$$

Molality of benzoic acid is 0.1547mol/kg

(b) Using $\Delta T = K_f m$;

From which $K_f = \frac{\Delta T}{m} = \frac{6.55℃}{0.1547\text{mol/kg}} = 42.34℃\text{kg/mol}$

The molal freezing point constant is $42.34℃\text{kg/mol}$.

(c) The K_f value will not change and will remain to be $42.34℃\text{kg/mol}$ (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. ($K_f = 1.86℃/m$)

Solution
Using $m = \rho V$;

Mass of the acid $= 1.06\text{g/mL} \times 0.6\text{mL} = 0.636\text{g}$

And mass of water $= 1\text{g/mL} \times 1000\text{mL} = 1000\text{g} = 1\text{kg}$

Using $\Delta T = K_f m = K_f \times \frac{m_{su}}{M_{su}\times m_{sv}\text{in kg}}$

From which; $M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv}\text{in kg}} = \frac{1.86\times 0.636}{0.0205\times 1}\text{g/mol} = 57.7\text{g/mol}$

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.

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:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+; N = 2$$

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:

(a) Molar mass of the solute.
(b) Vapour pressure of water at 298K.
(c) Why vapour pressure increased after further addition of 18g of water?

Solution

Using; $M_{su} = \frac{m_{su}\times M_{sv}\times P^{o}_{sv}}{m_{sv}\times \Delta P}$ where $\Delta P = P^{o}_{sv} - P_{soln} = P^{o}_{sv} - 2.8$

Before further addition of 18g of water.

$$M_{su} = \frac{30 \times 18 \times P^{o}_{sv}}{90 \times (P^{o}_{sv} - 2.8)} \ldots\ldots\ldots\ldots\ldots\ldots (i)$$

After further addition of 18g of water.

$$M_{su} = \frac{30 \times 18 \times P^{o}_{sv}}{108 \times (P^{o}_{sv} - 2.9)} \ldots\ldots\ldots\ldots\ldots\ldots (ii)$$

Equating (i) and (ii) gives;

$$\frac{30 \times 18 \times P^{o}_{sv}}{90 \times (P^{o}_{sv} - 2.8)} = \frac{30 \times 18 \times P^{o}_{sv}}{108 \times (P^{o}_{sv} - 2.9)}$$

From which $P^{o}_{sv} = 3.4\text{kPa}$

Substituting $P^{o}_{sv} = 3.4\text{kPa}$ in (i) gives;

$$M_{su} = \frac{30 \times 18 \times 3.4}{90 \times (3.4 - 2.8)}\text{g/mol} = 34\text{gmol}$$

Hence:

(a) Molar mass of the solute is 34g/mol and
(b) The vapour pressure of water is 3.4kPa
(c) 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

(a) Silver chloride is a non-volatile material, but does not dissolve in water. What effect will it have on the boiling point of water?
(b) Calculate the osmotic pressure of solution obtained by mixing 100cm^3 of 0.25M solution of urea and 100cm^3 of solution of 0.1M solution of cane sugar at 293K.

Solution

(a) 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) Using $M_3 = \frac{M_1V_1+M_2V_2}{V_1+V_2} = \frac{100\times0.25+100\times0.1}{100+100} = 0.175\text{M}$

Thus molarity of the solution containing solutes mixture is 0.175M

Using $\pi = [\quad]RT = 0.175 \times 0.082 \times 298\text{atm} = 4.3\text{atm}$

The osmotic pressure is 4.3atm.

Example 30

A 1.60g sample of a mixture of naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$) is dissolved in 20.0g benzene (C_6H_6). 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

$\Delta T = 5.51°C - 2.81°C = 2.7°C$

$\Delta T = K_f m = K_f \times \frac{n_{su}}{m_{sv}\text{ in kg}}$

From which; $n_{su} = \frac{\Delta T\times m_{sv}\text{ in kg}}{K_f} = \frac{2.7\times0.02}{5.12} = 0.01\text{mol}$

Let mass of naphthalene be n
Then mass of anthracene will be $1.6-\mathrm{n}$
Then using $\mathrm{n}=\frac{\mathrm{m}}{\mathrm{M_r}}$;
Number of moles of naphthalene $=\frac{\mathrm{n}}{128}$
Number of moles of anthracene $=\frac{1.6-\mathrm{n}}{178}$
It follows that: $\mathrm{n_{su}}=0.01=\frac{\mathrm{n}}{128}+\frac{1.6-\mathrm{n}}{178}; 23.04=50\mathrm{n}$
From which $\mathrm{n}=0.4608$ and $1.6-\mathrm{n}=1.6-0.4608=1.1392$
$\%\text{naphthalene}=\frac{0.4608\mathrm{g}}{1.6\mathrm{g}}\times 100\%=28.8\%$
$\%\text{anthracene}=\frac{1.1392\mathrm{g}}{1.6\mathrm{g}}\times 100\%=71.2\%$
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 $C_2H_4(OH)_2$
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, $C_6H_8O_6$) 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℃, 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℃, how many grams of water are present in the sample? K_f (2-methyl-2-propanol) = 4.68℃/m.

Question 15

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?
(c) At what temperature will the solution freeze? ($K_f = 1.86℃/m$)

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.

(i) What is the main aim of salting the road?
(ii) 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.

(i) Isotonic solutions at given temperature have the same boiling point elevation and freezing point depression.
(ii) Two different solutions with the same effective molality in the solution exhibit the same boiling point elevation.
(iii) 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$= 180\text{g/mol}$

Molar mass of cane sugar$= 342\text{g/mol}$

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 ($\text{Mwt} = 342\text{g/mol}$) at $20°\text{C}$

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 $27°\text{C}$

Question 32

Determine the osmotic pressure of a solution prepared by dissolving 25mg of K_2SO_4 in 2L of water at $25°\text{C}$, assuming that is completely dissociated

Question 33

An aqueous solution of nitrous acid (HNO_2) freezes at $-0.198°\text{C}$. 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°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 °C, what is the concentration of the solute within the solution in mole fraction? Vapour pressure of pure water at 25.0 °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 as 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; $$\mathbf{K_d} = \frac{\text{Concentration of the solute in the first solvent}}{\text{Concentration of the solute in the second solvent}} \ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

$$\mathbf{K_d} = \frac{\text{Concentration of the solute in the upper layer}}{\text{Concentration of the solute in the lower layer}} \ldots\ldots\ldots\ldots\ldots\ldots.. \text{(ii)}$$

Qualitatively, the partition coefficient gives relative solubility of the solute in the given solvents. So from equation (i), if $\mathbf{K_d}$ is large then the solute is more soluble in the first solvent and vice versa. For example, if $\mathbf{K_d}$ is 5, it means that the solute is 5 times more soluble in the first solvent than in the second solvent.

That is;

$$\frac{\text{concetration of solute in first solvent}}{\text{concentration of solute in second solvent}} = \frac{\text{solubility of solute in first solvent}}{\text{solubility of solute in second solvent}} = K_d$$

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.

$$K_d = \frac{\text{[solute] in the first solvent}}{\text{[solute] in the second solvent}}$$

But $\text{[solute]} = \frac{\text{mass concentration of solute}}{\text{molar mass of the solute}}$

It follows that:

$$K_d = \frac{\frac{\text{mass concentration of solute in the first solvent}}{\text{molar mass of the solute}}}{\frac{\text{mass concentration of solute in the second solvent}}{\text{molar mass of the solute}}}$$

$$= \frac{\text{mass concentration of solute in the first solvent}}{\text{mass concentration of solute in the second solvent}}$$

Hence: $K_d = \frac{\text{mass concentration of solute in the first solvet}}{\text{mass concentration of solute in the second solvent}}$

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.

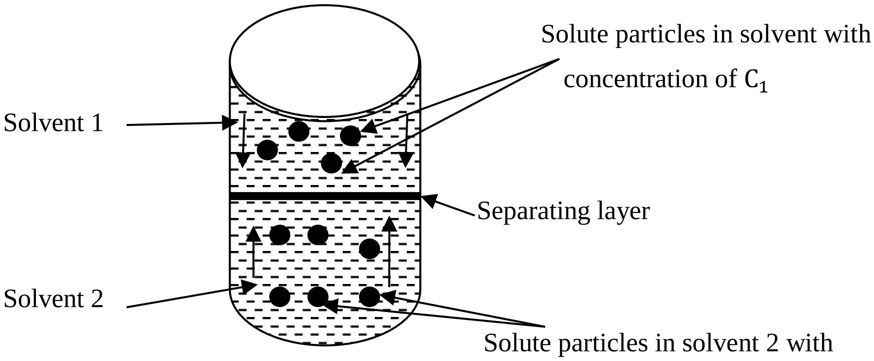


Figure 8.1 Distribution of solute in two immiscible solvents

The rate of diffusion of solute particles from one solvent to another in 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 $R_1 = K_1C_1 \ldots\ldots\ldots\ldots\ldots\ldots$ (i) (K_1 is the constant for proportionality)

And $R_2 \propto C_2$ or $R_2 = K_2C_2 \ldots\ldots\ldots\ldots\ldots\ldots$ (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: $K_1C_1 = K_2C_2$ 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 **d**istribution 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:

$$K_d = \frac{\text{Concentration of the solute in the extractive solvent}}{\text{Concentration of the solute in the residue solution}} \dots \dots \dots \dots \dots \dots \text{(iii)}$$

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, $\mathbf{K_d}$ should be large ($\mathbf{K_d}$>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.

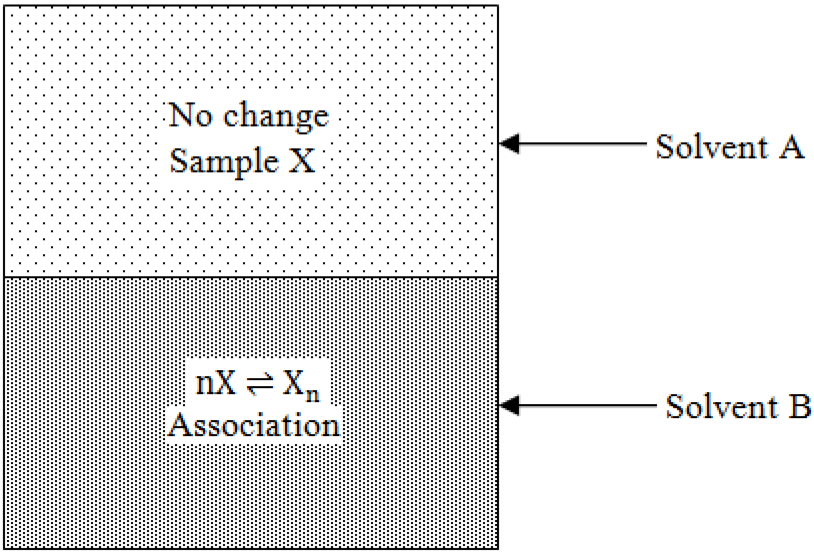


Figure 8.2 Distribution of solute in immiscible solvents with association of the solute in one of the solvents

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:

$\frac{C_1}{C_3} = K_d$……………………………………………………………… (i)

Also considering the equilibrium: $nX \rightleftharpoons X_n$

$$K_c = \frac{[X_n]}{[X]^n} = \frac{C_2}{(C_3)^n}$$

Or $(C_3)^n = \frac{C_2}{K_c}$

From which, $C_3 = \sqrt[n]{\frac{C_2}{K_c}}$ ………………………………………….(ii)

Substituting (ii) in (i) gives: $\frac{C_1}{\sqrt[n]{\frac{C_2}{K_c}}} = K_d$

Or $\frac{C_1 \times \sqrt[n]{K_c}}{\sqrt[n]{C_2}} = K_d$ 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

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:

$$\mathbf{K} = \frac{\mathbf{C_1}}{\sqrt[n]{\mathbf{C_2}}}$$

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.

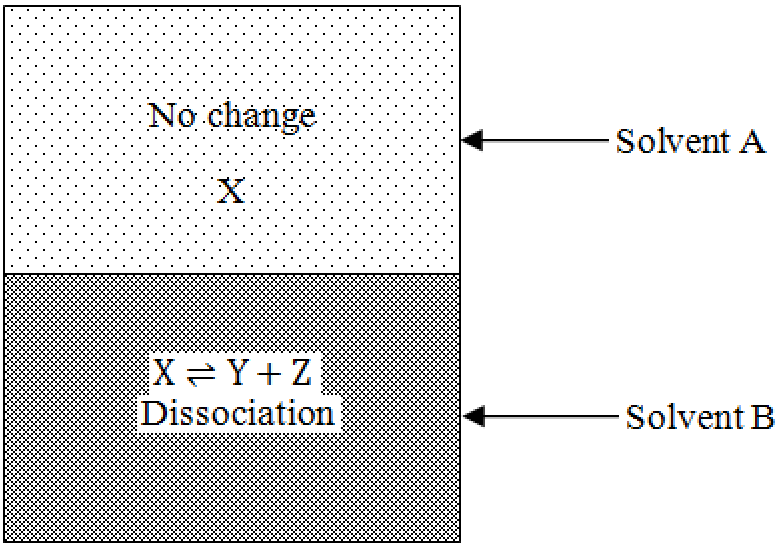


Figure 8.3 Distribution of solute in immiscible solvents with dissociation of the solute in one of the solvents

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:

	X	$\rightleftharpoons$	Y	$+$	Z
At equilibrium	$1-\alpha$		α		α

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;

$\mathbf{K_d} = \frac{\mathbf{C_1}}{\mathbf{C_2(1-\alpha)}}$ where $\boldsymbol{\alpha}$ 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 250 cm^3 in volume and contains 1g of Z. What is the partition coefficient of Z between ethoxyethane and water?

Solution

$\mathbf{K_d} = \frac{\text{Concentration of the solute in ethoxyethane (first solvent)}}{\text{Concentration of the solute in the water (second solvent)}}$

Then $\mathbf{K_d} = \frac{4g/50cm^3}{1g/250cm^3} = 20$

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 50 cm^3 of ethoxyethane and 500 cm^3 of water. On titration, 25 cm^3 of ethoxyethane layer required 22.5 cm^3 of 1 mol dm^{-3} sodium hydroxide solution while 25 cm^3 of the aqueous layer required 9 cm^3 of 0.1 mol dm^{-3} sodium hydroxide. Calculate the partition coefficient for the acid between ethoxyethane and water.

Solution

Equation for the neutralisation reaction: $RCOOH + NaOH \rightarrow RCOONa + H_2O$

From which $n_a = 1, \ n_b = 1$

Using $\frac{M_aV_a}{M_bV_b} = \frac{n_a}{n_b}$ But $n_a = n_b$

Then $M_aV_a = M_bV_b$ Or $M_a = \frac{M_bV_b}{V_a}$

For organic (ethoxyethane) layer:

$Va = 25cm^3, M_b = 1M$ and $V_b = 22.5cm^3$

Then $M_a = \frac{1 \times 22.5}{25} M = 0.9M$

For aqueous layer:

$V_a = 25cm^3, M_b = 0.1M$ and $V_b = 9cm^3$

Then $M_a = \frac{0.1 \times 9}{25} M = 0.036$

$$K_d = \frac{[\text{Acid] in organic layer}}{[\text{Acid] in aqueous layer}} = \frac{0.9}{0.036} = 25$$

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 dm^3

In CCl_4	17.50	15.80	13.20	6.50
In H_2O	0.200	0.180	0.150	0.075

(a) Calculate the distribution constant of iodine between these two solvents.
(b) What is the effect of shaking $1\ dm^3$ of water containing 0.3g of iodine with $10\ cm^3$ 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_2O/gdm^{-3}	0.200	0.180	0.150	0.075
$K = \frac{\text{Concentration of } I_2 \text{ in } CCl_4}{\text{Concentration of } I_2 \text{ in } H_2O}$	87.500	87.778	88.000	86.667

$$K_d = \frac{87.500 + 87.778 + 88.000 + 86.667}{4} = 87.486$$

(a) Hence the partition coefficient of Iodine between carbon tetrachloride and water is 87.486.
(b) Let mass of iodine extracted in CCl_4 be x.

Then mass of iodine left in water will be $0.3 - x$

So $87.486 = \frac{x/10}{0.3 - x/1000} = \frac{100x}{0.3 - x}$; $\quad x = 0.14g$ And $0.3 - x = 0.16g$

So iodine will distribute itself in the two solvents, such that 0.14g will be found in organic (CCl_4) 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 $1\ dm^3$ of an aqueous solution containing 25g by shaking with $100\ cm^3$ of trichloromethane?

Solution

The extractive solvent is trichloromethane ($CHCl_3$)

Let mass of x extracted in grams be y

Then mass of x which remains in the residue solution will be $25 - y$

Using:

$$K_d = \frac{\text{Concentration of X in } CHCl_3}{\text{Concentration of X in } H_2O}$$

But $K_d = 12$ (X is 12 times more soluble in $CHCl_3$ than in H_2O)

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.

(i) Calculate the partition coefficient for iodine between the organic solvent and water.
(ii) 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

$$K_d = \frac{[\text{Iodine}] \text{ in organic solvent}}{[\text{Iodine}] \text{ in water}} = \frac{0.01M}{0.004M} = 2.5$$

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 $0.0004 - a$

Thus $2.5 = \frac{\frac{a}{50}}{\frac{0.0004-a}{100}}; \; a = 0.00022$

Then $[\text{Iodine}]$ in organic solvent $= \frac{0.00022\text{mol}}{50\times10^{-3}\text{L}} = 0.0044M$

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:

(i) 100 cm^3 of ethoxyethane
(ii) Two successive portions of 50 cm^3 of ethoxyethane
(iii) 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;

That is $K_d = \frac{\text{Concentration of A in ethoxyethane}}{\text{Concentration of A in water}} = 90$

(i) Let mass of A extracted in grams be x

Then: $90 = \frac{x/_{100}}{5-x/_{500}} = \frac{5x}{5-x}$

$95x = 450, x = 4.74g$

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

Then $90 = \frac{m_1/50}{5-m_1/500} = \frac{10m_1}{5-m_1}$

$100m_1 = 450, m_1 = 4.5g$

Mass of A remained after the first extraction $= 5 - m_1 = (5 - 4.5)\ g = 0.5g$

Let mass of A extracted in the second extraction be m_2

Then $90 = \frac{m_2/50}{0.5-m_2/500} = \frac{10m_2}{0.5-m_2}$

$100m_2 = 45, m_2 = 0.45$

Total mass extracted $= m_1 + m_2 = (4.5 + 0.45)\ g = 4.95g$

Hence mass of A extracted by two successive portions of 50 cm^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:

$$\mathbf{W_r = W_o\left(\frac{V_b}{V_b + K_d V_a}\right)^n}$$

Where: $\mathbf{W_r}$ is the mass of solute which remain in residue solution after **n** extractions.

$\mathbf{W_o}$ is the original mass of the solute before extraction

$\mathbf{V_b}$ is the volume of residue solution

$\mathbf{V_a}$ is the volume of an extraction solvent used in each extraction (experiment)

n is the number extractions.

$\mathbf{K_d}$ is the partition coefficient obtained **according to the equation (iii)**

And in this question:

$\mathbf{W_o} = 5g$, $\mathbf{V_b} = 500cm^3$, $\mathbf{Va} = 50cm^3$, $\mathbf{K_d} = 90$ and $\mathbf{n} = 2$

Then $W_r = 5\left(\frac{500}{500+(50\times90)}\right)^2 = 0.05g$

Mass of A extracted after two extractions $= \mathbf{W_o} - W_r = (5 - 0.05)\ g = 4.95g$

Hence mass of A extracted by two successive portions of 50 cm^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 $\mathbf{K_d}$ (equation (iii) in **page 180** must be used). **If the extractive solvent is the lower layer and the given $\mathbf{K_d}$ is found according to equation (ii), the 'required' $\mathbf{K_d}$ is the reciprocal of the given $\mathbf{K_d}$.** 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:

$$K_d = \frac{\frac{W_o - W_1}{V_a}}{\frac{W_1}{V_b}}$$

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;

$K_d = \frac{V_b(W_o - W_1)}{V_a W_1}$ 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 $W_1(V_a K_d + V_b) = V_b W_o$

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;

$$W_2 = \frac{V_b W_1}{V_a K_d + V_b}$$

But $W_1 = \frac{V_b W_o}{V_a K_d + V_b}$;

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

Then $W_3 = \frac{V_b W_2}{V_a K_{d} + V_b} = \left(\frac{V_b}{V_a K_{d} + V_b}\right) W_o \left(\frac{V_b}{V_a K_{d} + V_b}\right)^2$

$= W_o \left(\frac{V_b}{V_a K_{d} + V_b}\right)^3$

Thus $W_3 = W_o \left(\frac{V_b}{V_a K_{d} + V_b}\right)^3$

For nth extraction;

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 secrete of extracting **M** from the petrol by using solvent **S**. The partition coefficient of M between petrol and S is 0.01

(a) What are the conditions necessary for the partition of the solute between the given solvents to remain constant?
(b) 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 50cm^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) $W_r = W_o\left(\frac{V_b}{V_b+K_dV_a}\right)^n$ .... (1)

The partition coefficient of **M** between petrol and **S** $= \frac{\text{Concentration of }\mathbf{M}\text{ in petrol}}{\text{Concentration of }\mathbf{M}\text{ in }\mathbf{S}} = 0.01$

But the extractive solvent is **S**, and the equation (1) requires **S** on numerator in K_d expression.

So the required $K_d = \frac{\text{Concentration of }\mathbf{M}\text{ in }\mathbf{S}}{\text{Concentration of }\mathbf{M}\text{ in petrol}} = \frac{1}{0.01} = 100$

So the useful K_d is 100.

First case: By using one portion of 100cm^3

$W_o = 5g, V_b = 1000cm^3, V_a = 100cm^3, K_d = 100, n = 1$

$$W_r = 5\left(\frac{1000}{1000 + (100 \times 100)}\right)^1 = 0.45g$$

Mass of **M** removed = $W_o - W_r = (5 - 0.45)g = 4.55g$

Second case: By using two 50 cm^3 portions of **S**

$W_o = 5g, V_b = 1000cm^3, V_a = 100cm^3, K_d = 100, n = 2$

$$W_r = 5\left(\frac{1000}{1000 + (100 \times 50)}\right)^2 = 0.14g$$

Total mass of **M** removed= $W_o - W_r = (5 - 0.14)g = 4.86g$

Alternative solution:

Given that: $K_d = \frac{\text{Concentration of }\mathbf{M}\text{ in petrol}}{\text{Concentration of }\mathbf{M}\text{ in }\mathbf{S}} = 0.01$

1st case:

By using one portion of $100cm^3$ of **S**

Let mass of **M** extracted by extractive solvent **S** be y

Then mass of **M** which remain in petroleum will be $5 - y$

Then $0.01 = \frac{5-y/_{1000}}{y/_{100}} = \frac{5-y}{10y}$ or $y = 4.55g$

Hence mass of **M** removed is 4.55g

2nd case:

By using two $50cm^3$ portions of **S**

Let mass of **M** extracted in the first extraction be m_1

Then $0.01 = \frac{5-m_1/1000}{m_1/50} = \frac{5-m_1}{20m_1}$

From which $m_1 = 4.17g$

Mass of **M** remained after first extraction $= 5 - m_1 = (5-4.17)\ g = 0.83g$

Let mass of **M** extracted in the second extraction be m_2

Then $0.01 = \frac{0.83-m_2/1000}{m_2/50} = \frac{0.83-m_2}{20m_2}$ or $m_2 = 0.69g$

Total mass of **M** extracted $= m_1 + m_2 = (4.17+0.69)g = 4.86g$

Example 8

If 10g of acid is dissolved in the mixture of $100cm^3$ of water and $100cm^3$ of ether. Calculate:

(i) The amount of acid extracted by $100cm^3$ of ether in one extraction only.
(ii) The amount of acid extracted by using four consecutive extractions of $25cm^3$ in each extraction.

Given that: $\frac{[\text{Acid}]\text{in water}}{[\text{Acid}]\text{ in ether}} = 0.2$

Solution

$W_r = W_o\left(\frac{V_b}{V_b+K_dV_a}\right)^n$ .... (1)

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.

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 $100cm^3$

$W_o = 10g, V_b = 100cm^3, V_a = 100cm^3, K_d = 5, n = 1$

$$W_r = 10\left(\frac{100}{100+(5\times 100)}\right)^1 = 1.7g$$

Mass of acid removed $= W_o - W_r = (10-1.7)g = 8.3g$

(i) The amount extracted by one extraction only is 8.3g

Second case: By using two 50 cm^3 portions of ether

$W_o = 10g, V_b = 100cm^3, V_a = 25cm^3, K_d = 5, n = 4$

$$W_r = 10\left(\frac{100}{100+(5\times 25)}\right)^4 = 0.4g$$

Total mass of acid removed$= W_o - W_r = (10-0.4)g = 9.6g$
(ii) 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 $\frac{C_1}{\sqrt{C_2}}$ = 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℃ and the zinc removed? (At 800℃ the solubility of silver in a given mass of zinc is 300 time 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 siver 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 xkg

Then mass of silver left in lead will be $(20 - \text{x})$kg

It follows that: $300 = \frac{{}^{x}/_{50}}{{}^{20-x}/_{1000}} = \frac{20x}{20-x}$, x $= 18.75$kg

Mass of silver extracted by zinc $= 18.75$kg

Thus mass of silver left in lead $= (20 - 18.75)$ kg $= 1.25$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 dm^3 of an aqueous solution containing 25g by shaking with 100 cm^3 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 $K_d = \frac{\text{Concentration of iodine in carbon disulphide}}{\text{Concenration of iodine in water}}$

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.

(i) In terms of intermolecular forces, explain why the shaking was different.
(ii) What is your expectation on the amount of time required for the liquid mixture to form the separating layer? Explain.
(iii) 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.

(i) What term is given to represent the process explained above?
(ii) What role does ether play in this process?
(iii) What features do ether possess that make it to fit that role (in (ii) above)?
(iv) Give at least other three substances which may substitute ether.

Question 13

Mr. Akilikubwa reported the following results for the distribution of acetic acid (CH_3CH_2COOH) 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 4.412gL^{-1}. The solubility of iodine in water at 25°C is 0.34gL^{-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 22.3mL of 0.01MHCl and the water layer requiring 13.6mL of 0.2MHCl for complete neutralisation. Find K_d for ammonia between silane and water.

Question 16

18g of compound **X** distribute themselves between water and equal volume of an immiscible solvent **Y** so that 2g of **X** are in water. Calculate to the nearest integer, the percentages **X** left in 1000cm^3 of water containing 1g of **X** are extracted by one litre of **Y**.

Question 17

An aqueous solution of succinic acid at 15°C, containing 0.07g in 10ml is in equilibrium with an ether solution which has 0.013g in 10ml. 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 0.024g in 10ml?

Question 18

An aqueous solution contains 10g of solute per litre. When 1litre of the solution is treated with 100mL of ether; 6g of the solute are extracted. How much more of the solute would be extracted from the aqueous solution by further 100mL 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

$100cm^3$ of a $0.15moldm^{-3}$ solution of aqueous methylamine was shaken with $75cm^3$ of an organic solvent at $25℃$ and left in the separating funnel to allow an equilibrium to be established. Only $50cm^3$ of the aqueous layer was run off and titrated against $0.225moldm^{-3}$ dilute hydrochloric acid with an end point of $14.1cm^3$ 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.
- (i) Azeotropes are compounds and not mixtures.
- (ii) Raoult's law of ideal solutions is applicable both to the liquid and vapour phase compositions.

(b)
- (i) Is the aqueous methanol solution ideal or non-ideal solution? Explain.
- (ii) 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 from 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.
- (i) Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg.
- (ii) 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)
- (i) 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.
- (ii) 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).
- (i) What is the vapour pressure of the resulting solution?
- (ii) 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. It 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 2×10^5Pa. When one more mole of B is added to the solution, the vapour pressure of the solution is 2.1×10^5Pa.
 (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℃ 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℃. 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℃. Calculate the percentage by mass of nitrobenzene in the distillate when the mixture is distilled at 1.013×10^5Pa given that the vapour pressure of water at 99℃ is 9.749×10^4Pa.

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.

That is $K_d = \frac{\text{concentration of acid in ether}}{\text{concentration of acid in water}} = 3$

A volume of 1000cm^3 of ether is available for the use in the extraction process. Two experiments were performed to extract acid from water. In the first experiment, 1000cm^3 of ether was used once in single extraction. In the second experiment, two extractions were performed, each using 500cm^3 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℃ at 760mmHg. The vapour of water at 91℃ 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/cm^3).

Question 23

(a)

(i) Identify whether the mixture of nitric acid and water shows positive or negative deviation from Raoult's law.
(ii) 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

(i) Use the above result to deduce whether phenol exists in normal state or dimerises in chloroform
(ii) 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'**:

(i) Associate in solvent **A** and remain normal in solvent **B**
(ii) Dissociate in solvent **A** and associate in solvent **B**
(iii) 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_2O 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 $1dm^3$ of tetrachloromethane and 2 dm^3 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 $50cm^3$ of tetrachloromethane and $50cm^3$ of water. $25cm^3$ of aqueous layer required $4.5cm^3$ 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) A vapour- composition curve for the solution of liquid **A** and **B**
(b) A temperature –composition curve for the solution of liquids **A** and **B**
(c) 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 ($CH_3CH_2CH_2OH$) were determined at various compositions, with the following data collected at 45°C:

X_{H_2O}	**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 $500 dm^3$ of an aqueous solution of uranium salt has been extracted with $200 dm^3$ 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:

$$\frac{(\text{Concentration of } \mathbf{X} \text{ in } \mathbf{Y})}{(\text{Concentration of } \mathbf{X} \text{ in } \mathbf{Z})} = \text{a constant}$$

   (i) What name is given to the constant.
   (ii) For $\mathbf{X} =$ phenylamine, $\mathbf{Y} =$ water and $\mathbf{Z} =$ ethoxyethane the value of the constant is 0.20. Calculate the mass of phenylamine extracted into the ethoxyethane layer when $100 cm^3$ of water containing 20g of phenylamine per dm^3 is treated with $100 cm^3$ 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:
   (i) Partition coefficient of the solute G between pentan-1-ol and water.
   (ii) Mass of the solute G which remained in the aqueous solution after a further shaking with 100 cm^3 of pentan-1-ol.

Question 33

Ethyl benzoate is liquid with a boiling point of 213℃. It is virtually insoluble in water

(a) The vapour pressures of water and ethyl benzoate at 50℃ are

Ethylbenzoate	0.2kPa
Water	12.25kPa

   (i) What would be the total vapour pressure of an equimolar mixture of the two liquids at 50℃?
   (ii) 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℃ 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:
   (i) Ideal solution
   (ii) Non-ideal solution with negative deviation
   (iii) Non-ideal solution with positive deviation
   (iv) Solid solution

(b) A solution consists of 3.88g benzene, C_6H_6, and 2.45g toluene , $C_6H_5CH_3$. 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?
   (i) The concentration of the solution.
   (ii) The forces between the particles in the solution.

(b) The vapour pressure of water at 95℃ is 635mmHg. A water insoluble organic liquid **X**, of relative molecular mass 160, steam distills at 95℃ 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:
   (i) Ideal solution is the solution which obeys Raoult's law.
   (ii) Non-ideal solution with positive deviation are warm to touch.

(b) Chlorobenzene which is soluble in water, steam distills at 91℃ 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℃.

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.

(i) How is vapour pressure related to intermolecular forces?
(ii) Why in measurement of vapour pressure, temperature must be '**given**'?
(iii) 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?

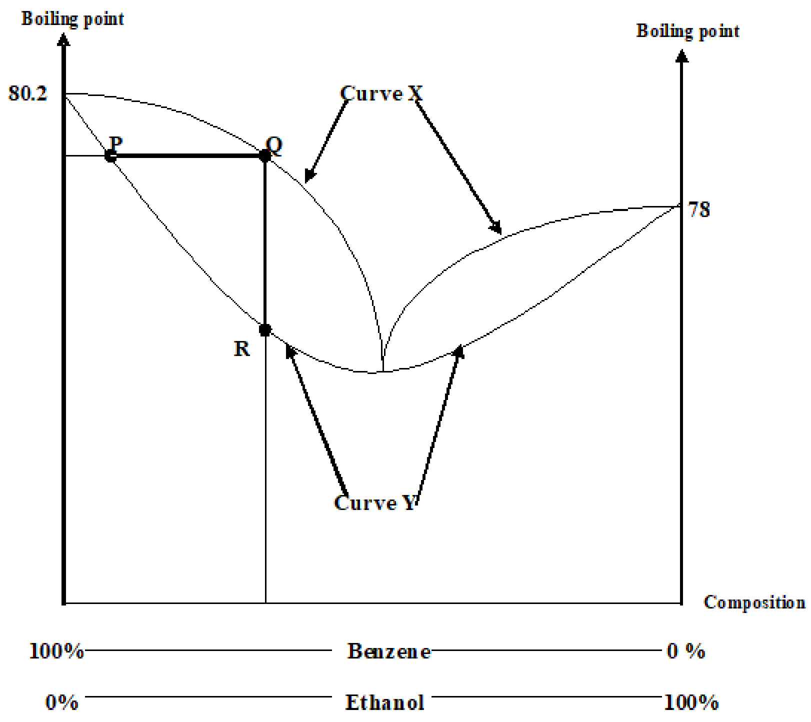
Question 39

(a) On your own words, give the meaning the following terms:
(i) Saturated vapour pressure
(ii) Azeotropic point
(iii) Ideal solution

(b) Ethanol and water form an azeotropic mixture which boils at 78.1℃ with 95.6% ethanol. The boiling point of pure ethanol and water are 78.4℃ and 100℃ respectively.
(i) Draw a temperature-mole fraction phase diagram of ethanol-water solution.
(ii) What happens when a solution of less than 50% ethanol is boiled?
(iii) 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.



(a) What do the curves **X** and **Y** represent?
(b) What is the relation between **P**, **Q** and **R**
(c) 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. ($K_f = 1.86°C kg mol^{-1}$).

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, $C_6H_{12}O_6$, is dissolved in 1kg of water in a saucepan. At what temperature will water boil at 1atm? K_b for water is $0.52 K kg mol^{-1}$.

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? ($K_f = 1.86°C kg mol^{-1}$)

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 ($K_f = 1.86°C kg mol^{-1}, K_b = 0.52°C kg mol^{-1}$)

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 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

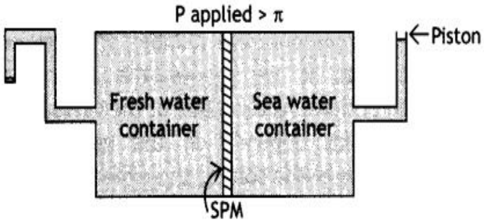
(a) Show that for very dilute solutions, molality ≅ molarity.
(b) A solid mixture contains $MgCl_2$ and NaCl. When 0.5g of this mixture is dissolved in enough water to form 1.0L of solution, the osmotic pressure at 25.0°C is observed to be 0.399atm. What is the mass percent of $MgCl_2$ in the solid?

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.



(i) Name and define the process occurring in the above plant.
(ii) To which container does the net flow of solvent take place?
(iii) What does SPM stand for?
(iv) Name one SPM which can be used in this plant.
(v) Give the main practical use of the plant.

(b) A solution containing 8.6g per litre of urea (Mwt=60g/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

(a) Why the boiling point 0.1m$BaCl_2$ solution is more than 0.1mNaCl solution?
(b) 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

(a) 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?
(b) 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℃ is 23.8mmHg.

Question 52

(a) Magnesium chloride is dissolved in water to make the solution in which its concentration is 0.1M.
(i) What is the theoretical value of Van't Hoff's factor of $MgCl_2$ in aqueous solution?
(ii) Explain why the value mentioned in (i) above cannot be realized in practice.
(iii) Explain what can be done to make the experimental value of Van't Hoff's factor of $MgCl_2(aq)$ to approach the theoretical value.
(b) 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

(a) The vapour pressure of water at 25℃ 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.
(b) The osmotic pressure of solution containing 0.2g of the monobasic acid **B** per litre was 94.6mmHg at 15℃ while a solution of 4g of **B** in 100g of benzene depressed freezing point of that solvent by 2.13℃. If an aqueous solution of **B** containing 0.5g required 10.9cm^3 of IM sodium hydroxide for neutralisation. What conclusion can you make about the state of **B** in water and benzene? (K_f of benzene is 49℃ per 100g)

Question 54

(a) Assuming the price per kilogram is the same:
(i) Which is a better salt to use for deicing wintry roads—NaCl or $MgCl_2$? Why?
(ii) Would magnesium chloride be an effective deicer at a temperature of −8°C?
(b) A solution of calcium nitrate contains 15g of anhydrous salt in 1000g of water freezes at −0.435℃. Calculate the degree of dissociation of the salt.

Given that: Freezing point constant for water, $K_f = 1.86°C kg mol^{-1}$

Question 55

(a) List the following solutions in order of increasing melting point:

$$0.1\text{m sugar}, 0.1\text{mNaCl}, 0.08\text{m } CaCl_2, 0.04\text{m}Na_2CO_3$$

(b) The freezing point of pure benzene was found to be 5.481°C. A solution of 0.321g hydrocarbon naphthalene ($C_{10}H_8$) 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 AB_2 or A_2B. 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) CH_3COOH dissolved in water.
   (ii) CH_3COOH dissolved in benzene.
   (iii) $CO(NH_2)_2$ dissolved in water.
(b) How many grams of urea ($(NH_2)_2CO$) 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 ($C_{12}H_{10}$) in 75.00g of benzene (C_6H_6). (The boiling point of benzene is 80.1°C and boiling point constant is $2.53°\text{Ckg/mol}$).

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 $BaCl_2$ per litres was found to be 3.2atm at 15°C. Calculate the apparent degree of dissociation of $BaCl_2$ 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 6dm^3 of water. What mass of ethylene glycol ($C_2H_6O_2$) 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 $= 1.86°\text{Ckg mol}^{-1}$)

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 $C_6H_{12}O_6$)

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, $C_{12}H_{22}O_{11}$, in water has a vapour pressure of $2311Nm^{-2}$ at 20°C. Pure water at this temperature has a vapour pressure of 2333 Nm^{-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 ($K = 0.52°C$ per 1000g of water).

Question 66

(a) List down four uses of freezing point depression.
(b) Calculate the relative molecular mass of benzene acid on the basic of the following experimental results: Mass of ethanol 16.150g.

Boiling Point/°C	Mass of benzoic acid dissolved/g
78.100	-
78.230	0.2400
78.360	0.4727
78.505	0.7470

$K = 1.07°C$ per 1000g of ethanol

Question 67

(a) Between $0.1MBaCl_2$ and $0.1MCaCl_2$ 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, $C_3H_8O_3$, 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℃.What mass of this compound in 250cm^3 of solution would give an osmotic pressure of 10 atmospheres at 10℃.

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℃. Calculate the relative molecular mass of the acid. At what temperature would you expect this solution to freeze? ($\text{K} = 1.86℃\text{kg/mol}$).

Question 72

(a) What do the following laws say?
  (i) Van't Hoff's law of osmotic pressure
  (ii) 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.
  (i) Mention three colligative properties apart from osmotic pressure.
  (ii) State two methods which employ colligative properties in the molar mass determination.
  (iii) In the determination of molar mass, is it better to use diluted or concentrated solution? Explain.
  (iv) 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℃ and 20℃ 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:
  (i) Meat can be classified as fresh (not frozen) even though it is stored at −1 ℃. Why wouldn't meat freeze at this temperature?
  (ii) 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℃ . 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:

$$0.01MC_2H_5OH, 0.01MBa_3(PO_4)_2, 0.01MNa_2SO_4, 0.01MKCl, 0.01MLi_3PO_4$$

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? ($K = 1.86°Ckg/mol$ 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 ($C_2H_6O_2$) 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? ($K = 5°C$ 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 freezing? (K_f of water $= 1.8°Ckg/mol$)

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 $K_b = 0.512°Ckgmol^{-1}$.
(Show your work clearly including manipulation of units).

Question 82

(a)
 (i) Is molarity or molality dependent on temperature? Explain your answer.
 (ii) 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 $1.891 \times 10^4 Nm^{-2}$. Calculate the approximate molecular mass of the solute given that, the vapour pressure of water at 60°C is $1.992 \times 10^4 Nm^{-2}$. Show your work clearly including manipulation of units.

Question 83

(a)
 (i) Why is the observed freezing point for electrolyte commonly less than the calculated value?
 (ii) 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:
 (i) Boiling point of water rise due to addition of table salt.
 (ii) 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 = $1.86°Cm^{-1}$)

Question 86

(a) Calculate the freezing point of a solution of 22.5g of cane sugar ($C_{12}H_{22}O_{11}$) 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 = $1.86°Ckgmol^{-1}$)

Question 87

(a) Calculate the boiling point and freezing point of a solution that is $3.725mCaCl_2$ in ethanol from the following data:

Solvent	Normal freezing point (°C)	Normal boiling point (°C)	$K_f(°Ckgmol^{-1})$	$K_b(°Ckgmol^{-1})$
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 $1.071gcm^{-3}$ 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 = $1.86°Ckgmol^{-1}$

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.

(i) Determine empirical formula of the organic solid.
(ii) Determine molecular formula of the organic solid.

Question 90

(a) Colligative properties are very useful in determination of molar mass of non-volatile solutes.
 (i) What is the non-volatile solute?
 (ii) 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?
(b) 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:
0.010mNa_3PO_4 in water
0.020m$CaBr_2$ in water
0.020mKCl in water
0.020MHF in water

(a) Complete the following table for the above solutions:

Solution	**Van't Hoff factor,i**	**Effective molality of solute,m**
0.010mNa_3PO_4		
0.020m$CaBr_2$		
0.020mKCl		
0.020mHF		

(b) Which solution(s) would have the same boiling point as 0.040m$C_6H_{12}O_6$ in water?
(c) Which solution(s) would have the lowest freezing point?
(d) Which solution(s) would have highest vapour pressure 30°C?
(e) Which solution(s) would have nearly the same osmotic pressure as 0.020m$C_6H_{12}O_6$ in water?

Question 92

(a) Explain what is mostly likely to happen when cucumber is placed in a concentrated salt solution.
(b) 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.

(a) Calculate the freezing point of a solution containing 651g of ethylene glycol in 2505 g of water.
(b) 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

(a) Does seawater boil at the same temperature as distilled water? If not, which has the higher boiling point? Explain your answer.
(b) 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°C. (The normal freezing point of benzene is 5.50°C and the molal freezing point depression constant, K_f for benzene is $5.12°C/molal$)

(a) Determine the empirical formula of the unknown substance.
(b) Using the data gathered from the freezing point depression method, calculate the molar mass and hence molecular formula of the unknown substance.
(c) Calculate the mole fraction of benzene in the solution described above.
(d) The vapour pressure of pure benzene at 35°C is 150mmHg.Calculate the vapour pressure of benzene over the solution described above at 35°C .

Question 96

(a) The boiling point of diethyl ether is 34.6°C. Would this compounds be considered non-volatile? Give reason.
(b) 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

(a) 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?
(b) Vapour pressure of CCl_4 at 25°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

(a) Colligative properties are very special physical property of the solution. They are very special in different perspective; from their origin to their useful application.
 (i) List down three things which make colligative properties special.
 (ii) Mention at least four properties of solution which are **not** regarded as colligative properties.
(b) 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

(a) 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?
(b) 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°C.
 (i) Calculate the osmotic pressure of a 4.0% aqueous NaCl solution at 25°C.
 (ii) 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°C?

Question 100

(a) 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°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°C. If a mixture of 1.00g of an unknown compound with 100.0g of biphenyl has a melting point of 68.86°C, what is the molar mass of the unknown compound?

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 1kg/dm^3.That is 1kg of solvent is contained in 1dm^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) 4.505×10^{-2}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) 1.5×10^{-3}% (ii) 1.26×10^{-4}m

10. 3.22g

9. 4m

11. 8.764×10^{-4} 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. 1.6×10^{-4}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$= 455.55\text{torr}$; Partial vapour pressure of A in the solution $= 256.2\text{torr}$

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 $100℃$ 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℃

Hint:

A liquid starts to boil when its vapour matches the atmospheric pressure (in this case, 1atm)

$P_{soln} = X_{Acetone}\ P^{\circ}_{Acetone} + X_{water}P^{\circ}_{water} = 1atm$

Then calculate mole fraction of each component from the given data get:

$X_{Acetone} = {}^{1}/_{3}$; $X_{water} = {}^{2}/_{3}$

This gives: $1atm = {}^{1}/_{3}\, P^{\circ}_{Acetone} + {}^{2}/_{3}\, P^{\circ}_{water}$

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℃

That is ${}^{1}/_{3} \times 2.12 + {}^{2}/_{3} \times 0.456 = 1.01atm$

41. (a) $P_{Benzene} = 406torr$; $P_{Toluene} = 133torr$ (b) 540torr (c) $X_{Benzene} = 0.75$; $X_{Toluene} = 0.25$

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: $P_{benzene} = X_{benzene}P^{\circ}_{benzene}$

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; $P_{benzene} < X_{benzene}P^{\circ}_{benzene}$

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℃, 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℃(normal boiling point of water)
- The combined water and ethyl benzoate vapour pressure reach 101.325kPa at temperature less than 100℃ (boiling point of immiscible liquid mixture is less than either of the two components) and hence the mixture must boil somewhere between 99℃ and 100℃.

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. 0.10m $C_2H_4(OH)_2$ > 0.10m KNO_3 > 0.10m $BaCl_2$ > 0.10m Na_3PO_4

$\xrightarrow{\text{Decrease in freezing point}}$

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

13. 69.6g/mol.

14. 0.35g

15. (a) 17.95m (b)9.1M (c) $-33.4℃$

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 elevation 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 $A = 25.59\text{amu}$**;** Atomic mass of $B = 42.64\text{amu}$

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. $100.24℃$

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 $= 18.75\text{g}$

Mass of X remained in water layer $= (25 - 18.75)\text{g} = 6.25\text{g}$

Using $K_d = \frac{\text{Concentration of X in } CHCl_3}{\text{Concentration of X in } H_2O}$

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
2) Chloroform
3) Hexane
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 ($K_d > 1$).

EXAMINATION QUESTIONS SOLUTIONS

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; $P_{soln} = X_{CP}^{L}P_{CP}^{o} + X_{CH}^{L}P_{CH}^{o}$ (Mixture of cyclopentane and cyclohexane is ideal solution).

Where $X_{CP}^{L} = \frac{1}{1+3} = 0.25$

And $X_{CH}^{L} = 1 - X_{CP}^{L} = 1 - 0.25 = 0.75$

Substituting: $P_{soln} = 0.25 \times 331\text{mmHg} + 0.75 \times 113\text{mmHg} = 167.5\text{mmHg}$

Then $X_{CP}^{V} = \frac{X_{CP}^{L}P_{CP}^{o}}{P_{soln}} = \frac{0.25 \times 331\text{mmHg}}{167.5\text{mmHg}} = 0.494$

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 $P_A = X_AP_A^o$ and $P_B = X_BP_B^o$. 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 $P_{soln} = X_AP_A^o + X_BP_B^o$

(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 $m = n \times M_r = 0.8\text{mol} \times 32\text{gmol}^{-1} = 25.6\text{g} = 0.0256\text{kg}$

The molality $= \frac{n_{su}}{m_{sv}\text{ in kg}} = \frac{0.2\text{mol}}{0.0256\text{ kg}} = 7.8125\text{mol/kg}$

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 $P_{soln} = X_X^LP_X^o + X_Y^LP_Y^o$

For the first case;

$$550\text{mmHg} = \left(\frac{3\text{mol}}{3\text{mol} + 1\text{mol}}\right)P_X^o + \left(\frac{1\text{mol}}{3\text{mol} + 1\text{mol}}\right)P_Y^o$$

From which;

$$\frac{3}{4}P_X^o + \frac{1}{4}P_Y^o = 550 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\text{(i)}$$

For the second case;

$560\text{mmHg} = \left(\frac{4\text{mol}}{4\text{mol} + 1\text{mol}}\right) P_X^o + \left(\frac{1\text{mol}}{4\text{mol} + 1\text{mol}}\right) P_Y^o$

From which;

$\frac{4}{5}P_X^o + \frac{1}{5}P_Y^o = 560 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. \text{(ii)}$

Solving the two equations above gives;

$P_X^o = 600\text{mmHg}$ and $P_Y^o = 400\text{mmHg}$

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 $P_{soln} = X_P^L P_P^o + X_H^L P_H^o$

But $X_H^L = 1 - X_P^L$

It follows that; $P_{soln} = X_P^L P_P^o + (1 - X_P^L)P_H^o$

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

$n_A = \frac{100\text{g}}{140\text{gmol}^{-1}} = 0.7143\text{mol}$

$n_B = \frac{1000\text{g}}{180\text{gmol}^{-1}} = 5.5556\text{mol}$

Using; Mole fraction, $X = \frac{n}{n_T}$

$X_A = \frac{0.7143\text{mol}}{(0.7143 + 5.5556)\text{mol}} = 0.114$

And $X_B = 1 - X_A = 1 - 0.114 = 0.886$

Assuming the solution obeys Raoult's law;

$P_{soln} = X_A P_A^o + X_B P_B^o$

Then 475= $0.114P_A^o + 0.886 \times 500$

From which $P_A^o = 281\text{torr}$

And $P_A = X_A P_A^o = 0.114 \times 281\text{torr} = 32\text{torr}$

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 weakens 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;

$P_{soln} = X_A P_A^o + X_B P_B^o$

But $X_B = 1 - X_A$

Then $P_{soln} = X_A P_A^o + (1 - X_A)P_B^o$

Substituting $600 = 450X_A + (1 - X_A) \times 700$

From which $X_A = 0.4$ or 40% and $X_B = 1 - 0.4 = 0.6$ or 60%

Hence liquid composition by mole is 40%A and 60%B

$X_A^V = \frac{X_A P_A^o}{P_{soln}} = \frac{0.4 \times 450mmHg}{600mmHg} = 0.3$ or 30%

And $X_B^V = 1 - X_A^V = 1 - 0.3 = 0.7$ 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.

Thus $P_{soln} = X_B P_B^o + X_T P_T^o$; where $X_T = 1 - X_B$

Substituting $0.83 = 1.1X_B + (1 - X_B) \times 0.7$

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

$= \frac{X_B P_B^o}{P_{soln}} = \frac{0.375 \times 1.1atm}{0.83atm} = 0.497$ 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 $m = nM_r$;

Mass of benzene $= 0.497mol \times 78gmol^{-1} = 38.766g$

Mass of toluene $= 0.503mol \times 92gmol^{-1} = 46.276g$

%benzene by mass$= \frac{m_b}{m_{total}} = \frac{38.766g}{(38.766+46.276)g} = \frac{38.766g}{85.042g} \times 100\% = 45.58\%$

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 $= 25mL \times 0.63g/mL = 15.75g$

Mass of hexane $= 45mL \times 0.66g/mL = 29.7g$

Then using; $n = \frac{m}{M_r}$

Number of moles of pentane, $n_P = \frac{15.75g}{72gmol^{-1}} = 0.21875mol$

Number of moles of hexane, $n_H = \frac{29.7g}{86gmol^{-1}} = 0.34535mol$

Using; Mole fraction, $X = \frac{n}{n_T}$

$X_P = \frac{0.21875mol}{(0.21875 + 0.34535)mol} = 0.3878$

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;

Thus $P_{soln} = X_P P_P^o + X_H P_H^o$

Substituting: $P_{soln} = 0.3878 \times 511mmHg + 0.6122 \times 150mmHg = 289.9958mmHg$

$X_P^V = \frac{X_P P_P^o}{P_{soln}} = \frac{0.3878 \times 511mmHg}{289.9958mmHg} = 0.68$

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 $\frac{m_Q}{m_w} = \frac{P_Q M_Q}{P_w M_w}$

Where $P_Q = 100900Pa - P_w = (100900 - 94300)Pa = 6600Pa$

Substituting $\frac{m_Q}{m_w} = \frac{6600Pa \times 120gmol^{-1}}{94300Pa \times 18gmol^{-1}} = 0.4666$

From which percentage of Q $= \left(\frac{0.4666}{0.4666+1}\right) \times 100\% = 31.8\%$

And percentage of water is $(100 - 31.8)\% = 68.2\%$

Hence the composition of distillate is 31.8% and 62.8% 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.

Thus $P_{soln} = X_M^L P_M^o + X_P^L P_P^o$

But $X_M^L = 1 - X_P^L$

It follows that; $P_{soln} = X_P^L P_P^o + (1 - X_P^L)P_M^o$

Substituting $174 = 44.6X_P^L + (1 - X_P^L)303$

From which $X_P^L = 0.499$ or 49.9%

And $X_M^L = 1 - 0.499 = 0.501$ 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 $P_{soln} = X_A P_A^o + X_B P_B^o$

Substituting: $P_{soln} = 0.8x + 0.2y$

$X_A^V = \frac{X_A P_A^o}{P_{soln}} = \frac{0.8x}{0.8x+0.2y}$ and $X_B^V = \frac{X_B P_B^o}{P_{soln}} = \frac{0.2y}{0.8x+0.2y}$

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, $X_T^V = 1 - X_B^V = 1 - 0.65 = 0.35$

Using $X_T^V = \frac{X_T^L P_T^o}{P_{soln}}$

From which $0.35 = \frac{0.7X_T^L}{P_{soln}}$……………………….(i)

But the mixture of benzene and toluene forms ideal solution and therefore it obeys Raoult's law.

Thus $P_{soln} = X_T^L P_T^o + X_B^L P_B^o$; where $X_B^L = 1 - X_T^L$

It follows that: $P_{soln} = X_T^L P_T^o + (1 - X_T^L)P_B^o$……………..(ii)

Substituting (ii) to (i);

$$0.35 = \frac{0.7X_T^L}{X_T^L P_T^o + (1 - X_T^L)P_B^o}$$

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 $P_{soln} = X_A^L P_A^o + X_M^L P_M^o$

But $X_M^L = 1 - X_A^L$

It follows that; $P_{soln} = X_A^L P_A^o + (1 - X_A^L) P_M^o$

But at the boiling point, vapour pressure of the solution is equal to the external pressure.

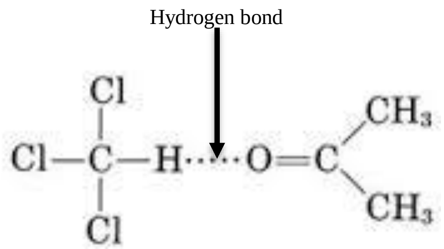
Thus $0.248\text{atm} = 0.342X_A^L + 0.188(1 - X_A^L)$

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, $P_M' = X_M^L P_M^o$

Substituting $P_M' = 0.305 \times 96\text{torr} = 29.28\text{torr}$

Hence vapour pressure of methyl alcohol is 29.28torr

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, $X = \frac{n}{n_T}$

Mole fraction of dichloroethane, $X_{DC} = \frac{0.03\text{mol}}{(0.03 + 0.05)\text{mol}} = 0.375$

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;

Thus $P_{soln} = X_{DC}P_{DC}^o + X_{DB}P_{DB}^o$

Substituting:

$P_{soln} = 0.375 \times 133\text{torr} + 0.625 \times 11.4\text{torr} = 57\text{torr}$

$X_{DC}^{V} = \frac{X_{DC}P_{DC}^{o}}{P_{soln}} = \frac{0.375 \times 133\text{torr}}{57\text{torr}} = 0.875$

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 2×10^5Pa to 2.1×10^5Pa)

(ii) Since the solution is ideal; $P_{soln} = X_A P_A^o + X_B P_B^o$

Initially:

$X_A = \frac{n_A}{n_A + n_B} = \frac{1\text{mol}}{(1+2)\text{mol}} = \frac{1}{3}$ and $X_B = 1 - \frac{1}{3} = \frac{2}{3}$

Then $2 \times 10^5 = \frac{1}{3} P_A^o + \frac{2}{3} P_B^o$……………….(i)

After addition of one mole of B:

$n_B = (1 + 2)\text{ mol} = 3\text{mol}$

$X_A = \frac{n_A}{n_A + n_B} = \frac{1\text{mol}}{(1+3)\text{mol}} = \frac{1}{4}$ and $X_B = 1 - \frac{1}{4} = \frac{3}{4}$

Then $2.1 \times 10^5 = \frac{1}{4} P_A^o + \frac{3}{4} P_B^o$……………….(ii)

Solving (i) and (ii) simultaneously gives:

$P_A^o = 1.2 \times 10^5\text{Pa}$ and $P_B^o = 2.4 \times 10^5\text{Pa}$

Question 17

(a) Raoult's law relates the partial vapour pressure of a particular component in ideal solution to its mole fraction.

(b) Using; $n = \frac{m}{M_r}$

Number of moles of heptane, $n_H = \frac{5.32\text{g}}{86\text{gmol}^{-1}} = 0.06186\text{mol}$

Number of moles of octane, $n_O = \frac{8.8\text{g}}{114\text{gmol}^{-1}} = 0.07719\text{mol}$

Using; Mole fraction, $X = \frac{n}{n_T}$

$X_H = \frac{0.06186\text{mol}}{(0.06186 + 0.07719)\text{mol}} = 0.4449$

And $X_O = 1 - X_O = 1 - 0.4449 = 0.5551$

Since the solution is ideal, it obeys Raoult's law;

Thus $P_{soln} = X_H P_H^o + X_O P_O^o$

Substituting: $P_{soln} = 0.4449 \times 0.522\text{atm} + 0.5551 \times 0.238\text{atm} = 0.36435\text{atm}$

$X_O^V = \frac{X_O P_O^o}{P_{soln}} = \frac{0.5551 \times 0.238\text{atm}}{0.36435\text{atm}} = 0.36$

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℃.

(b) Using $\frac{m_o}{m_w} = \frac{P_o \times M_o}{P_w M_w}$

But $\frac{m_o}{m_w} = 0.48,\ P_o = 5.3\text{kPa}, P_w = 95\text{kPa}$ and $M_w = 18\text{g/mol}$

Then $0.48 = \frac{5.3\text{kPa} \times M_o}{95\text{kPa} \times 18\text{g/mol}}$

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.

Partial vapour pressure of benzene, $P_B = X_B P_B^o = 0.09 \times 75.2\text{mmHg} = 6.768\text{mmHg}$

Partial vapour pressure of ethanol, $P_E = X_E P_E^o$

But $X_E = 1 - X_B = 1 - 0.09 = 0.91$

If follows that, $P_E = 0.91 \times 43.6\text{mmHg} = 39.676\text{mmHg}$

Using $P_{soln} = P_B + P_E$ (Dalton's law of partial pressure)

$P_{soln} = (6.768 + 39.676)\text{mmHg} = 46.444\text{mmHg}$

(i) Hence total vapour pressure of the mixture is 46.444mmHg

(ii) $X_B = \frac{P_B}{P_{soln}} = \frac{6.768}{46.444} = 0.146$

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;

$P_N + P_W = \text{atmospheric pressure} = 1.013 \times 10^5 P_a$

Then $P_N = 1.013 \times 10^5 \text{Pa} - P_W = (1.013 \times 10^5 - 9.749 \times 10^4)P_a = 3810\text{Pa}$

Also $M_W = 18\text{gmol}^{-1}$ and $M_N = 127\text{gmol}^{-1}$

Then $\frac{M_N}{M_w} = \frac{3810\text{Pa} \times 127\text{gmol}^{-1}}{9.749 \times 10^4\text{Pa} \times 18\text{gmol}^{-1}} = 0.2757$

$\% \left(\frac{m}{m}\right) \text{Nitrobenzene} = \left(\frac{0.2757}{1 + 0.2757}\right) \times 100\% = 21.6\%$

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; $\mathbf{W_r} = \mathbf{W_o}\left(\frac{\mathbf{V_b}}{\mathbf{V_b + K_d V_a}}\right)^{\mathbf{n}}$

Where:

$\mathbf{W_r}$ is the mass of solute which remain in residue solution after **n** extractions.

$\mathbf{W_o}$ is the original mass of the solute before extraction

$\mathbf{V_b}$ is the volume of residue solution

$\mathbf{V_a}$ is the volume of an extraction solvent used in each extraction (experiment)

n is the number extractions.

$\mathbf{K_d}$ is the partition coefficient

First case:

$\mathbf{W_o} = 50\text{g}, \mathbf{V_b} = 1000\text{cm}^3, \mathbf{V_a} = 1000\text{cm}^3, \mathbf{K_d} = 3$ and $\mathbf{n} = 1$

Then $W_r = 50\left(\frac{1000}{1000+(1000\times3)}\right)^1$

$= 12.5\text{g}$

The mass remained by using single extraction is 12.5g

Second case:

$\mathbf{W_o} = 50\text{g}, \mathbf{V_b} = 1000\text{cm}^3, \mathbf{V_a} = 500\text{cm}^3, \mathbf{K_d} = 3$ and $\mathbf{n} = 2$

Then $W_r = 50\left(\frac{1000}{1000+(500\times3)}\right)^2 = 8\text{g}$

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℃

$\frac{n_c}{n_w} = \frac{760-540}{540} = \frac{11}{27}$ 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.

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:
Mass of chlorobenzene in the distillate = $\frac{90}{100}\times 20g = 18g$

If m_T is the total mass of the distillate

If follows that $\frac{71.8 m_T}{100} = 18g$ or $m_T = \frac{100\times 18g}{71.8} = 25g$

Using $V = \frac{m}{\rho}$

Total volume of distillate = $\frac{25}{1.1}cm^3 = 22.72cm^3$

Hence total volume of distillate obtained is 22.72 cm^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 grater 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.

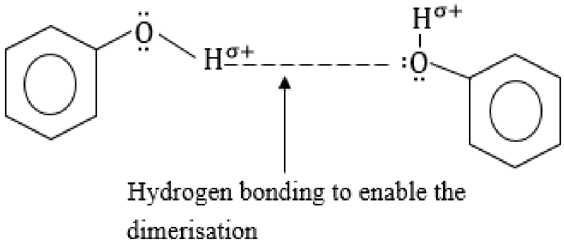
(b)

(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) $K = \frac{\sqrt[n]{C_1}}{C_2}$

(ii) $K = \frac{C_1(1-\alpha)}{\sqrt[n]{C_2}}$

(iii) $K = \frac{C_1}{C_2(1-\alpha)}$

(b) Iodine and sodium thiosulphate reacts together according to the following equation:

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

From which mole ratio of I_2 to $Na_2S_2O_3$ is 1:2

But number of moles, $n = [\quad]V$

Thus the product of molar concentration of each solution and its respective volume must satisfy the mole ratio.

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

For CCl_4 layer: $\frac{[I_2] \times 25}{0.1 \times 27.7} = \frac{1}{2}$ or $[I_2] = 0.0554M$

For water layer: $\frac{[I_2] \times 25}{0.01 \times 3.15} = \frac{1}{2}$ or $[I_2] = 0.00063M$

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

For CCl_4 layer: $\frac{[I_2] \times 25}{0.1 \times 21.2} = \frac{1}{2}$ or $[I_2] = 0.0424M$

For water layer: $\frac{[I_2] \times 25}{0.01 \times 2.4} = \frac{1}{2}$ or $[I_2] = 0.00048M$

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

For CCl_4 layer: $\frac{[I_2] \times 25}{0.1 \times 14} = \frac{1}{2}$ or $[I_2] = 0.028M$

For water layer: $\frac{[I_2] \times 25}{0.01 \times 1.6} = \frac{1}{2}$ or $[I_2] = 0.00032M$

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

It follows that: $87.9 = \frac{5 - x/1}{x/2} = \frac{2(5-x)}{x}$; $x = 0.1112g$

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.

$$A \ldots\ldots..\ldots A = B.\ldots\ldots\ldots..B = A \ \ldots\ldots\ldots\ldots B$$

Where; ... ... represents intermolecular forces.

(b) Iodine reacts with sodium thiosulphate according to the following equation:

$$I_2 + 2Na_2S_2O_3 \quad \rightarrow \quad Na_2S_4O_6 + 2NaI$$

From which mole ratio of I_2 to $Na_2S_2O_3$ is 1:2

Thus $\frac{[I_2]\times \text{Volume of iodine solution}}{[Na_2S_2O_3]\times \text{Volume of thiosulphate solution}} = \frac{1}{2}$

For aqueous layer: $\frac{[I_2] \times 25}{0.01 \times 4.5} = \frac{1}{2}$ or $[I_2] = 0.0009\text{M}$

Number of moles of I_2 in 50cm^3 of aqueous solution $= \frac{50}{1000}\times 0.0009\text{moles} = 4.5\times 10^{-5}\text{moles}$ (n=MV)

Mass of I_2 in 50cm^3 of aqueous solution $= 4.5 \times 10^{-5} \times 254\text{g} = 0.01143\text{g}$ $(m = nM_r)$

Mass of I_2 in 50cm^3 in tetrachloromethane$(CCl_4) = (1 - 0.01143) = 0.98857\text{g}$

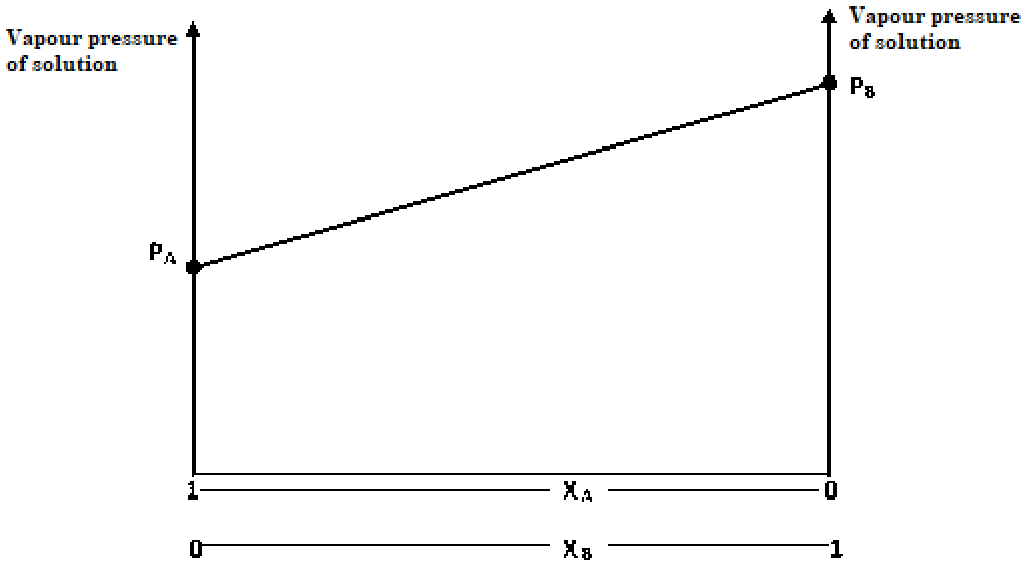
$K_d = \frac{\text{Concentration of } I_2 \text{ in } CCl_4 \text{ layer}}{\text{Concentration of } I_{2 \text{ in aqueous layer}}} = \frac{0.98857}{0.01143}$

(Mass in equal volume of 50 cm^3 of each layer) $= 86.5$

Hence the distribution constant of iodine between tetrachloromethane and water is 86.5.

Question 26

(a)



Where $\mathbf{P_A}$ is the vapour pressure of pure **A**

$\mathbf{P_B}$ is the vapour pressure of pure **B**

(b)

Where $\mathbf{T_A}$ is the boiling point of pure **A**

$\mathbf{T_B}$ 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 74torr and 71.9torr). 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

$n_{Acetone} = \frac{50g}{58gmol^{-1}} = 0.862mol$

$n_{Methanol} = \frac{50g}{32gmol^{-1}} = 1.5625mol$

$n_T = n_{Acetone} + n_{Methanol} = 2.4245mol$

$X_{Acetone} = \frac{n_{Acetone}}{n_T} = \frac{0.862mol}{2.4245mol} = 0.36$

$X_{Methanol} = \frac{n_{Methanol}}{n_T} = \frac{1.5625mol}{2.4245mol} = 0.64$

From Raoult's law;

$P_{soln} = X_{Acetone}P^{\circ}_{Acetone} + X_{Methanol}P^{\circ}_{Methanol} = 0.36 \times 271torr + 0.64 \times 143torr = 189.08torr$

The vapour pressure of the solution is approximately 189torr

$X^{V}_{Acetone} = \frac{X_{Acetone}P^{\circ}_{Acetone}}{P_{soln}} = \frac{0.36 \times 271torr}{189torr} = 0.52$

And $X^{V}_{Methanol} = 1 - X^{V}_{Acetone} = 1 - 0.52 = 0.48$

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;

$P_{soln} = X^{L}_{A}P^{\circ}_{A} + X^{L}_{B}P^{\circ}_{B}$

Where $X^{L}_{B} = 1 - X^{L}_{A}$

Substituting; $600 = 450X^{L}_{A} + (1 - X^{L}_{A})700$

From which $X^{L}_{A} = 0.4$

And $X^{L}_{B} = 1 - 0.4 = 0.6$

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;

$X^{V}_{A} = \frac{X^{L}_{A}P^{\circ}_{A}}{P_{soln}} = \frac{0.4 \times 450}{600} = 0.3$

$X^{V}_{B} = 1 - X^{V}_{A} = 1 - 0.3 = 0.7$

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)

(i) 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)

1. Propanol-ethanol solution
2. Toluene-benzene solution
3. Heptane-hexane solution

(iii)

1. Intermolecular forces between the components in the solution is the same as those intermolecular forces in pure components.
2. 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

Then from; $K_d = \frac{[\text{Uranium}]\text{in organic layer}}{[\text{Uranium}]\text{in water layer}}$

Substituting; $50 = \frac{\frac{n_o}{200}}{\frac{n_w}{500}} = \frac{500n_o}{200n_w}$

From which; $\frac{n_o}{n_w} = \frac{50\times200}{500} = 20$

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

(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

Then $\frac{20-x/100}{x/100} = 0.2$, $\frac{20-x}{x} = 0.2$ or $x = 16.67\text{g per dm}^3$

But exact volume used was 100cm^3

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)

(i) 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.

(ii) 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.

(iii) 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.

(b) Using; $K_d = \frac{\text{Mass concentration of G in pentan-1-ol (in gdm}^{-3})}{\text{Mass concentration of G in aqueous solution (in gdm}^{-3})}$

Where: Mass concentration of G in pentan-1-ol $= \frac{\text{mass of G}}{V_{Soln}\text{ in dm}^3}$

But $V_{Soln} = 100\text{ cm}^3 = \frac{100}{1000}\text{dm}^3 = 0.1\text{dm}^3$

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℃, 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℃ (normal boiling point of water).
The combined water and ethyl benzoate vapour pressure reach 101.325kPa at temperature less than 100℃ (boiling point of immiscible liquid mixture is less than either of the two components) and hence the mixture must boil somewhere between 99℃ and 100℃.

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.

Then $P_{\text{soln}} = X_{\text{benzene}}P^o_{\text{benzene}} + X_{\text{toluene}}P^o_{\text{toluene}}$

$P_{\text{soln}} = (0.65 \times 75)\text{mmHg} + (0.35 \times 22)\text{mmHg} = 56.45\text{mmHg}$

Then $X^V_{\text{benzene}} = \frac{P_{\text{benzene}}}{P_{\text{soln}}}$

But $P_{\text{toluene}} = X_{\text{benzene}}P^o_{\text{benzene}} = (0.65 \times 75) = 48.75\text{mmHg}$

So $X^V_{\text{benzene}} = \frac{48.75\text{mmHg}}{56.45\text{mmHg}} = 0.86$

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; $P_{soln} = X_A P_A^o + X_B P_B^o$

From which; $P_B^o = \frac{P_{soln} - X_A P_A^o}{X_B}$

But at normal boiling point of the solution; $P_{soln} = 1\text{atm}$

Then substituting $P_B^o = \frac{(1-(0.72\times0.7))\text{atm}}{0.28} = 1.771\text{atm}$

The vapour pressure of pure B is 1.771atm

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 at 95°C $= 760\text{mmHg} - P_w = (760 - 635)\text{ mmHg} = 125\text{mmHg}$

Using $\frac{m_x}{m_w} = \frac{P_x M_x}{P_w M_w}$

Substituting given values: $\frac{m_x}{m_w} = \frac{125\times160}{635\times18} = \frac{2000}{1143}$ or $m_x : m_w = 2000 : 1143$

If m_x = 40g; then $\frac{40\text{g}}{m_w} = \frac{2000}{1143}$

$m_w = \frac{1143\times40}{2000}\text{g} = 22.86\text{g}$

So mass of water in the distillate is 22.86g

And mass of X in the distillate is 40g (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) Using $\frac{m_c}{m_w} = \frac{P_c M_c}{P_w M_w}$

M_c = molar mass of Chlorobenzene (C_6H_5Cl) = 112.5g/mol

M_w = molar mass of water = 18g/mol

Then $\frac{23.7}{10} = \frac{112.5P_c}{18P_w}$ or $\frac{P_c}{P_w} = 0.3792$

Thus $P_c - 0.3792P_w = 0$ … … … … … … … … … … … … (i)

But $P_c + P_w = 101300$ … … … … … … … … … … … ….(ii)

Solving the two equations simultaneously gives:

$P_c = 27852\text{Pa}$ and $P_w = 73448\text{Pa}$

The vapour pressure of water is 73448Pa and the vapour pressure of chlorobenzene is 27852Pa.

Question 38

(a)

(i) Vapour pressure becomes smaller as intermolecular forces becomes stronger.

(ii) 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.

(iii) 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: $P_{soln} = X_C P_C^o + X_M P_M^o$ (where C stands for chloroform and M stands for methanol).

But $X_C + X_M = 1$

Or $X_M = 1 - X_C$

So $P_{soln} = X_C P_C^o + (1 - X_C)P_M^o$

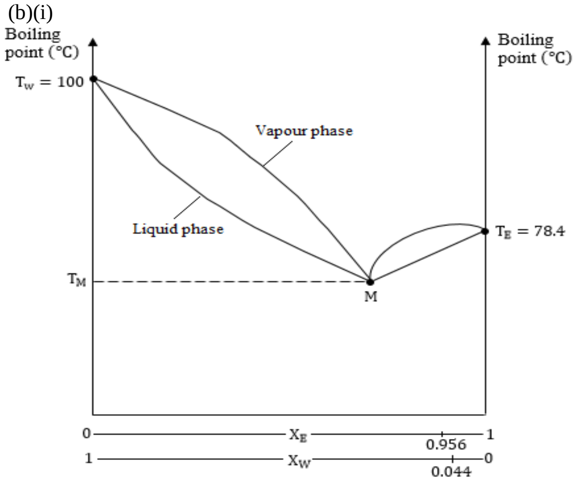
$P_{soln} = X_C(P_C^o - P_M^o) + P_M^o$

Or $X_C = \frac{P_{soln} - P_M^o}{P_C^o - P_M^o} = \frac{(0.255 - 0.192)\text{atm}}{(0.311 - 0.192)\text{atm}} = 0.53$

The mole fraction of chloroform in the solution is 0.53.

Question 39

(a) (i) Is the saturated vapour pressure is the vapour pressure of the liquid in equilibrium with excess liquid at **given temperature.**
(ii) Azeotropic point is the boiling point of the azeotropic mixture.
(iii) Ideal solution is the mixture of substances of similar chemical structures and polarities.
(b)(i)



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%.

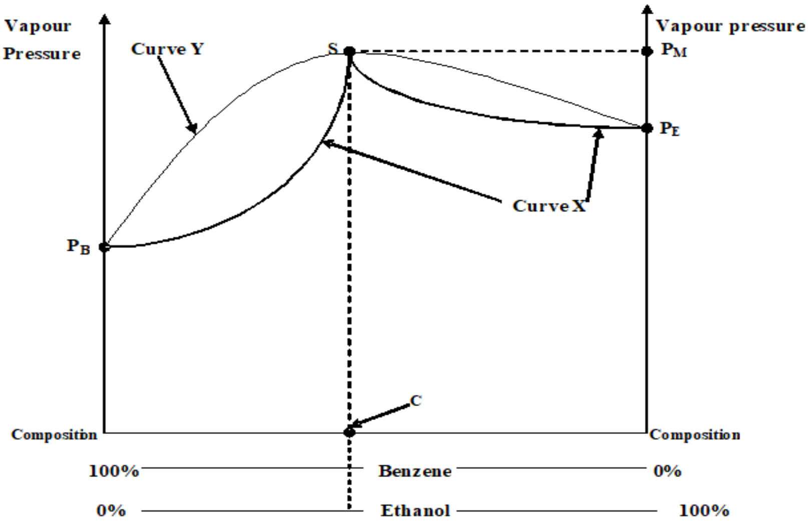
Question 40

(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, $\Delta T = 0°C - (-0.415\ °C) = 0.415°C$

Using $\Delta T = iK_f m$ or $i = \frac{\Delta T}{K_f m} = \frac{0.415°C}{1.86°Ckgmol^{-1} \times 0.118m} = 1.89$

From $\pi V = inRT$ or $\pi = \frac{inRT}{V} = iCRT$

Substituting $\pi = iCRT = 1.89 \times 0.118 \times 0.082 \times 283 = 5.18atm$.

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) Using $\Delta T = K_b m = K_b \times \frac{m_{su}}{M_{su} \times m_{sv} \text{in kg}}$

Substituting $\Delta T = 0.52Kkgmol^{-1} \times \frac{18g}{180g/mol \times 1kg} = 0.052K$

But boiling point of pure water is 373K

Hence boiling point of solution= $(373 + 0.052)K = 373.052K$

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:

By Raoult's law: $P_{sv} = X_{sv}P^o_{sv}$

and $P_{su} = X_{su}P^o_{su}$

Where:

$P_{sv}$and P_{su} are partial vapour pressures exerted in solution by solvent and non-volatile solute respectively.

P^o_{sv} and P^o_{su} 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: $P_{soln} = X_{sv}P^o_{sv} + X_{su}P^o_{su}$

But for non-volatile solute, $P^o_{su} = 0$

Then $P_{soln} = X_{sv}P^o_{sv}$

But $X_{sv} = 1 - X_{su}$ $(X_{sv} + X_{su} = 1)$

The $P_{soln} = (1 - X_{su})P^o_{sv}$ or $P_{soln} = P^o_{sv} - X_{su}P^o_{sv}$ Or $X_{su}P^o_{sv} = P^o_{sv} - P_{soln}$

But $P^o_{sv} - P_{soln}$ = Lowering in the vapour pressure of the solvent, ΔP

It follows that: $\Delta P = X_{su}P^o_{sv}$

But P^o_{sv} 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 $\Delta T = iK_f m$

Or $m = \frac{\Delta T}{iK_f} = \frac{(0-(-1.95))°C}{2\times1.86°Ckgmol^{-1}} = 0.5242mol/kg$

Using $m = nM_r$;

Mass of the solute (KI) in 1kg (1000g) of the solvent $= 0.5242mol \times 166g/mol = 87g$

Mass of the solution= $m_{su} + m_{sv} = (1000 + 87)g = 1087g$

Thus mass of solution containing 87g of solute is 1087g

Also using $\pi V = inRT$ or $\pi = \frac{inRT}{V} = iCRT$

From which $C = \frac{\pi}{iRT} = \frac{25}{2\times0.082\times298}mol/L = 0.51154mol/L$

Using $\text{mass concentration} = \text{molarity} \times \text{molar mass}$

Mass concentration of the solute (KI) in the solution $= 0.51154mol/L \times 166g/mol = 85g/L$

Using $\text{volume of solution} = \frac{\text{mass of solute}}{\text{volume of solution}}$

Volume of solution containing 87g of solute $= \frac{87g}{85g/L} = 1.0235L = 1023.5mL$

Thus mass of solution containing 87g of solute is 1023.5mL

Hence 1087g of the solution corresponds to 1023.5mL of the solution.

Using $\text{density of solution}, \rho = \frac{\text{mass of solution}}{\text{volume of solution}}$

Thus $\rho = \frac{1087g}{1023.5mL} = 1.062g/mL$

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:

$\pi V = nRT$ or $\pi = CRT$ 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$= 100 + 0.00304 m_{su}$

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 $= 105$

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)

(i) 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.

(ii) 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; $n = \frac{m}{M_r}$	$\frac{42.9\text{g}}{12\text{g/mol}} = 3.575\text{mol}$	$\frac{2.4\text{g}}{1\text{g/mol}} = 2.4\text{mol}$	$\frac{16.6\text{g}}{14\text{g/mol}} = 1.1857\text{mol}$	$\frac{38.1\text{g}}{16\text{g/mol}} = 2.38125\text{mol}$
Divide by smallest to get simplest ratio	$\frac{3.575\text{mol}}{1.1857\text{mol}} = 3$	$\frac{2.4\text{mol}}{1.1857\text{mol}} = 2$	$\frac{1.1857\text{mol}}{1.1857\text{mol}} = 1$	$\frac{2.38125\text{mol}}{1.1857\text{mol}} = 2$

$m_{sv} = \rho V = 0.779 \text{ g/mL} \times 75.0\text{mL} = 58.425\text{g} = 0.058425\text{kg}$

$\Delta T = 6.5°C - 0°C = 6.5°C$

Using $\Delta T = K_f m = K_f \times \frac{m_{su}}{M_{su} \times m_{sv} \text{in kg}}$

From which; $M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{in kg}} = \frac{20.2 \times 3.16}{6.5 \times 0.058425} \text{g/mol} = 168 \text{g/mol}$

Let the molecular formula be $(C_3H_2NO_2)_n$

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)

(i) 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.

(ii) It is easier to measure volume and hence molarity with greater accuracy than to measure mass and hence molality.

(iii) 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 $100\text{g} - 18.2\text{g}$ or 81.8g

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

$n_{su} = \frac{18.2g}{162g/mol} = 0.1123mol$ and $n_{sv} = \frac{81.8g}{18g/mol} = 4.5444mol$

$$X_{su} = \frac{n_{su}}{n_{su} + n_{sv}} = \frac{0.1123mol}{0.1123mol + 4.5444mol} = 0.0241$$

Using $\Delta P = iX_{su}P_{sv}^{o}$

From which $i = \frac{\Delta P}{X_{su}P_{sv}^{o}} = \frac{(26.02-23.51)torr}{0.0241\times 26.02torr} = 4$

Hence the electrolyte dissociates into 4 ions per formula unit.

Question 47

(a) 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 $1kg/dm^3$.That is 1kg of solvent is contained in $1dm^3$.

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 $= \text{volume of solvent} + \text{volume of solute}$

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 $\text{numerical values of molality} = \text{numerical value of molarity}$ if the solution is very dilute.

(b) Using $\pi_{ob}V = n_{ob}RT$

Thus observed number of solute particles in the solution, $n_{ob} = \frac{\pi_{ob}V}{RT} = \frac{0.399\times 1}{0.082\times 298}mol = 0.01633mol$

Assuming complete ionisation of each given salt:

$MgCl_2$ gives three ions per formula unit,

NaCl gives two ions per formula unit.

It follows that if x is the mass of $MgCl_2$ in the mixture, then: π_{ob} for $MgCl_2 = 3 \times \frac{xg}{95g/mol} = \frac{3x}{95}mol$

And $\pi_{ob}$for $NaCl = 2 \times \frac{(0.5-x)g}{58.5g/mol} = \frac{1-2x}{58.5}mol$

Thus $\frac{3x}{95} + \frac{1-2x}{58.5} = 0.01633; 95 - 14.5x = 90.75$

From which; $x = 0.2931g$

$$\%MgCl_2 = \frac{0.2931}{0.5} \times 100\% = 58.62\%$$

Hence the mass percent of $MgCl_2$ 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 $= (1800 - 312.3)\text{g} = 1478.7\text{g} = 1.4787\text{kg}$

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, $i = 2$)

$$= 2 \times 0.52℃\text{kgmol}^{-1} \times 1.4787\text{mol/kg} = 1.54℃$$

But boiling point of pure water is $100℃$

Hence the normal boiling point of the solution $= 100℃ + 1.54℃ = 101.54℃$

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 $\rho_{solution} = \rho_{water} = 1\text{g/mL}$

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, $0.1\text{m}BaCl_2$ has higher solute concentration leading to larger boiling point elevation and hence higher boiling point of the solution.

(b) $P_{soln} = \frac{80}{100} \times P^o_{sv} = 0.8P^o_{sv}$

Then $\Delta P = P^o_{sv} - P_{soln} = 0.2P^o_{sv}$

Using $M_{su} = \frac{m_{su}\times M_{sv}\times P^o_{sv}}{m_{sv}\times \Delta P}$

From which $m_{su} = \frac{m_{sv} \times \Delta P \times M_{su}}{M_{sv} \times P_{sv}^o} = \frac{114g \times 0.2P_{sv}^o \times 40g/mol}{114g/mol \times P_{sv}^o} = 8g$

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

$$n_{su} = \frac{50g}{342g/mol} = 0.1462mol$$

$$n_{sv} = \frac{500g}{18g/mol} = 27.7778mol$$

$$X_{su} = \frac{n_{su}}{n_{su} + n_{sv}} = \frac{0.1462mol}{0.1462mol + 27.7778mol} = 0.0052$$

Using $\Delta P = X_{su} P_{sv}^o = 0.0052 \times 23.8mmHg = 0.124mmHg$

Hence the vapour pressure lowering is 0.124mmHg

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) $\Delta P = \frac{5}{100} \times P_{sv}^o = 0.05P_{sv}^o$

Using $M_{su} = \frac{m_{su} \times M_{sv} \times P_{sv}^o}{m_{sv} \times \Delta P}$

From which $m_{su} = \frac{m_{sv} \times \Delta P \times M_{su}}{M_{sv} \times P_{sv}^o} = \frac{100g \times 0.05P_{sv}^o \times 60g/mol}{18g/mol \times P_{sv}^o} = 16.67g$

Hence the mass of the solute is approximately 17g

Using molality $= \frac{n_{su}}{m_{sv} \text{ in kg}} = \frac{m_{su}}{M_{su} \times m_{sv} \text{ in kg}} = \frac{17g}{60g/mol \times 0.1kg} = 2.8mol/kg$

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

From $M_r = \frac{mRT}{\pi V} = \frac{0.2 \times 0.082 \times 288 \times 760}{94.6 \times 1} g/mol = 37.9g/mol$

Thus molar mass of **B** in water is 37.9g/mol

Second case: Calculating molar mass of monobasic acid **B** using freezing point depression:

$$\Delta T = K_f m = \frac{K_f m_B}{M_B \times m_{benzene} \text{in kg}}$$

From which: $M_B = \frac{K_f \times m_B}{\Delta T \times m_{benzene} \text{in kg}}$

But $K_f = K_{1000} = \frac{K_{100}}{10} = \frac{49}{10} = 4.9$ per 1000g

Substituting given values: $M_B = \frac{4.9 \times 4}{2.13 \times 0.1} g/mol$

Thus molar mass of **B** in benzene is 92g/mol

Third Case: calculating molar of monobasic acid **B** by using volume of neutralisation of the acid.

Equation for the reaction: $HA + NaOH \rightarrow NaA + H_2O$

From which mole ratio of HA to NaOH is 1: 1

Number of mole of NaOH $= \frac{10.9\times1}{1000}$moles $= 0.0109$moles

Thus number of moles of HA was also 0.0109moles

From $n = \frac{m}{M_r}, M_r = \frac{m}{n}$

Molar mass of **B** in water $= \frac{0.5}{0.0109}$ g/mol $=$ 46g/mol

Thus formula mass of **B** (if there would be neither dissociation nor association of **B**) is 46g/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; $\Delta T = 0°C - (-0.435)°C = 0.435°C$ (Pure water freezes at 0°C)

$$M_{su} = \frac{\frac{1.86\times15}{0.435\times1}g}{mol} = 64g/mol$$

Observed molar mass of calcium nitrate ($Ca(NO_3)_2$) is 64g/mol

But expected molar mass of $Ca(NO_3)_2 = 40 + (62 \times 2) = 164g/mol$

$$i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{164}{64} = 2.5625$$

Calcium nitrate dissociate according to the following equation.

$Ca(NO_3)_2 \rightleftharpoons Ca^{2+} + 2NO_3^{2-}$; $N = 3$

$$\alpha = \frac{i-1}{N-1} = \frac{2.5625-1}{3-1} = 0.78125 \text{ or } 78.125\%$$

Hence degree of dissociation of the salt is 78.125%

Question 55

(a) $0.08m\ CaCl_2 < 0.1mNaCl < 0.04mNa_2CO_3 < 0.1m$ sugar

(b) When naphthalene is dissolved in benzene:

Freezing point depression, $\Delta T = (5.481 - 4.91)°C = 0.571°C$

Using $\Delta T = \frac{K_f\times m_{su}}{M_{su}\times m_{sv}\text{in kg}}$

$0.571 = \frac{K_f\times0.321}{128\times0.025}$ From which $K_f = 5.7°Ckg/mol^{-1}$

So the molar freezing point depression constant for 1000g of benzene, K_f is $5.7°Ckg/mol^{-1}$

When benzoic is dissolved in benzene:

Using $M_{su} = \frac{K_f\times m_{su}}{\Delta T\times m_{sv}\text{in kg}} = \frac{5.7\times0.305}{(5.481-5.226)}$ g/mol $=$ 273g/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 $m_{sv} = m_{water} = \rho_{water} = 25mL \times \frac{0.997g}{mL} = 24.925g$

Boiling point of pure water is 100ºC

So boiling elevation, $\Delta T = (100.45 - 100)°C = 0.45°C$

Then $M_{su} = \frac{0.52\times1.5}{0.45\times0.024925}$ g/mol $= 69.5$g/mol

(a) The molar mass of the compound if it is non-electrolyte is 69.5g/mol

(b) **Ideally,** the ionic compound exists as ions i.e. it tends to ionises completely according to the following equations:

$$AB_2 \rightarrow A^{2+} + 2B^- \text{ or } A_2B \rightarrow 2A^+ + B^{2-}$$

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)

$$\text{i} = \frac{\text{Observed number of particles}}{\text{Expected number of particles}} = \frac{3}{1} = 3$$

Vant 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:

$CO(NH_2)_2$ being non-electrolyte undergoes neither dissociation nor association in water.

(b) Using $\Delta P = \frac{m_{urea} \times M_{water} \times P_{water}}{M_{urea} \times m_{water}}$

Substituting given values: $2.5 = \frac{m_{urea} \times 18 \times 31.8}{60 \times 450}$

$m_{urea} = 117.9\text{g}$

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) $\Delta P = P - P_{soln} = (0.196 - 0.194)\text{atm} = 0.002\text{atm}$

Using: $M_{su} = \frac{m_{su} \times M_{sv} \times P}{\Delta P \times m_{sv}}$

Substituting given values: $M_{su} = \frac{2 \times 18 \times 0.196}{0.002 \times 90.1} = 39\text{g/mol}$

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) $\Delta T = \frac{K_b \times m_{su}}{M_{su} \times m_{sv} \text{in kg}} = \frac{2.53 \times 2.4}{154 \times 0.075}°C = 0.53°C$

Boiling point of solution $= T_o + \Delta T = (80.1 + 0.53)°C = 80.63°C°C$

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 $M_r = \frac{mRT}{\pi V}$;

Substituting given values: $M_r = \frac{10\times0.082\times288}{3.2\times1} = 73.8g/mol$

Thus the observed molar mass of $BaCl_2$ is $73.8g/mol$

But the expected molar mass of $BaCl_2 = 137 + (2 \times 35.5) = 208g/mol$

$$i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{208}{73.8} = 2.818$$

$BaCl_2$ dissociate according to the following equation:

$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-; N = 3$

$$\alpha = \frac{i-1}{N-1} = \frac{2.818-1}{3-1} = 0.909 \text{ or } 90.9\%$$

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 $(NH_4)_3PO_4$, 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;

$\Delta T = \frac{K_f m_{su}}{M_{su}\times m_{sv} \text{in kg}}$;

$$m_{sv} = m_{water} = \rho V = 6000cm^3 \times \frac{1g}{cm^3} = 6000g = 6kg$$

Then $13 = \frac{1.86\times m_{su}}{62\times6}$; $m_{su} = 2600g$ or $2.6kg$

Mass of ethylene glycol required is 2.6kg

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) From $\pi V = \frac{mRT}{M_r}$, $\frac{m}{v} = \frac{\pi M_r}{RT}$

So $C = \frac{\pi M_r}{RT} = \frac{2.32\times180}{0.082\times285} = 17.9g/dm^3$

Hence concentration of glucose is $17.9g/dm^3$

Question 63

(a) Isotonic solutions have the same osmotic pressure which means equal concentration and hence osmosis will not occur.

(b) Using $\Delta P = \frac{m_{su}\times M_{sv}\times P_{sv}}{M_{su}\times m_{sv}} = \frac{4.1\times78\times10000}{128\times60} Nm^{-2} = 416.4Nm^{-2}$

Thus the lowering in vapour pressure of benzene is $416.4Nm^{-2}$

New vapour pressure of benzene in the solution = $(10000 - 416.4)\ Nm^{-2} = 9583.6Nm^{-2}$

Hence the vapour pressure of benzene in the solution will be decreased to $9583.6Nm^{-2}$ 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) Using $\Delta P = \frac{m_{su}\times M_{sv}\times P_{sv}}{M_{su}\times m_{sv}}$

Where: $\Delta P = P_{sv} - P_{soln} = (2333 - 2311)Nm^{-2} = 22Nm^{-2}$

$M_{su} = 342g/mol$

$M_{sv} = 18g/mol$

$P_{sv} = 2333Nm^{-2}$

Then $22 = \left(\frac{m_{su}}{m_{sv}}\right) \times \frac{18\times2333}{342}$, $\frac{m_{su}}{m_{sv}} = \frac{342\times22}{18\times2333} = 0.1792$

Neglecting volume of sucrose, so that $V_{soln} = V_{water}$

Then $m_{sv} = \rho_{water} \times V_{soln}$

But $\rho_{water} = 1gcm^{-3} = 1000g/dm^3$

$$\text{So } \frac{m_{su}}{V_{soln}\times 1000gdm^{-3}} = 0.1792, \quad \frac{m_{su}}{V_{soln}} = 0.1792 \times 1000gdm^{-3} = 179.2gdm^{-3}$$

But $\frac{m_{su}}{V_{soln}} = \text{mass concentration of solute(sucrose)}$

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 ($[PbCl_4]^{2-}$), 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)g = 98g

Using $M_{su} = \frac{K_b \times m_{su}}{\Delta T \times m_{sv} \text{in kg}} = \frac{0.52 \times 2}{(99.877 - 99.7) \times 0.098} = 60\text{g/mol}$

The relative molecular mass of the compound is 60

Question 66

(a)

1. In determining molar mass of non-volatile solute.
2. In estimating degree of dissociation of solute in a solvent.
3. In making anti-freeze (mixture of ethylene glycol and water) to prevent freezing of radiator in automobiles.
4. In salting roads so as to prevent formation of ice over the road in cold regions.

(b) Using $M_{su} = \frac{K_b \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}}$

Where boiling point of pure ethanol is 78.1ºC

$K_b = 1.07°\text{C mol}^{-1}\text{kg and } m_{sv} = 16.15\text{g} = 0.01615\text{kg}$

Boiling point/℃	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

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 $M_{su} = \frac{K_b \times m_{su}}{\Delta T \times m_{sv} \text{in kg}}$

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

Then 32n = M_r = 252 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) = $(4000 - y)$g.

Using $\Delta T = \frac{K_f \times m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$

It follows that: $6 = \frac{1.86y \times 1000}{92 \times (4000 - y)}$ or y= 923g

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) Using $\frac{\pi_2}{T_2} = \frac{\pi_1}{T_1}$, $\pi_2 = \frac{T_2}{T_1} \times \pi_1$

Where$T_1 = 15°C = 288K, T_2 = 0\ °C = 273K, \pi_1 = 100000Nm^{-2}$

Then $\pi_2 = \frac{273}{288} \times 100000Nm^{-2} = 94792Nm^{-2}$

Hence the osmotic pressure at 0ºC 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) $C_1 = \frac{7g}{100cm^3} = 0.07g/cm^{-3}$

$\pi_1 = 9.3atm, T_1 = 18°C = 291K, \pi_2 = 10atm, T_2 = 10°C = 283K$

Using $\frac{\pi_1}{C_1T_1} = \frac{\pi_2}{C_2T_2}$

From which $C_2 = \left(\frac{\pi_2}{\pi_1}\right)\left(\frac{T_1}{T_2}\right)C_1 = \frac{10\times291\times0.07}{9.3\times283}gcm^{-3} = 0.0774gcm^{-3}$

But the volume of second solution is 250 cm^3

Using m = CV

Then required mass of the compound is $0.0774 \times 250g = 19.35g$

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 changed Fe^{3+} than Na^{+}in NaCl, is more covalent in character and hence it has lower degree of ionisation than NaCl.

(b) Using $M_r = \frac{mRT}{\pi V}$

Then M_r for the acid $= \frac{1\times0.082\times285\times760}{288\times1}gmol^{-1} = 61.67gmol^{-1}$

Hence the relative molecular mass of the acid is 61.67

$$\Delta T = \frac{K_f \times m_{su}}{M_{su} \times m_{sv}\text{ in kg}} = \frac{1.86 \times 1}{61.67 \times 1} = 0.03°C$$

(Assuming density of solution = density of water = $1kg/dm^3$)

Freezing point depression = $0.03°C$

Freezing point = $0°C - 0.03°C = -0.03°C$

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) **For urea solution:** $\pi V = \frac{mRT}{VM_r}$ or $\pi = \frac{mRT}{M_r}$

but $\frac{m}{v}$ = Mass concentration, C

$$\text{Thus } \pi = \frac{CRT}{M_r} = \frac{1.754RT}{60} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

For sugar solution:$\pi = \frac{CRT}{M_r} = \frac{10RT}{M_r} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(ii)}$

Since the two solutions are isotonic (have the same osmotic pressure)

Then (i) = (ii) or $\frac{10RT}{M_r} = \frac{1.754RT}{60}$ or $M_r = \frac{60\times10}{1.754}\text{gmol}^{-1} = 342\text{gmol}^{-1}$

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: $\pi_A = \frac{C_A\times R\times 273}{M_{glucose}}$

For solution B: $\pi_B = \frac{C_B\times R\times 293}{M_{glucose}}$ but $\pi_A = \pi_B$

It follows that: $\frac{C_B\times R\times 293}{M_{glucose}} = \frac{C_A\times R\times 273}{M_{glucose}} = 324100$

For $\dfrac{C_B \times 0.082 \times 293}{180} = \dfrac{324100}{103100}$; $C_B = 23.55\text{g/dm}^3$

For $\dfrac{C_A \times 0.082 \times 273}{180} = \dfrac{324100}{103100}$; $C_A = 25.28\text{g/dm}^3$

$C_A - C_B = (25.28 - 23.55)\text{g/dm}^3 = 1.73\text{g/dm}^3$

Hence there is 1.73g more grams of glucose per dm^3 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 $\text{atmdm}^3\ \text{K}^{-1}$** 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 = $\frac{R_1+R_2+R_3+R_4}{4} = \frac{0.083+0.080+0.081+0.080}{4} = 0.081\text{atmdm}^3\text{K}^{-1} \approx$ 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) $0.01MBa_3(PO_4)_2 < 0.01MLi_3PO_4 < 0.01MNa_2SO_4 < 0.01MKCl < 0.01MC_2H_5OH$

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 $Ba_3(PO_4)_2$, Li_3PO_4, Na_2SO_4, KCl and finally C_2H_5OH which does not ionise at all and hence the freezing points of solutions follow the reverse order.

(b) Molarity of monobasic acid, $HA = 1mol/dm^3$ (A molar solution)

But for very dilute solution

Volume of solution = Volume of water (solvent) $= 1dm^3$

And density of solution = Density of water $= 1kg/dm^3$

So mass of water (solvent) $1kg/dm^3 \times 1dm^3 = 1kg$

Therefore molality of monobasic acid $= 1mol/kg$

(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, $\Delta T = K_f m = 1.86 \times 1°C = 1.86°C$

But observed freezing point depression $= 0°C - (-1.93°C) = 1.93°C$

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:

$HA \rightleftharpoons H^+ + A^-; N = 2$

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% $\pi = \frac{inRT}{V}$

But $\frac{n}{V} = [\quad] = 1M$

Thus $\pi = i[\quad]RT = 1.0376 \times 1 \times 0.082 \times 285atm = 24.25atm$

Hence the osmotic pressure of the solution is 24.25atm

Question 76

(a)

(i) Is the process of measuring freezing point depression so as determine molar mass of non – volatile solute.

(ii) Is the process of measuring boiling point elevation so as to determine molar mass of the non-volatile solute.

(b) 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:

$NaCl \rightleftharpoons Na^+ + Cl^-; N = 2$

So if the compound ionises completely (entirely dissociated), $i = N = 2$.

And $\Delta T = \frac{iK_f m_{NaCl}}{M_{NaCl} \times m_{sv} \text{ in kg}} = \frac{2 \times 3K_f}{58.5 \times 1} = \frac{4K_f}{39}$

So $\Delta T = \frac{4K_f}{39} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (i)$

For $CaCl_2$ solution

$CaCl_2$ ionises according to the following equation:

$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-; N = 3$

So if the compound ionises completely, $i = 3$.

If the required mass of $CaCl_2$ is m

Then $\Delta T = \frac{3K_f \times m}{111 \times 0.1} = \frac{10mK_f}{37} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (ii)$

Since freezing point depression is the same for the two solutions. It follows that by equating (i) and (ii) gives: $\frac{4K_f}{39} = \frac{10mK_f}{37}$

or $m = \frac{4 \times 37}{39 \times 10} g = 0.379g$

The mass of anhydrous calcium chloride per 100g of water is 0.379g

Question 77

(a)

(i) 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.

(ii) 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.

(iii) 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.

(iv) 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 $N = 2$

Then $0.97 = \frac{i-1}{2-1}$ or $i = 1.97$;

It follows that $\Delta T = iK_f m = \frac{iK_f m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$

$1dm^3$ of water $=$ 1kg of water;

Then $\Delta T = \frac{1.97 \times 20K_f}{58.5} = \frac{394K_f}{585} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (i)$

For glycerol (covalent solute which neither associate nor dissociate in the solution)

$\Delta T = \frac{m_g K_f}{62 \times 1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (ii)$

Equating (i) and (ii) (The two solutions have the same anti-freezing effect)

$\frac{394K_f}{585} = \frac{m_g K_f}{62}$, $m_g = \frac{62 \times 394}{585} g = 41.76g$

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:**

$K_f = \frac{\Delta T \times M_{su} \times m_{sv} \text{ in kg}}{m_{su}} = \frac{0.167 \times 58 \times 0.09}{0.47} = 1.85°\text{Ckgmol}^{-1}$

For zinc chloride solution

Using $M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}} = \frac{1.85 \times 2.9}{0.111 \times 1} \text{gmol}^{-1} = 48.33\text{g/mol}$

Observed molar mass of zinc chloride $=$ 48.33g/mol

But expected molar mass of zinc chloride ($ZnCl_2$)

$$= 65 + (2 \times 35.5) = 136\text{g/mol}$$

Using $i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{136}{48.33} = 2.814$

$ZnCl_2$ Ionises (dissociates) according to the following equation:

$ZnCl_2 \rightleftharpoons Zn^{2+} + 2Cl^-$; $N = 3$

$\alpha = \frac{i-1}{N-1} = \frac{2.814 - 1}{3-1} = 0.907$ 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) 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, CH_3COOH 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: $KI \rightarrow K^+ + I^-$; $N = 2$

So since the salt ionises (dissociates) completely, $i = 2$

Using $\Delta T = \frac{iK_f m_{su}}{M_{su} \times m_{sv} \text{ in kg}} = \frac{2 \times 1.8 \times 1.66}{166 \times 0.1}°C = 0.36°C$

Freezing point of solution = $T_o - \Delta T$

Where T_o is the freezing point of pure water $0°C$

Freezing point of the solution = $0°C - 0.36°C = -0.36°C$

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; $\Delta T = (104.4 - 100)°C = 4.4°C$ (100°C is the boiling point of pure water).

And $K_b = 0.512°C\text{kgmol}^{-1}$ (Given)

Substituting $4.4\ \cancel{°C} = 1.8 \times 0.512\cancel{°C}\text{kgmol}^{-1} \times \text{Molality}$

$\text{Molality} = 4.7743\ \text{mol/kg}$

Thus the required molality for the NaCl solution to boil at 104.4°C is $4.7743\ \text{mol/kg}$

But $\%\left(\frac{m}{m}\right)$ of NaCl $= \left(\frac{\text{mass of NaCl}}{\text{mass of solution}}\right) \times 100\%$

And mass of NaCl $= n_{NaCl} \times M_{NaCl} = 4.7743\text{mol} \times 58.5\text{g/mol} = 279.29655\ \text{g}$

The mass of solution mass of NaCl (solute) + mass of H_2O (solvent) $= (279.29655\ \text{g}) + (1000\text{g}) = 1279.29655\text{g}$

Thence $\%\left(\frac{m}{m}\right)$ of NaCl $= \left(\frac{279.29655\ \text{g}}{1279.29655\text{g}}\right) \times 100\% = 21.8\ \%$

Whence in terms of mas 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°.

Using mass = Density × Volume

Mass of the given solution $= 1.12\text{g}/\cancel{\text{mL}} \times 100\cancel{\text{mL}} = 112\text{g}$

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 in grams.

It follows that $21.8 = \left(\frac{15.12+x}{112+x}\right) \times 100$; 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:

$X_{su} = \frac{\Delta P}{P^o_{sv}}$; but $X_{su} = \frac{n_{su}}{n_{su}+n_{sv}}$

And for very dilute solution; $n_{su} + n_{sv} \approx n_{sv}$

Thence $\frac{n_{su}}{n_{sv}} = \frac{\Delta P}{P^o_{sv}}$

But $n_{su} = \frac{m_{su}}{M_{su}}$ and $n_{sv} = \frac{m_{sv}}{M_{sv}}$

Then $\frac{m_{su} \times M_{sv}}{M_{su} \times m_{sv}} = \frac{\Delta P}{P^o_{sv}}$

From which $M_{su} = \frac{m_{su} \times M_{sv} \times P^o_{sv}}{m_{sv} \times \Delta P}$

Where:

M_{sv} =molar mass of water (solvent) = $18\ \text{g/mol}$

P^o_{sv} = vapour pressure of pure water = $1.992 \times 10^4 Nm^{-2}$

ΔP =Lowering in vapour pressure = $P^o_{sv} - P_{soln} = (1.992 - 1.891) \times 10^4\ Nm^{-2} = 1.01 \times 10^4 Nm^{-2}$

m_{su} = mass of solute = 10.6 g

m_{sv} = mass of solvent (water) = 90g

Substituting $M_{su} = \frac{10.6\cancel{g} \times 18g/mol \times 1.992 \times 10^4 \cancel{Nm^{-2}}}{90\cancel{g} \times 1.01 \times 10^3 \cancel{Nm^{-2}}} = 41.8\ g/mol$

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) Using $\Delta T = K_f m = \frac{K_f \times m_{su}}{M_{su} \times m_{sv}\ \text{in kg}}$

Where $\Delta T = (25.5 - 24.59)°C = 0.91°C$

$M_{su} = 18gmol^{-1}$

$m_{sv} = 10g = 0.01kg$

Substituting $0.91 = \frac{9.1 \times m_{su}}{18 \times 0.01}$

From which**;** $m_{su} = 0.018g$

The mass of water in the sample is 0.018g

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 mole of particles = 6.02×10^{23} particles

But mass of 1 particle = 10^{-9}g

Thus molar mass of particles = $10^{-9}g/\cancel{particle} \times 6.02 \times 10^{23}\ \cancel{particles}/mol = 6.02 \times 10^{14}g/mol$

Then using; molarity = $\frac{\text{Mass concentration in g/L}}{\text{Molar mass}}$

Molarity of solid particles = $\frac{60\ \cancel{g}/L}{6.02 \times 10^{23}\cancel{g}/mol} = 9.9668 \times 10^{-14}\cancel{mol}/L$

Then from; $\pi v = nRT$; $\pi = \left(\frac{n}{v}\right)RT$ or $\pi = [\quad]RT$

Substituting; $\pi = 9.9668 \times 10^{-14}\cancel{mol}/\cancel{L} \times 0.082atm\cancel{Lmol^{-1}}\cancel{K^{-1}} \times 298\cancel{K} = 2.44 \times 10^{-12}atm$

Hence the osmotic pressure of the suspension is 2.44×10^{-12}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) Using $\Delta T = iK_f m$

From which $i = \frac{\Delta T}{K_f m}$

Substituting $i = \frac{0.265}{1.86 \times 0.05} = 2.85$

Calcium nitrate dissociates according to the following equation:

$Ca(NO_3)_2(aq) \rightleftharpoons Ca^{2+}_{(aq)} + 2NO_3^-(aq); N = 3$

Using $\alpha = \frac{i - 1}{N - 1}$

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, $\Delta T = K_f m$

Where $m = \frac{n_{su}}{m_{sv}\text{ in kg}} = \frac{m_{su}}{M_{su} \times m_{sv}\text{ in kg}}$

Then $\Delta T = \dfrac{K_f \times m_{su}}{M_{su} \times m_{sv}\text{in kg}}$

Where:

m_{su} = mass of solute = 22.5g
M_{su} = molar mass of solute = 342g/mol
m_{sv} = mass of solvent = 450g = 0.45kg
Substituting $\Delta T = \frac{1.86 \times 22.5}{342 \times 0.45}℃ = 0.27℃$

Then the freezing point, $T_f = 0℃ - \Delta T = (0 - 0.27)℃ = -0.27℃$

Then freezing point of solution is $-0.27℃$

(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:

$CaCl_2(aq) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq); N = 3$
Thus assuming complete ionisation, Van't Hoff's factor, $i = N = 3$

Using $\Delta T = iK_b m = 3 \times 1.22℃kg/mol \times 3.725mol/kg = 13.6℃$

Boiling point of the solution, $\mathbf{T_b = (78.5 + 13.6)℃ = 92.1℃}$

Also $\Delta T = iK_f m = 3 \times 1.99℃kg/mol \times 3.725mol/kg = 22.2℃$

Freezing point of the solution, $\mathbf{T_f = (-117.3 - 22.2)℃ = -139.5℃}$

(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

$\rho_{soln} = 1.071gcm^{-3} = 1071gdm^{-3}$

Thus; Mass of solution in $1dm^3$ of the solution is 1071g

Then mass of the solute(NaCl)in $1dm^3 = \frac{1}{100} \times 1071g = 10.71g$

Using $\pi V = nRT$;

From which $\pi = \frac{nRT}{V} = \frac{mRT}{VM_r}$

Expected osmotic pressure, $\pi_{ex} = \frac{1071g \times 0.082atmdm^3mol^{-1}K^{-1} \times 298K}{1dm^3 \times 58.5gmol^{-1}} = 4.47atm$

Then Van't Hoff's factor, $i = \frac{\pi_{ob}}{\pi_{ex}} = \frac{7.83atm}{4.47atm} = 1.75$

NaCl ionises according to the following equation;

$NaCl(aq) \rightleftharpoons Na^+(aq) + Cl^-(aq); N = 2$

Then using; $\alpha = \frac{i-1}{N-1}$

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, $\Delta T = iK_f m = \frac{i \times K_f m_{su}}{m_{su} \times m_{sv}\text{in kg}}$

$$\Delta T = \frac{1.75 \times 1.86℃kgmol^{-1} \times 1g}{58.5gmol^{-1} \times 0.099kg} = 0.562℃$$

Freezing point of the solution, $T_f = 0℃ - \Delta T = 0℃ - 0.562℃ = -0.562℃$

The freezing point of the solution -0.562℃

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=$\frac{m}{M_r}$	$\frac{19.93}{12gmol^{-1}} = 1.66mol$	$\frac{26.7g}{16gmol^{-1}} = 1.67mol$	$\frac{46.7g}{14gmol^{-1}} = 3.336mol$	$\frac{6.67g}{1gmol^{-1}} = 6.67mol$
Dividing by smallest to get simpler ratio	$\frac{1.66mol}{1.66mol} = 1$	$\frac{1.67mol}{1.66mol} = 1$=1	$\frac{3.336mol}{1.66mol} = 2$	$\frac{6.67mol}{1.66mol} = 4$

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:

$\Delta T = (82.3 - 80.2)℃ = 21℃$

$m_{su} = 5g$

$m_{sv} = 100g = 0.1kg$

Substituting: $m_{su} = \frac{2.53 \times 5}{2.1 \times 0.1} gmol^{-1} = 60gmol^{-1}$

Let the molecular formula be $(CON_2H_4)_n$

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

$$n_{glucose} = \frac{50\cancel{g}}{180\cancel{g}mol^{-1}} = 0.2778mol$$

$$n_{water} = \frac{60\cancel{g}}{18\cancel{g}mol^{-1}} = 33.3333mol$$

$X_{water} = \frac{n_{water}}{n_{total}} = \frac{33.3333\cancel{mol}}{0.2778\cancel{mol}} = 0.9917$

From Raoult's law and Dalton's law of partial pressure;

$P_{soln} = X_{water}P^o_{water} + X_{glucose}P^o_{glucose}$

Since glucose is non-volatile solute; $P^o_{glucose} = 0$

Thus $P_{soln} = X_{water}P^o_{water} = 0.9917 \times 23.8torr = 23.6torr$

The vapour pressure of the solution is 23.6torr.

Question 91

(a)

Solution	**Van't Hoff factor,i**	**Effective molality of solute, m**
$0.010mNa_3PO_4$	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) $0.010mNa_3PO_4$ and 0.020mKCl (Both have effective molality of 0.04m).

(c) $0.020\text{m}CaBr_2$ (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) $\Delta T = (0 - (-2.24))°C = 2.24°C$

Using $\Delta T = K_f m$
But $m = \frac{n_{su}}{m_{sv}\text{ in kg}}$

It follows that: $\Delta T = \frac{K_f \times n_{su}}{m_{sv}\text{ in kg}}$

From which $n_{su} = \frac{\Delta T \times m_{sv}\text{ in kg}}{K_f} = \frac{2.24 \times 0.15}{1.86} = 0.18$

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 $m = \frac{n_{su}}{m_{sv}\text{ in kg}}$ and $n_{su} = \frac{m_{su}}{M_{su}}$

It follows that: $\Delta T = \frac{K_f \times m_{su}}{M_{su} \times m_{sv}\text{ in kg}} = \frac{1.86 \times 651}{62 \times 2.505} = 7.8°C$

Freezing point $= 0°C - 7.8°C = -7.8°C$

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 ikg 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, $n=\frac{m}{M_r}$	$\frac{49.02g}{12gmol^{-1}}$ $= 4.085mol$	$\frac{2.743g}{1gmol^{-1}}$ $= 2.743molmol$	$\frac{48.23g}{35.5gmol^{-1}}$ $= 1.378mol$
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 C_3H_2Cl

Using $\Delta T = K_f m = \frac{K_f \times m_{su}}{M_{su} \times m_{sv} in\ kg}$

From which:

$M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} in\ kg}$

Where: $\Delta T = (5.5 - 1.12)°C = 4.38°C$, $m_{su} = 3.15g$, $m_{sv} = 25g = 0.025kg$

Substituting: $m_{su} = \frac{5.12 \times 3.15}{4.38 \times 0.025} gmol^{-1} = 147gmol^{-1}$

Let the molecular formula be $(C_3H_2Cl)_n$

Then $36n + 2n + 35.5n = M_r = 147$

$73.5n = 60; n = 2$

The molecular formula is $C_6H_4Cl_2$

Mass of water (solvent) is $100g - 18.2g$ or $81.8g$

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

$n_{su} = \frac{3.15g}{147g/mol} = 0.0214mol$ and $n_{sv} = \frac{25g}{78g/mol} = 0.32mol$

$X_{benzene} = X_{sv} = \frac{n_{sv}}{n_{su} + n_{sv}} = \frac{0.32mol}{0.0214mol + 0.32mol} = 0.937$

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) Using $\pi V = nRT = \frac{m}{M_r}RT$ 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 $\rho_{solution} = \rho_{water} = 1g/mL$

Thus 100g of the solution is equivalent to 100mL (0.1L) of the solution.

Then for cane sugar:

$$\pi_c = \frac{m_c RT}{VM_u} = \frac{5g \times RT}{0.1L \times 342g/mol}$$

And for another solute, X:

$$\pi_x = \frac{m_x RT}{VM_x} = \frac{1g \times RT}{0.1L \times M_x}$$

But $\pi_u = \pi_x$(isotonic solutions)

$$\frac{5g \times RT}{0.1L \times 342g/mol} = \frac{1g \times RT}{0.1L \times M_x}$$

From which $M_x = \frac{342g/mol}{5} = 68.4g/mol$

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 $100mL \times 1.58g/mL = 158g$

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

$n_{su} = \frac{0.5g}{65g/mol} = 0.0076923mol$ and $n_{sv} = \frac{158g}{154g/mol} = 1.025974mol$

$$X_{sv} = \frac{n_{sv}}{n_{su} + n_{sv}} = \frac{1.025974mol}{1.025974mol + 0.0076923mol} = 0.99256$$

Using $P_{soln} = X_{sv}P_{sv}^o = 0.99256 \times 143mmHg = 141.94mmHg$

Vapour pressure of the solution is 141.94mmHg.

Question 98

(a)

(i)

1. Colligative properties depend on concentration of solute in the solution and not on the nature of solute.
2. Colligative properties are tied together in a manner that changing concentration of solute in the solution changes all colligative properties at the same time.
3. Colligative properties are useful in determination of molar mass of non-volatile substances.

(ii) Non-colligative properties include the following:

1. Viscosity
2. Density
3. Surface tension
4. Solubility
5. Electrolytic conductivity

(b) Using $\pi = i \times [\quad]RT$

Then for glucose (i = 1): $\pi_g = 0.01M \times RT$

And for sodium sulphate: $\pi_s = i \times 0.004M \times RT$

But $\pi_g = \pi_s$(isotonic solutions); $0.01M \times RT = i \times 0.004M \times RT$

From which; $i = 2.5$

Na_2SO_4 ionises in water according to the following equation: $Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}$; $N = 3$

$$\alpha = \frac{i-1}{N-1} = \frac{2.5-1}{3-1} = 0.75 \text{ or } 75\%$$

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 $V_{soln} = \frac{100g}{1.02g/mL} = 98mL = 0.098L$

Using $\pi = i \times \frac{nRT}{V} = i \times \frac{m_{NaCl}RT}{M_{NaCl}V}$

Assuming complete dissociation of NaCl, $i = 2$.

Then $\pi = 2 \times \frac{4 \times 0.082 \times 298}{58.5 \times 0.098} atm = 34atm$

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 $C_2 = \frac{C_1 \times \pi_2}{\pi_1} = \frac{0.3 \times 34}{7.3} = 1.4M$

The concentration to be synthesized$= C_2 - C_1 = (1.4 - 0.3)M = 1.1M$

Hence the yeast cell must synthesize $\mathbf{1.1M}$ 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 $m = \frac{n_{su}}{m_{sv} \text{ in kg}}$ and $n_{su} = \frac{m_{su}}{M_{su}}$

It follows that: $\Delta T = \frac{K_f \times m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$

From which $K_f = \frac{\Delta T \times M_{su} \times m_{sv} \text{ in kg}}{m_{su}}$

For biphenyl-naphthalene mixture:

Where $\Delta T = (69 - 68.5)°C = 0.5°C$

m_{sv} in kg $= \frac{100}{1000} kg = 0.1kg$ and $M_{su} = 128g/mol$

Substituting; $K_f = \frac{0.5 \times 128 \times 0.1}{2.67} = 2.4°Ckgmol^{-1}$

The freezing point depression constant is $2.4°Ckgmol^{-1}$

Using $\Delta T = \frac{K_f \times m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$

From which; $M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}}$

Substituting (for biphenyl-unknown compound mixture): $M_{su} = \frac{2.4 \times 1}{(69 - 68.86) \times 0.1} = 171g/mol$

Molar mass of the unknown compound is 171g/mol.