Question 1

Define the following terms with reference to gases:

- (i) Critical temperature
- (ii) Critical volume
- (iii)Critical pressure

Solution

- (i) Is the temperature at and above which a gas cannot be liquefied, no matter how much pressure is applied.
- (ii) Is the volume occupied by one mole of a gas at critical temperature and pressure.
- (iii) Is the pressure required to liquefy a gas at its critical temperature

Question 2

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

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

Solution

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

By Boyle's law:
$$P_iV_i = P_fV_f$$

But $P_i = 3$ atm, $P_f = 1$ atm
Then $3V_i = 1 \times V_f$
Hence $V_f = 3V_i$

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

$$\begin{aligned} &\text{Using } \frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} & \text{(General gas equation)} \\ &\text{Where, } P_i = \ 2 \text{ atm, } P_f = \ 3 \text{ atm,} T_i = 200 \text{K, } T_f = 300 \text{K} \\ &\text{Then } \frac{2 V_i}{200} = \frac{3 V_f}{300} \end{aligned}$$

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

By Charles's law:
$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$
Where $T_1 = 400 \text{K}$ and $T_2 = 100 \text{K}$
Then $\frac{V_i}{400} = \frac{V_f}{100}$
Hence $V_f = \frac{V_i}{4}$

Question 3

Hence $V_f = V_i$

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

Solution

The concept of pressure directly follows from the theory because each collision imparts forces on the wall it hits, and so when very large number of collisions each second hit a unit area of a container's wall, the collective force per area is just the sum of force of all the individual collisions. Since $P = \frac{Force}{Area}$, the collective force per area associated with the collisions is the pressure of the gas.

Question 4

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

$$Cl_2$$
, O_2 , F_2 , N_2

Solution

The molecular speed is high if the molecular mass is small and hence the correct order will be as follows:

$$\frac{\text{Cl}_2 < \text{F}_2 < \text{O}_2 < \text{N}_2}{\text{Increase in molecular speed}}$$

Question 5

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

Solution

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

From PV = nRT

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

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

Thus the partial pressure of oxygen gas, P_{0_2} is 8atm

For helium gas

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

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

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

Hence partial pressure of Helium is 2.4atm

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

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

Hence total pressure in the tank is 10.4 atm

Alternative solution

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

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

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

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

Hence the partial pressure of oxygen gas is 8atm

For Helium gas:
$$P_1 = 1$$
atm, $V_1 = 12$ L, $V_2 = 5$ L

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

Hence the partial of oxygen gas is 2.4atm

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

Hence the total pressure in the tank is 10.4atm

Question 6

When the molecular weight of a volatile liquid is calculated from the mass, volume, temperature, and pressure of a sample of the liquid when vapourised, the assumption is usually made that the gases behave ideally. In fact at a temperature not far above the boiling point of the liquid, the liquid gas is not ideal. Explain how this would affect the results of the molecular weight determination.

Solution

The experimental molecular weight would be greater than the true value.

Explanation

Molecular weight of the vapourised liquid is calculated from the following formula:

$$M_r = \frac{mRT}{PV}$$

Significant intermolecular forces of attraction exists at temperature not far above boiling point. Therefore, the compressibility of the gas is greater and the value of PV is smaller than predicted. This would lead to a higher value of the molecular weight than the true value..

Question 7

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

Solution

By definition:

Vapour density (relative density of a gas) =
$$\frac{Density \text{ of the gas}}{Density \text{ of hydrogen gas}}$$

= $\frac{Mass \text{ of given volume of the gas}}{Mass \text{ of an equal volume of hydrogen gas}}$

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

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

If follows that:

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

But mass of one mole = Molar mass

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

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

Or Molar mass of the gas = Vapour density \times 2g/mol

Question 8

The relative vapour density of a sample of ozone at a certain temperature was 18.3. What is the degree of dissociation of ozone into oxygen under these conditions? (Ozone is O_3 , trioxygen)

Solution

 O_3 dissociates according to the following equation:

$$20_3(g) \rightleftharpoons 30_2(g)$$

Rewriting the equation to show number of molecule of O_2 produced by one molecule of ozone by dividing with 2 throughout the above equation gives: $O_3(g) \rightleftharpoons \frac{3}{2}O_2(g)$

So
$$N = \frac{3}{2} = 1.5$$

Using $\alpha = \frac{i-1}{N-1}$ Where α is the degree of dissociation and i is the Van't Hoff's factor.

But $i = \frac{\text{Expected relative vapour density}}{\text{Observed relative vapour density}}$

Where Expected relative vapour density = $\frac{\text{Expected molar mass (of O}_3)}{2g/\text{mol}} = \frac{48g/\text{mol}}{2g\text{mol}} = 24$

Then $i = \frac{24}{18.3} = 1.31$

It follows that $\alpha = \frac{1.31-1}{1.5-1} = 0.62$

Hence the degree of dissociation is 0.62 or 62%

Question 9

The Van der Waals equation of state for one mole of real gas is as follows:-

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

For any given gas, the values of the constants, 'a and 'b' can be determined experimentally.

- (i) Indicate which physical properties of molecule determine the magnitudes of the constants 'a' and 'b'
- (ii) Which of the two molecules, H₂ or H₂S, has the higher value for 'a' and which has the higher value for 'b'? Explain
- (iii) One of the Van der Waals constants can be correlated with the boiling point of a substance. Specify which constant and how it is related to the boiling point.

Solution

(i)

- 'a' indicates the intermolecular forces of attraction between molecules of real gases (Greater intermolecular forces, greater value of 'a').
- **'b'** indicates actual volume of a molecule of real gas (Greater size or molecular weight of the molecule, greater value of **'b'**).
- (ii) H₂S has higher value of 'a'

Reason:

 H_2S molecules exhibit stronger intermolecular forces of attraction since it has stronger Van der Waals dispersion forces (H_2S has greater molecular weight than H_2) and also has dipole-dipole forces in additional to the dispersion forces while H_2 has the dispersion forces only.

H₂S has higher value of 'b'

Reason:

Having greater molecular weight, H₂S molecule has greater size and therefore greater volume than H₂.

(iii) 'a' is correlated to boiling point. The greater value of 'a' means stronger intermolecular forces of attraction and whence higher boiling point.

Question 10

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

Solution

(a) Using PV=nRT

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

Substituting given values

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

Hence the pressure of vapour in the container is 0.43atm

Question 11

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

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

Solution

- (i) Reducing the temperature of a gas reduces the average kinetic energy (or speed) of the gas molecules. This would reduce the frequency of collisions of gas molecules with the walls of the balloon and also would make those collisions less energetic. In order to maintain constant pressure against the external pressure, the volume must decrease (shrink).
- (ii) The molecules of the gas do have volume, when they are cooled sufficiently, the forces of attraction that exist between them cause them to liquefy or solidify.

Question 12

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

Solution

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

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

Where
$$m = 1.82g$$
, $R = 0.082atmLmol^{-1}K^{-1}$, $T = 25^{\circ}C = (25 + 273)K = 298K$

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

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

Hence molecular mass of the compound is 23g/mol.

Question 13

Predict which of the substances;

- (i) The smallest Van der Waals 'a' constant
- (ii) The largest 'b' constant

Solution

- (i) N₂(Has a weakest intermolecular force of attraction. Among the non-polar, N₂ has smallest molecular weight and therefore smallest Van der Waals dispersion forces. NH₃ has a stronger intermolecular force than N₂ despite the fact that has smallest molecular weight because it is polar covalent molecule with hydrogen bond.
- (ii) CCl₄(It has much greater molecular weight and therefore greatest size making its molecule to occupy greatest volume).

Question 14

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

Solution

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

Substituting given value: 75.9 + 6.37 + %N = 100

From which %N = 17.73%

Then calculating empirical formula of the given compound as follows;

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

Hence t e empirical formula of the compound is $C_5H_5\ N$

Calculating molar mass of the compound

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

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

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

Where
$$\rho = \frac{2.12g}{L}$$
, $R = 0.082 atm Lmol^{-1} K^{-1}$, $T = 110^{\circ} C = 383 K$, $P = 630 mmHg = \frac{630}{760}$ atm

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

Let molecular formula of the compound be $(C_5H_5N)_n$

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

Hence the molecular formula of the compound is C₅H₅N

Question 15

Explain each of the following observations in terms of kinetic molecular theory of gases:

- (i) When NH₃ gas is introduced at one end of a long tube and HCl gas is introduced simultaneously at the other end, a ring of white ammonium chloride is observed to form in the tube after a few minutes. This ring is closer to the HCl end of the tube than the NH₃ end.
- (ii) A flag waves in wind.

Solution

- (i) The molecules of gas are in constant motion, so the HCl and NH₃ diffuse along the tube. Where they meet, the solid NH₄Cl is formed. Since HCl has greater molar mass, its speed is lower, therefore, it does not diffuse as fast as the NH₃.
- (ii) The wind is moving molecules of air that are going mostly in one direction. Upon encountering a flag, they transfer some of their Kinetic energy to it and cause it to move.

Question 16

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

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

Solution

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

Where M_g is the molar mass of the gas

But from PV = nRT

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

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

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

P = standard pressure = 1atm

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

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

$$R = 0.082atmLmol^{-1}K^{-1}$$

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

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

Hence relative density is 14.38

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

Hence normal density of the gas is 1.197g/L

Question 17

From the ideal gas equation, deduce the following:

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

Solution

(i) From ideal gas equation: PV = nRT

For fixed mass of a gas, n is constant

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

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

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

(ii) From ideal gas equation: PV = nRT

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

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

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

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

(iii) From ideal gas equation: PV = nRT

For given mass of a gas, n is constant

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

And from PV = nRT

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

So $P = constant \times T$

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

(iv) From ideal gas equation: PV = nRT

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

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

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

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

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

Thus
$$P_TV = (n_A + n_B + n_C)RT$$

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

Rewriting equation $P_TV = (n_A + n_B + n_C)RT$; $P_TV = n_ART + n_BRT + n_CRT$

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

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

Where PA, PB and PC are partial pressures of A, B and C respectively

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

Question 18

In running diffusion experiment, ammonia is found to diffuse 30.0cm during the time hydrogen chloride moves 20.0cm. Calculate the percentage deviation from Grahm's law.

Solution

Theoretically;

$$\frac{\text{Rate of diffusion of ammonia}}{\text{Rate of diffusion of hydrogen chloride}} = \frac{\text{Distance moved by ammonia}}{\text{Distance moved by hydrogen chloride}} = \sqrt{\frac{M_{H_{Cl}}}{M_{NH_3}}} = \text{Theoretical ratio}$$

$$\text{Thus the theoretical ratio} = \sqrt{\frac{M_{H_{Cl}}}{M_{NH_3}}} = \sqrt{\frac{36.5 \text{g/mol}}{17 \text{g/mol}}} = 1.4653$$

But experimentally;

$$\frac{\text{Distance moved by ammonia}}{\text{Distance moved by hydrogen chloride}} = \frac{30\text{cm}}{20\text{cm}} = 1.5 = \text{Experimentally determined ratio}$$

Then the percentage deviation =
$$\frac{|\text{Experimental ratio-Theoretical ratio}|}{\text{Theoretical ratio}} \times 100\% = \frac{1.5-1.4653}{1.4653} \times 100\% = 2.37\%$$

Hence the given experimental data shows the deviation of 2.37% from Grahm's law of diffusion.

Question 19

From the standpoint of the kinetic molecular theory, explain briefly the properties of gas molecules that cause deviations from ideal behaviour

Solution

- 1. Real gas molecules exhibit finite volume, thus excluding some volume from compression.
- 2. Real gas molecules exhibit intermolecular forces of attraction, thus leading to fewer and less energetic collisions with the walls of the container and hence lower pressure.

Question 20

At 25°C and 1 atmosphere pressure, which of the following gases shows greatest deviation from ideal behaviour? give two reasons for your choice

$$CH_4$$
 SO_2 O_2 H_2

Solution

SO₂ shows greatest deviation

Reasons:

- 1. A molecule of SO₂ has largest size (or volume)
- 2. SO₂ molecule exhibit strongest intermolecular forces of attraction (With largest molecular weight, SO₂ has strongest Van-der-Waals dispersion forces. Also SO₂ has dipole-dipole forces in additional to the strongest dispersion forces while other gases have dispersion forces only).

Question 21

Oxygen can be converted to ozone according to the reaction equation:

$$3O_2(g) \rightarrow 2O_3(g)$$

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

Solution

From the given equation: $30_2(g) \rightarrow 20_3(g)$

Mole ratio of O_2 to O_3 is 3:2

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

Thus 3L of O_2 produces 2L of O_3

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

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

Question 22

Real gases approach ideality at low pressure, high temperature or both. Explain these observations.

Solution

High temperature results in high kinetic energy which overcomes intermolecular forces of attraction.

Low pressure increases distance between molecules leading to greater volume occupied and therefore molecules comprise a small part of the volume and (due to greater distance apart between molecules) the intermolecular forces of attraction become very small.

Question 23

From kinetic equation of gases, derive a mathematical equation of kinetic energy of one mole of a gas and hence show that the kinetic energy varies directly proportional to absolute temperature.

Solution

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

But the kinetic energy of N molecules = $\frac{1}{2}$ Nmc²

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

So from K. E = $\frac{1}{2}$ Nmc², Nmc² = 2K. E

Then substituting Nmc² = 2K. E to the above kinetic equation gives: PV = $\frac{2}{3}$ K. E

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

But from ideal gas equation: PV = nRT

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

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

Since **R** is constant, $\frac{3}{2}$ **R** is also constant and therefore K. E = constant × T or K. E \propto T.

Hence the result of kinetic energy the kinetic energy of gas molecules varies directly proportional to the absolute temperature.

Question 24

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

Solution

Using
$$n = \frac{m}{Mr}$$

Number of moles of $CH_4 = \frac{6.4}{16} \text{ mol} = 0.4 \text{mol}$

Number of moles of $C_2H_6 = \frac{9}{30}$ mol = 0.3mol

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

Then
$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

But $T_1 = T_2 = T$ (temperature is constant)

If follows that: $\frac{P_1V_1}{n_1} = \frac{P_2V_2}{n_2}$

Substituting $\frac{05atm \times 2L}{0.4mol} = \frac{P_2 \times 1L}{0.3mol}$

From which $P_2 = 0.75$ atm

Hence the pressure is 0.75 atm

Question 25

- (i) State Boyle's law
- (ii) At what conditions Boyle's law obeys strictly?

Solution

- (i) The volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature.
- (ii) Bayle's law is obeyed by the gases at **high temperature** and **low pressure**.

Question 26

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

Solution

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

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

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

If temperature and number of moles (mass) of N₂ remain constant

$$P_1V_1 = P_2V_2$$
 (Boyle's law)

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

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

Hence the volume would be 278mL

Question 27

- (i) Explain the concept of absolute zero of temperature.
- (ii) Why absolute temperature cannot be negative?

Solution

- (i) The temperature, at which volume or pressure of any gas reduces to zero, is referred to as absolute zero temperature. Its value is equal to at 0K or -273°C. The absolute zero temperature is just hypothetical temperature because practically all gases become liquefied before reaching -273°C.
- (ii) Negative absolute temperature implies negative volume of gases. Since the volume cannot be negative, it is not possible for absolute temperature to be negative.

Question 28

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

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

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

Solution

From the given equation: $4\text{FeS}_2(s) + 110_2(g) \rightarrow 2\text{Fe}_20_3(s) + 8\text{SO}_2(g)$

8L of SO_2 are produced by 11L of O_2 (For gases: mole ratio = volume ratio)

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

Thus 75L of SO_2 is produced by 103.125L of O_2

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

Where P = 1.04atm, V = 103.125L, $M_r = 32$ g/mol, R = 0.082atmLmol⁻¹K⁻¹

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

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

Hence mass of oxygen is 112.2g

Question 29

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

- (a) What is the pressure in the flask
- (b) When 3g of nitrogen gas is introduced in the flask (still containing oxygen gas)
 - (i) What is the total pressure exerted by the gaseous mixture in the flask?
- (ii) What is the total number of molecules.
- (iii) The mixture is exploded so that nitrogen gas and oxygen gas react according to the equation.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$
, what is the new pressure in the flask?

Solution

(a) From ideal gas equation: PV = nRT

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

Where:
$$m = 4g$$
, $R = 0.082atmLmol^{-1}K^{-1}$, $T = 27^{\circ}C = (27 + 273)K = 300K$, $M_r = 32g/mol$

$$V = 2dm^3$$

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

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

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

By Dalton's law of partial pressure; total pressure exerted by gaseous mixture in the flask is given by; $P_T = P_{O_2} + P_{N_2}$

But from ideal gas equation: PV = nRT

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

Then
$$P_{O_2} = \frac{n_{O_2}RT}{V}$$
 and $P_{N_2} = \frac{n_{N_2}RT}{V}$

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

$$P_{T} = \left(n_{O_2} + n_{N_2}\right) \frac{RT}{V}$$

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

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

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

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

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

Using
$$N = nN_A$$

Where N is the number of molecules of a gas

n is the number of moles of the gas

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

Hence total number of molecules = $0.125 \times 6.02 \times 10^{23} + 0.107 \times 6.02 \times 10^{23}$ = 1.39664×10^{23} molecules

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

(iii) If the mixture is allowed to explode: (Explosion implies that the gaseous mixture was allowed to react).

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

Since mole ratio of N₂ to O₂ is 1:1, oxygen gas present in excess.

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

From above equation; mole ratio of N₂ (limited reactant) to NO is 1:2

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

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

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

Then by Dalton's law of partial pressure:

$$P_{T} = P_{O_{2}} + P_{NO} = \frac{n_{O_{2}}RT}{V} + \frac{n_{NO}RT}{V} = (n_{O_{2}} + n_{NO})\frac{RT}{V}$$
$$= (0.214 + 0.018) \times \frac{0.082 \times 300}{2} = 2.8536 \text{atm}$$

Hence the new pressure in the flask is 2.8536atm

Question 30

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

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

Solution

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

But $n = \frac{m}{M_r}$
Thus V = $\frac{mRT}{PM_r} = \frac{8 \times 0.082 \times 298}{5 \times 32} \, dm^3 = 1.2218 dm^3$

Hence the volume of the vessel is 1.2218dm³

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

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

But
$$n_{0_2} = \frac{8}{32}$$
 moles = 0.25 moles

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

Thus the final pressure is 25atm.

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

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

1mol 0.25mol

From above equation; mole ratio of oxygen to hydrogen is 1:2, thus 0.25 moles of oxygen required (2×0.25) moles = 0.5 moles of hydrogen.

Thus (1 - 0.5) moles = 0.5 moles of hydrogen remains unreacted at the end of the reaction.

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

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

The final pressure in the vessel is 10atm

Question 31

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

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

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

- (i) The partial pressure of HCl(g) at 327°C.
- (ii) The amount of ammonium chloride originally present in the bulb.

Solution

- (i) Gases which present at 327°C are (after decomposition of solid NH₄Cl):
 - Helium gas
 - Ammonia (NH₃) gas and
 - Hydrogen chloride (HCl) gas

By Dalton's law of partial pressure, total pressure exerted by gaseous mixture at 327°C is given by; $P_T = P_{He} + P_{NH_3} + P_{HCl}$

But from the given equation, mole ratio of NH₃ to HCl is 1:1

Thus
$$n_{HCl} = n_{NH_3} = n$$

And hence
$$P_{HCl} = P_{NH_3} = P$$

So
$$P_T = P_{He} + 2P$$

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

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

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

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

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

Thus P_{He} at 327°C is 228mmHg

But
$$P_T = P_{He} + 2P = 908$$
mmHg

Then
$$908 = 228 + 2P$$

Or
$$P = 340$$
mmHg

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

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

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

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

But for helium:

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

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

Then substituting the value o f V in $n_{HCl} = \frac{340V}{760 \times 0.082 \times 600}$

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

But from the given equation

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

Moles ratio of NH₄Cl to HCl is 1:1

Thus number of moles of NH₄Cl originally present in the flask was also 0.0149 moles

Using $m = nM_r$

Where molar mass of NH₄Cl is 53.5g

Then
$$m = 0.0149 \times 53.5g = 0.797g$$

Hence amount of NH₄Cl was approximately 0.8g

Question 32

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

$$MgCO_3(S) \rightarrow MgO(s) + CO_2(g)$$

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

- (i) The partial pressure of CO_2 .
- (ii) The amount of MgCO₃ originally present in the vessel.

 (In your calculation neglect the volume of the solid and the change of volume of the container).

Solution

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

Then for air:

$$P_1 = 1 atm T_1 = 20$$
°C = 293K and $T_2 = 800$ °C = 1073K

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

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

By Dalton's law of partial pressure:

$$P_T = P_{CO_2} + P_{air}$$
 or $P_{CO_2} = P_T - P_{air} = 5atm - 3.66atm = 1.34atm$

Hence the partial pressure of CO₂ is 1.34 atm.

(ii) Using
$$n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{1.34 \times 1}{0.082 \times 1073}$$
 moles = 0.0152moles

From the given equation:

Mole ratio of CO_2 to $MgCO_3$ is 1:1

Thus number of moles of CO_2 = number of moles of $MgCO_3$ = 0.0152mol

Using $m = nM_r$

Mass of
$$MgCO_3 = 0.0152 \times 84g = 1.2768g$$

Hence amount of MgCO₃ was approximately 1.3g.

Question 33

Explain the following:

- (i) Air pressure in a car tire increases during driving.
- (ii) A hot-air balloon floats in air.

(iii) Propane tanks should not be kept at extreme temperatures.

Solution

- (i) During driving, temperature of air inside car tire increases while its volume remains constant which in turn means that the pressure in the tire will increase in accordance to Gay-Lussac's pressure-temperature law.
- (ii) According to Charles's law; hot air inside the balloon has larger volume than cold air outside the balloon. With the addition of the fact that the air molecules in the greater volume are of more distant to each other and therefore making them to exert weaker attraction between them, the air molecules inside the balloon tend to spread out even further making them to have significant lower density than the air outside and hence the balloon floats.
- (iii) **Extreme high temperature** will cause high increase in pressure in accordance to Gay-Lussac's law and therefore the tank will burst leading to the explosion while **extreme low temperature** cause large decrease in pressure of the gas in accordance to the same law.

Question 34

A sample of butane (C_4H_{10}) of unknown mass is introduced into a vessel of volume, V at 28°C and 560mmHg. To this vessel is introduced 8.6787g of Neon gas until the final pressure in the vessel is 1420 mmHg at the same temperature. Calculate the volume of the vessel and the mass of butane introduced (Atomic mass of Ne is 20).

Solution

For Butane:

$$P_hV = n_hRT$$
(i)

When Neon is introduced in the vessel:

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

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

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

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

And it is given that: $P_T = 1420$ mmHg, $P_b = 560$ mmHg

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

From which $n_b = 0.2826$ moles

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

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

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

Thus mass of butane, $m_b = n_b M_b$

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

Then
$$M_b = 0.2826 \times 58g = 16.3908g$$

Hence mass of butane was approximately 16.4g

Alternative solution

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

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

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

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

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

Hence the volume of the vessel is 9.5 dm³.

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

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

Hence mass of butane was approximately 16.4g

Question 35

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

Solution

Good flavour of chips is maintained by high pressure in the bag which ensures freshness of preservative chemicals added during the manufacture of the chips. Placing the bag in the freezer causes a reduction in pressure in accordance to Gay-Lussac's law, and hence good flavour is lost.

Question 36

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

Solution

Given that:

Pressure at $127^{\circ}C = 950 \text{mmHg}$

Pressure at 27°C = 380mmHg

Volume of flask = $600 \text{cm}^3 = 0.6 \text{L}$

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

Thus at 27°C:

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

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

Using
$$P_T = \frac{\left(n_{H_2O} + n_{N_2}\right)RT}{V}$$
, Then $\frac{950}{760} = \frac{\left(n_{H_2O} + 0.0122\right) \times 0.082 \times 400}{0.6}$

From which $n_{H_2O} = 0.011$ moles

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

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

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

Question 37

State whether you agree or you disagree in each of the following statements. In each case, give brief explanation to support your answer.

- (i) According to Boyle's law, equal mass of hydrogen and oxygen kept in different containers of the same volume at the same temperature exerts the same pressure.
- (ii) According to Charles's law increasing the temperature of the gas from 10°C to 20°C doubles its volume.
- (iii) 2mol of oxygen gas in 5L container at 25°C shows greater deviation from ideal behaviour than 1mol of the oxygen gas in the container of the same volume at the same temperature.

Solution

(i) Disagree

Explanation

Amount of pressure exerted by a gas does not directly depend on the mass of the gas; it depends on the number of gas molecules (particles). With equal mass of hydrogen and oxygen, hydrogen having smaller molar mass will possess greater number of gas molecules $\left(n = \frac{m}{M_T}\right)$ and hence greater pressure of hydrogen than that of oxygen despite the fact that the two have equal mass.

(ii) Disagree

Explanation

For the volume of the gas to double in accordance to Charles's law the temperature in Kelvin (absolute temperature) must double too. Although the given temperature seems in to double in Celsius scale but converting them to Kelvin gives 283K and 393K respectively which is clear that the latter is not twice of the former.

(iii) Agree

Explanation

Greater number of gas molecules means greater of both pressure deviation and volume deviation from their corresponding ideal results. This is because, with greater number of gas molecules the intermolecular forces will be higher with more gas molecules pulling the gas molecules backward before hitting the container's wall and hence more decrease in real pressure. Also greater number of gas molecules means greater volume occupied by gas molecules which in turn means less empty space is left compared to the volume of the container.

Ouestion 38

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

Solution

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

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

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

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

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

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

Question 39

According to one of postulates of kinetic theory of gases, "Gas exerts pressure in the container due to collision between gas molecules and the container's wall." Based on this postulate, explain clearly the effect of the each of the following factors on the pressure exerted by the gas:

- (i) Decreasing the volume of the container at the same temperature.
- (ii) Increasing the temperature of the container.
- (iii) Adding amount of the gas in the container at the same temperature

Solution

- (i) Decreasing the volume of the container will decrease the distance between walls of the container and therefore gas molecules will hit the container's walls more frequent leading to higher pressure.
- (ii) Increasing temperature, increases the speed of gas molecules and therefore making collisions between gas molecules and container's walls more energetic and more frequent and hence higher pressure.
- (iii)Adding amount of the gas in the container increases the concentration of the gas leading to more frequent collision between gas molecules and container's walls and hence higher pressure.

Ouestion 40

A gas diffuse through a porous plug at the rate of 143cm³/s. Carbon dioxide diffuses through the plug at the rate of 0.43 cm³/s. Calculate the molar mass of the gas.

Solution

By Grahm's law of diffusion:

$$\frac{R_{CO_2}}{R_g} = \sqrt{\frac{M_g}{M_{CO_2}}} \ \, \text{or} \, \, M_g = M_{CO_2} \left(\frac{R_{CO_2}}{R_g}\right)^2 = 44 \left(\frac{0.43}{143}\right)^2 = 3.98 \times 10^{-4} \text{g/mol}$$

Hence molar mass of the gas is 3.98×10^{-4} g/mol.

Question 41

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

Solution

Oppose.

Explanation

To be valid, Gay-Lussac's needs the temperature to be in Kelvin (absolute temperature). So in Kelvin scale the increase in temperature is from 300K to 600K from which it is clear that the latter is the twice of the former and hence the pressure should in accordance to Gay-Lussac's law as suggested by John.

Ouestion 42

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

Solution

From Grahm's law of diffusion: $\frac{R_e}{R_{CO_2}} = \sqrt{\frac{M_{CO_2}}{M_e}}$

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

Then
$$\frac{R_e}{R_{CO_2}} = \frac{V_e/_{t_e}}{V_{CO_2}/_{t_{CO_2}}} = \frac{V_e t_{CO_2}}{V_{CO_2} t_e} = \sqrt{\frac{M_{CO_2}}{M_e}}$$

Where:

$$M_{CO_2} = 44 \text{gmol}^{-1}, M_e = \text{molar mass of ethane } (C_2 H_6) = 30 \text{gmol}^{-1}, V_{CO_2} = 25 \text{cm}^3,$$

 V_e = volume of ethane diffused = 10.25cm³, t_e = time taken by ethane to diffuse = 40s

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

From which $t_{CO_2} = 118s = 1min58sec$

Hence the time taken by CO₂ is 1min58 sec.

Question 43

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

- (i) the molar mass of oxide
- (ii) the formula of oxide of nitrogen.

Solution

By Grahm's law of diffusion;
$$\frac{t_O}{t_{H_2}} = \sqrt{\frac{M_O}{M_{H_2}}}$$
 or $M_O = M_{H_2} \left(\frac{t_O}{t_{H_2}}\right)^2$

Where $t_0=10 min23 sec=623 sec, t_{\rm H_2}=2 min10 sec=130 sec, M_{\rm H_2}=2 g/mol$

Thus
$$M_0 = 2 \times \left(\frac{623}{130}\right)^2 = 46g/\text{mol}$$

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

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

Hence the formula of oxide is NO_2 .

Question 44

- (a) State the following:
- (i) Boyle's law
- (ii) Charles's law

Solution

- (i) Volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature.
- (ii) The volume of fixed mass of a gas varies directly proportional to its absolute temperature at constant pressure.

Question 45

Laws stated in **Question 44** above may be combined to give single gas equation. Derive and give name of the equation.

Solution

From Boyles' law: $V \propto \frac{1}{p} \dots \dots \dots \dots \dots \dots (i)$ (n and T are constant).

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

Hence $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3} = \cdots = \frac{P_nV_n}{T_n}$ (n is constant)

Name of the equation: Combined gas law.

Question 46

Nickel forms a carbonyl $Ni(CO)_n$. Deduce the value of n from the fact that: Carbon monoxide diffuse 2.46 times faster than the carbonyl compound. (Atomic mass of Ni is 59)

Solution

By Grahm's law of diffusion:

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

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

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

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

Then: 59 + 28n = 169

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

Hence the value of n is 4.

Question 47

Explain the following:

- (i) Doubling number of moles of a real gas in a container at given temperature does not double its pressure.
- (ii) Pressure deviation of real gas from ideal pressure is maximum at its boiling temperature.

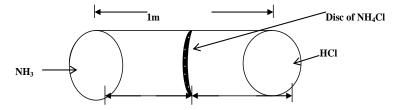
Solution

- (i) Doubling the pressure as result of doubling is the ideal behaviour which neglects presence of intermolecular forces. In real gas, doubling number of moles means more intermolecular forces which results into more pressure deviation making the increase in pressure to be less than one could expect if the gas would be ideal.
- (ii) Kinetic energy of gas decreases as the temperature decreases toward its boiling point. At boiling point kinetic energy is so small that it unable to break intermolecular forces to the extent that the liquefaction of the gas starts to take place.

Question 48

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

Solution



From Grahm's law of diffusion:
$$\frac{R_{NH_3}}{R_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}}$$

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

Thus
$$\frac{R_{NH_3}}{R_{HCl}} = \frac{l_{NH_3}}{l_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}}$$
; Then $\frac{x}{1-x} = \sqrt{\frac{36.5}{17}}$

Solving above equation gives x = 0.59m

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

Ouestion 49

Arrange the following gases in order of increasing their magnitude of volume correction in Van-der-Waals equation.

Solution

The magnitude of volume correction increases as molecular size (volume) of gas increases. Gases with larger molecular size have large molecular weight. So the order is as follows:

$$SF_6 < CO_2 < CO < NH_3 < He$$

Question 50

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

Solution

From the Graham's law of diffusion: $\frac{t_{mixture}}{t_{Br_2}} = \sqrt{\frac{M_{mixture}}{M_{Br_2}}}$ but $t_{mixture} = \frac{1}{2}t_{Br_2}$

Then
$$\frac{\frac{1}{2}t_{Br_2}}{t_{Br_2}} = \sqrt{\frac{M_{mixture}}{M_{Br_2}}} = \sqrt{\frac{M_{mixture}}{160}}$$

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

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

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

Where molar masses of CO and CO₂ are 28g/mol and 44g/mol respectively

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

$$28x + 4400 - 44x = 4000$$

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

Hence:

The percentage of CO is 25%

The percentage of CO₂ is 75%

Question 51

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

Solution

(i) From Boyle's law: $V \propto \frac{1}{p}$; constants: n and T

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

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

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

Where R is the proportionality constant; and the which is known as universal molar gas constant

Hence PV = nRT (ideal gas equation).

(ii) Because it shows relationship between all variables (pressure, volume, number of molecules and temperature) of gaseous state.

Ouestion 52

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

Solution:

By Graham's law of diffusion:

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

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

Let the percentage by volume of NO₂ be x

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

Where molar mass of NO₂ is 46g/mol

Molar mass of N_2O_4 is 92 g/mol

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

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

$$46x = 2000$$

$$x = 43.5$$

And
$$100 - x = 100 - 43.5 = 56.5$$

Hence: The percentage of NO₂ is 43.5 %

The percentage of N₂O₄ is 56.5%

Question 53

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

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

Solution

- (i) Pressure of the gas decreases as the volume increases (or pressure of the gas increases as the volume decreases).
- (ii) Temperature, number of gas molecules

Question 54

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

Solution

By Dalton's law of partial pressure:

$$P_T = P_{H_2} + P_U$$

But
$$P_T = 6$$
atm and $P_{H_2} = \frac{n_{H_2}RT}{V} = \frac{0.7 \times 0.082 \times 300}{3}$ atm = 5.74atm

So
$$P_U = P_T - P_{H_2} = 6atm - 5.74atm = 0.26atm$$

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

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

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

Thus
$$\frac{V_{H_2}}{V_U} = \frac{n_{H_2}}{n_U} = \sqrt{\frac{M_U}{M_{H_2}}}$$

From which;
$$M_U = M_{H_2} \left(\frac{V_{H_2}}{V_{U}} \right)^2 = 2 \left(\frac{0.7}{0.0317} \right)^2 \text{gmol}^{-1} = 975 \text{gmol}^{-1}$$

Hence the molecular weight of unknown gas is 975gmol⁻¹

Question 55

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

Solution

No. (CO and O_2 reacts, so direct application of Dalton's law of partial pressure is not allowed).

At 30°C, CO reacts with O₂ According to the following equation:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

From which 3atm of CO reacts with 1.5atm $(^{1}/_{2} \times 3atm)$ of 0_{2} to give 3atm (For gases pressure ratio is equal to mole ration).

So after the reaction there are:

- 0atm of CO (all of it reacted)
- 0.5atm (2atm-1.5atm) of unreacted O_2
- 3atm of produced CO₂

Then by Dalton's law of partial pressure; the total pressure in the container is given by;

$$P_T = P_{O_2} + P_{CO_2} = (3 + 0.5)atm = 3.5atm$$

Hence the correct total pressure is 3.5atm.

Question 56

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

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

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

Solution

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

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

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

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

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

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

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

Hence the time required by gas J is 306 seconds

Ouestion 57

Explain the effect of dissociation and association in the experimental determination of molar mass of volatile substances.

Solution

Both association and dissociation lead to abnormal result of experimental determination of molar mass of volatile substances as explained below:

Dissociation

Dissociation is splitting of a large molecule into two or more smaller molecules. It leads to increase in number of gas molecules and whence the increase in volume of the gas. So from the ideal gas equation which can be written as $PV = \frac{m}{M_r}RT$; it is clearly understood that the volume (V) of the gas varies inversely proportional to its molar mass (M_r) . So the increase in volume of the gas as the result of dissociation leads to decrease in molar mass of the gas. Hence dissociation makes the measured molar mass of volatile substance to be smaller than that suggested by its normal molecular formula.

Association

Association is the combining of more than one small molecule to form one larger molecule. It leads to decrease in number of gas molecules and whence decrease in volume of the gas. So from the ideal gas equation; $PV = \frac{m}{M_r}RT$ where volume of the gas varies inversely proportional to its molar mass, the molar mass of the gas must increase as result of association. Hence association makes the measured molar mass of volatile substance to be greater than suggested by its normal molecular formula.

Question 58

In a Victor Meyer determination; 0.292g of a substance displaced 61cm³ of air at 22°C and 755mmHg. Calculate molar mass of the substance.

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

Solution

Volume of air displaced = volume of the sample = $61cm^3 = 0.061dm^3$

Mass of the sample = 0.292g

Pressure e exerted by the vapour of the sample = Total pressure - Vapour pressure of water

$$= (755 - 22)$$
mmHg $= 733$ mmHg

From general gas equation;

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$
; $V_2 = \frac{P_1V_1T_2}{P_2T_1}$

Volume of the gas at stp(T = 273, P = 760mmHg) may be found if;

$$P_1 = 733$$
mmHg, $P_2 = 760$ mmHg, $V_1 = 0.061$ dm³

$$T_1 = 295K \text{ And } T_2 = 273K$$

Substituting
$$V_2 = \frac{733 \times 0.061 \times 273}{760 \times 295} \text{ dm}^3 = 0.0544 \text{dm}^3$$

But at stp, 1mol of the gas, occupies $22.4dm^3$ and therefore mass of the gas in $22.4dm^3$ (at stp) is the molar mass of the gas

- Also it is given that 0.292g of the gas occupies 0.061dm³
- Then 22.4dm³ of the gas corresponds to:

$$\frac{22.4}{0.0544} \times 0.292$$
 or 120.2g/mol

Hence molar mass of the substance is 120.2g/mol

Alternative solution:

The easier method of calculating molar mass from the result obtained from Victor Mayer's apparatus is by using ideal gas equation, PV = nRT from which it can be shown that; $M_r = \frac{mRT}{PV}$.

With:

$$m = 0.292g$$
, $T = 295K$, $P = 733mmHg$, $V = 0.061dm^3$;

$$\label{eq:Mr} \rm M_r = \frac{0.292 \times 0.082 \times 295}{\frac{733}{760} \times 0.061} \ or \ 120.1g/mol$$

Question 59

Define Van't Hoff's factor,i and give its basic mathematical formula.

Solution

It is the ratio of observed number of particles to expected number of particles.

Thus
$$i = \frac{Observed number of particles}{Expected number of particles}$$

Question 60

Give an interpretation for each of the following Van't Hoff's factor (i) values:

- (i) i > 1
- (ii) i < 1
- (iii) i = 1

Solution

- (i) If i > 1; it means that observed number of particles > expected number of particles which implies that there is dissociation.
- (ii) If i < 1; it means that observed number of particles < expected number of particles which implies that there is dissociation.
- (iii) If i = 1; it means that observed number of particles = expected number of particles which implies that there is neither dissociation nor association.

Question 61

Calculate the relative molecular mass of volatile liquid X from the following data:

Mass of Dumas bulb full of air at 10°C and 770 mmHg = 25.700g

Mass of bulb sealed full of vapour of X at 100°C and 770mmHg = 25.759g

Mass of bulb full of water = 265.1 g

Given: 1 dm³ of air of s.t.p has mass of 1.293 g

Solution

Mass of water which fill the bulb = (265.1 - 25.7)g = 239.4g

Volume of bulb = volume of water =
$$\frac{m}{\rho} = \frac{239.4g}{1g/cm^3} = 239.4cm^3$$

But at s.t.p 1dm³ of air contain 1.293g

$$P_1 = 760 \text{mmHg}, V_1 = 1 \text{dm}^3, T_1 = 273 \text{K}$$

$$P_2 = 770 \text{mmHg}, T_2 = 283 \text{K}, V_2 = ?$$

$$V_2 = \left(\frac{283}{273}\right) \left(\frac{760}{770}\right) \times 1 dm^3 = 1.0232 dm^3$$

Thus mass of air filled in the bulb = $\frac{0.2394 \times 1.293}{1.0232} = 0.303g$

So mass of the bulb is (25.7 - 0.303) g = 25.397g

Mass of vapour of X = (25.759 - 25.397) g = 0.362g

$$M_r = \frac{mRT}{PV} = \frac{0.362 \times 0.082 \times 383 \times 760}{770 \times 0.2394} = 46.9g/mol$$

Hence the relative molecular mass of X is 46.9g/mol

Question 62

One molecule of hypothetical gas $A_{XN}B_{YN}$ is dissociates into N molecules of A_XB_Y . If i is Van't Hoff's factor of the gas and α is its degrees of dissociation, prove that:

$$\alpha = \frac{i-1}{N-1}$$

Solution

Equation to show the dissociation of given compound is shown below:

 $A_{XN}B_{YN}(g) \Rightarrow NA_XB_Y$

Initial number of molecules before dissociation

Number of molecules after dissociation

 $1 - \alpha$

0 Να

Where α is numerically equal to degree of dissociation = fraction of the molecules dissociated.

From the above equation:

Expected number of molecules (without dissociation) = 1

Observed number of molecules (after dissociation) = $1 - \alpha + N\alpha = 1 + \alpha (N - 1)$

Then
$$i = \frac{Observed \ number \ of \ particles}{Expected \ number \ of \ particles} = \frac{1 + \alpha(N-1)}{1} \ or \ i = 1 + \alpha(N-1)$$

Hence
$$\alpha = \frac{i-1}{N-1}$$

Question 63

The relative molar mass of nitrogen dioxide at 25°C is 80. What is the percentage of molecules in the mixture is N_2O_4 ?

Solution

Expected molar mass of N_2O_4 is $92g/mol((2 \times 14) + (4 \times 16)) = 92g/mol$

Measured molar mass of N₂O₄ is 80g/mol

Using i =
$$\frac{\text{Expected molar mass}}{\text{Measured molar mass}} = \frac{92 \text{gmol}^{-1}}{80 \text{gmol}^{-1}} = 1.15$$

From the equation: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; N = 2

$$1 - \alpha$$
 2α After association

Using
$$\alpha = \frac{i-1}{N-1} = \frac{1.15-1}{2-1} = 0.15$$
 or 15%

But total number of molecules of N₂O₄ after dissociation:

=
$$1 - \alpha + 2\alpha = (1 + \alpha)$$
 Molecules

$$\%N_2O_4$$
 in the mixture $=\frac{n_{N_2O_4}}{n_T} \times 100\% = \frac{1-\alpha}{1+\alpha} \times 100\% = \left(\frac{1-0.15}{1+0.15}\right) \times 100\% = 73.9\%$

Hence the percentage of N_2 in the mixture is 73.9%

Question 64

N molecules of the hypothetical gas $A_X B_Y$ undergoes association to give 1 mole of $A_{XN} B_{YN}$. If i is Van't Hoff's factor of the gas and α is its degrees of dissociation. Prove of that:

$$\alpha = \frac{i-1}{\frac{1}{N} - 1}$$

Solution

Equation to show the association of given compound is shown below:

 $NA_XB_Y(g) \Rightarrow A_{XN}B_{YN}(g)$

Initial number molecules before association N

0

Number of molecules after association

 $N - N\alpha$

α

Where α is the degree of association.

Expected number of molecules (without association) = N

Observed number of molecules (after association) = $N - N\alpha + \alpha = N + \alpha (1 - N)$

Then
$$i = \frac{Observed\ number\ of\ particles(molecules)}{Expected\ number\ of\ particles(molecules)} = \frac{N + \alpha(1-N)}{N}\ or\ \alpha = \frac{iN + N}{1-N}$$

Dividing by N throughout the expression
$$\frac{iN+N}{1-N}$$
 gives $\alpha=\frac{i-1}{\frac{1}{N}-1}$

Hence degree of association is given by; $\;\alpha = \frac{i-1}{\frac{1}{N}-1}$

Ouestion 65

Nitrogen dioxide exists in an equilibrium mixture: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

A 10.32g of AlCl₃ are allowed to vapourise in 1dm³ vessel at 80°C a pressure of 1.7×10^5 Nm⁻² develops. What is the degree of association of AlCl₃ into Al₂Cl₆.

Solution

An equation to show association of $AlCl_3$ into Al_2Cl_6

$$2AlCl_3(g) \rightleftharpoons Al_2Cl_6(g); N = 2$$

From PV =
$$\frac{m}{M_r}$$
RT or $M_r = \frac{mRT}{PV}$

Where: m = 10.32g, R = 8.314, $T = 80^{\circ}C = 353K$, $P = 1.7 \times 10^{5} \text{ Nm}^{-2}$

$$V = 1 dm^3 = 103 m^3$$

$$M_{r} = \frac{10.32 \times 8.314 \times 353}{1.7 \times 10^{5} \times 10^{-3}} \text{gmol}^{-1} = 178 \text{gmol}^{-1}$$

 $i = \frac{Expected \ molar \ mass}{Measured(observed) \ molar \ mass}$

But expected molar mass of AlCl₃ = $(27 + (3 \times 35.5)) = 133.5$ gmol

$$i = \frac{133.5}{178} = 0.75$$

Degree of association,
$$\alpha$$
 is given by; $\alpha = \frac{i-1}{\frac{1}{N}-1} = \frac{0.75-1}{\frac{1}{2}-1} = 0.5\%$ or 50%

Hence degree of association of AlCl₃ into Al₂Cl₆ is 50%

Question 66

If helium gas is cooled, will the distribution of velocities look more like that of H₂ or of H₂O? Explain your answer.

Solution

 H_2O . Cooling slows the velocities of the He atoms, causing them to behave as though they were heavier.

Question 67

20.85g of phosphorous (V) chloride are allowed to vapourise in 5 dm 3 vessel at 175°C.A pressure of 1.04 \times 10⁵ Pa develops. Calculate the degree of dissociation of PCl₅ into PCl₃ and Cl₂.

Solution

An equation to show the dissociation of PCl₅;

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

$$N = 2$$

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

Where m =
$$20.85g$$
, R = 8.314 , T = 175° C = 448 K, P = 1.04×10^{5} Pa

$$V = 5 dm^3 = 5 \times 10^{-3} m^3$$

$$M_r = \frac{20.85 \times 8.314 \times 448}{1.04 \times 10^5 \times 5 \times 10^{-3}} \text{gmol}^{-1} = 149 \text{gmol}^{-1}$$

But expected molar mass of PCl₅ is 208.5 gmol⁻¹

$$i = \frac{\text{Expected molar mass}}{\text{Measured molar mass}} = \frac{208.5}{149} = 1.4$$

Using
$$\alpha = \frac{i-1}{N-1} = \frac{1.4-1}{2-1} = 0.4$$
 or 40%

Hence degree of dissociation of phosphorous (V) chloride is 0.4 or 40%

Question 68

Calculate the relative molecular mass of Iron (III) chloride.

Solution

Molecular mass of FeCl₃

$$= 55 + (3 \times 35.5) = 161.5$$
g/mol

Hence molecular mass of Iron (III) chloride is 161.5g/mol.

Question 69

Calculate another value from the following data.

When 1g of Iron (III) chloride was volatilised at 300°C, its vapour displaced 76cm³ of air measured at 27°C and 101 KPa (758mmHg) pressure.

Comment on your two values of parts (a) and (b) (r. a. m. Cl = 35.5, Fe = 55)

Solution

Volume of air displaced at 27°C is 76cm³

That is
$$V_1 = 76 \text{cm}^3$$
, $T_1 = 27 \text{°C}$ or 300K

So the volume of air at 300°C (573K) may be found by applying Charles's law as follows:

From Charles's law:
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
 or $V_2 = \left(\frac{T_2}{T_1}\right) V_1 = \frac{573}{300} \times 76 \text{cm}^3 = 145.16 \text{cm}^3$

But volume of air displaced = volume of Iron (III) chloride vapour

Thus the volume of FeCl₃ vapour is 145.16cm³

Using
$$M_r = \frac{mRT}{PV} = \frac{1 \times 0.082 \times 573 \times 760}{758 \times 145.16 \times 10^{-3}} = 324.5 \text{g/mol}$$

Hence molar mass of FeCl₃ is 324.5g/mol

Comment:

The obtained molar mass in (b) is approximately twice the value obtained in (a) because in the vapour phase two molecules of Iron (III) chloride associates (dimerises) to form a dimer which corresponds to the molecular formula of Fe_2Cl_6

Ouestion 70

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

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

Solution

- (i) The number of molecules in the gas increases as the volume increases.
- (ii) Temperature, pressure

Question 71

 140 cm^3 of water vapour measured at 150°C and 100700 Nm^{-2} (755mmHg) pressures have a mass of 0.071g. Show that these figures are in accordance with the formula H_2O for steam.

Solution

Given that:

$$v = 140 \text{cm}^3 = \frac{140}{1000} \text{dm}^3$$
; $T = 150 \text{°C} = 423 \text{K}$

$$P = 755 \text{mmHg} = \frac{755}{760} \text{atm}, m = 0.071 \text{g}$$

From
$$PV = \frac{M}{Mr} RT$$

$$Mr = \frac{mRT}{PV} = \frac{0.071 \times 0.082 \times 423 \times 760 \times 1000}{755 \times 140} = 17.7g/mol$$

Thus the measured molar mass of water is approximately 18g/mol

But the molecular formula H₂O suggests molecular mass of water to be 18g/mol

Hence the given figures are in accordance with the formula H₂O for steam

Question 72

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

Solution

Bicycle tyre absorb heat energy from the sun raising its temperature which in turn will raise its pressure in accordance to Gay-Lussac's law. If the pressure in the tyre rises beyond its limit, the tyre will burst.

Question 73

Beryllium chloride was known to contain 11.3% of beryllium but the oxidation number of the metal was uncertain. The chloride was found to have a relative vapour density of 40. Determine the oxidation number of beryllium in the compound and hence it's relative atomic mass.

Solution

If the oxidation number of Beryllium (Be) in the compound is x, then the molecular formula of its chloride will be $BeCl_x$

Where x = oxidation number of Be = number of moles of chlorine atoms in the compound

But percentage of Be in the Compound is 11.3%

So the percentage of chlorine atoms in the compound is (100 - 11.3)% = 88.7%

And molar mass of the compound (BeCl_x) = Relative vapour density \times 2 = 40 \times 2 = 80

Thus mass of chlorine atoms in the compound $\frac{88.7}{100} \times 80 = 70.96g$

Therefore number of moles of chlorine atoms in the compound $=\frac{70.96}{35.5}$ mol = 2mol

So oxidation number of Be in the compound is 2

The molecular formula of the compound is then become BeCl₂

It follows that y + 71 = 80; where y is atomic mass of Be

From which y = 9

Hence the relative atomic mass of Be is 9

It should be noted that:

In the question it was asked to find the relative atomic mass of Be from the result of its oxidation number and not otherwise.

Ouestion 74

(a) Which of the following gases diffuse more slowly than oxygen?

Solution

Gases whose molar masses are larger than that of oxygen gas will diffuse more slowly than oxygen. These are: F_2 , N_2O , Cl_2 and H_2S

Question 75

In a diffusion experiment, the time required for water to cover the space between two marks on a tube as oxygen diffused out of it was 240 seconds. In identical conditions, the time required for another gas, X, was three and three – quarters minutes. Calculate the relative molecular mass of X

Solution

From Grahm's of diffusion

$$\frac{t_x}{to_2} = \sqrt{\frac{M_x}{M_0}} \text{ or } M_x = Mo_2 \left(\frac{t_x}{to_2}\right)^2$$

Where $Mo_2 = 32g/mol$

 $to_2 = 240$ seconds, $t_x = 3\frac{3}{4}$ minutes = 225 seconds

Then
$$M_x = 32 \times \left(\frac{225}{240}\right)^2 = 28g/\text{mol}$$

Hence the relative molecular mass of X is 28

Question 76

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

Solution

From the first postulate of kinetic molecular theory, the gas consists of very small molecules in a random motion of which there is a collision between gas molecules themselves and the collision between gas molecules and the walls of the container. This makes the direction of the motion of the gas to be completely random whereby the gas will continue to spread out until it is evenly distributed throughout the volume of the container.

Question 77

A certain volume of hydrogen diffuses from an apparatus in one minute. Calculate the time required for the diffusion of the same volume of ozonide oxygen, containing 10% of ozone by volume, from the apparatus under identical conditions. (ozone is 0_3 trioxygen).

Solution

Ozone always exists in a mixture with oxygen as result of its dissociation according to the following equation:

$$20_3(g) \approx 30_2(g)$$

So if the percentage of O_3 is 10%

Then the percentage of O_2 will be (100 - 10) % = 90%

So average molecular mass of gases

$$= \frac{10}{100} M_{O_3} + \frac{90}{100} M_{O_2}$$
$$= \left(\frac{10}{100} \times 48\right) + \left(\frac{90}{100} \times 32\right) = 33.6 \text{ g/mol}$$

If M_m and t_m is the average molecular mass of the mixture and time taken by mixture to diffuse respectively;

Then by Grahm's law of diffusion:
$$\frac{t_m}{t_{H_2}} = \sqrt{\frac{M_m}{M_{H_2}}}$$
 or $t_m = t_{H_2} \sqrt{\frac{M_m}{M_{H_2}}}$

So, tm =
$$1\sqrt{\frac{33.6}{2}}$$
 = 4.1minutes = 246 second

Hence the time required for ozonide oxygen is 246 seconds

Question 78

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

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

Solution

- (i) Avogadro's law.
- (ii) Identical balloons have the same volume and therefore they both contain the same number of particles (molecules) in accordance to Avogadro's law. Since one atom of helium has smaller mass than one molecule of oxygen, with equal number of particles for each, the helium balloon will be lighter.

Question 79

The relative vapour density of nitrogen dioxide at 1050°C is 24; calculate the degree of dissociation (by mass) of the gas in these conditions.

Solution

Since NO₂ and N₂O₄ are at equilibrium according to the following equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

If follows that:

Observed molar mass of N_2O_4 = observed molar mass of NO_2

But $M_r = 2 \text{ g/mol} \times \text{Relative vapour density} = 2 \times 24 = 48 \text{ g/mol}$

Using
$$i = \frac{Expected molar mass}{Observed molar mass}$$

Then Vant'hoff factor for $N_2O_4 = \frac{92}{48} = 1.92$

Using
$$\alpha = \frac{i-1}{N-1}$$
 where $N = 2$

Then
$$\alpha = \frac{1.92-1}{2-1} = 0.92$$
 or 92%

Hence degree of dissociation of the gas is 92%

Question 80

Show that Boyle's law and Charles's law are contained in the kinetic equation of gases.

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

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

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

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

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

If T is constant:

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

Hence $V \propto \frac{1}{p}$ which is is Boyle's law.

If P is constant:

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

Hence $\mathbf{V} \propto \mathbf{T}$ which is Charles's law.

Since both laws can be derived from the kinetic equation of gases as shown above, the two laws are contained in the equation.

Question 81

If phosphorous pentachloride is 20% dissociated at a certain temperature, calculate the relative vapour density of the equilibrium mixture of the pentachloride, trichloride and chlorine at this temperature.

Solution

PCl₅ (Phosphorous pentachloride) dissociates according to the following equation:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$N = 2$$

Using
$$\alpha = \frac{i-1}{N-1}$$

Where
$$\alpha = 20\% = 0.2$$

So
$$0.2 = \frac{i-1}{2-1}$$
 or $i = 1.2$

But
$$i = \frac{Expected molar mass}{Observed molar mass}$$

From which Observed molar mass
$$=$$
 $\frac{\text{Expected molar mass}}{i} = \frac{208.5}{1.2} = 173.75g$

But relative vapour density =
$$\frac{\text{Molar mass}}{2\text{g/mol}} = \frac{173.75}{2} = 86.875$$

Hence the relative vapour density for dissociated mixture is 86.875.

Ouestion 82

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

Solution

False

Reason

The amount of the gas which directly determine amount of pressure is the number of gas molecules and not mass. With smaller molecular mass, 2g of hydrogen possess greater number of molecules (1mol) than 4g of oxygen (0.125mol). So although the mass of oxygen is twice the mass of hydrogen the pressure exerted by hydrogen will be 8 times (greater by far) the pressure of oxygen.

Question 83

The relative vapour density of iodine at 1 atmosphere pressure and 125°C is 87. Calculate the percentage dissociation of iodine, I₂ into its corresponding atoms in these conditions.

Solution

Iodine dissociates according to the following equation: $I_2 \rightleftharpoons 2I$; N = 2

 $M_r = 2g/mol \times relative vapour density$

So the observed molar mass of iodine = $2 \times 87 = 174$ g/mol

$$i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{254}{174} = 1.46$$

$$\alpha = \frac{i-1}{N-1} = \frac{1.46-1}{2-1} = 0.46$$
 or 46%

Hence the percentage dissociation of I₂ is 46%

Question 84

Show that if kinetic equation of gases is valid, Grahm's law of diffusion must be valid too.

Solution

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

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

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

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

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

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

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

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

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

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

Rate of diffusion $\propto \frac{1}{\sqrt{\rho_g}}$ which is the mathematical form of Grahm's law of diffusion.

Since the Grahm's law can be derived from kinetic equation of gases, the validity of the kinetic equation confirms the validity of the Grahm's law.

Question 85

1g of hydrogen iodide was heated to a certain temperature and the products suddenly cooled. The iodine which had been liberated required 15cm³ of 0.1M sodium thiosulphate for complete reaction. Calculate the percentage by mass of hydrogen iodide which remained undissociated at that temperature.

Solution

Hydrogen iodide (HI) dissociate according to the following equation: $2HI \rightleftharpoons H_2 + I_2$

The liberated iodine reacts with sodium thiosulphate according to the following equation:

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

Where mole ratio of I_2 to $Na_2S_2O_3$ is 1:2

But number of moles of Na₂S₂O₃ in 15cm³ of its solution

$$= \frac{15}{1000} \times 0.1 \text{ moles} = 1.5 \times 10^{-3} \text{ moles (using n = MV)}$$

So number of moles of liberated $I_2 = \frac{1.5 \times 10^{-3}}{2}$ moles = 7.5×10^{-4} moles

HI contain 1/128 moles = 7.8125×10^{-3} moles

Thus 7.8125×10^{-3} moles of HI dissociates to give 7.5×10^{-4} moles of I_2

2HI
$$\rightleftharpoons$$
 H₂ + I₂

After dissociation $7.8125 \times 10^{-3} - 2x$

X X

Where $x = 7.5 \times 10^{-4}$ moles

Degree of dissociation =
$$\frac{\text{Number of moles dissociated}}{\text{Original number of moles before dissociation}} = \frac{2x}{7.8125 \times 10^{-3}}$$

$$= \frac{2 \times 7.5 \times 10^{-4}}{7.8125 \times 10^{-3}} = 0.192 \text{ or } 19.2\%$$

Since $n = \frac{m}{M_r}$ and for given element, M_r is constant and hence percentage by mass of HI = percentage by moles

So percentage by mass of HI which remain undissociated is

$$(100 - 19.2) \% = 80.8\%$$

Question 86

Clearly differentiate ideality of gas at its boiling temperature and its critical temperature.

Solution

At boiling point the kinetic energy is too small to break intermolecular forces and therefore the deviation of real pressure from ideal pressure is maximum. Also the small kinetic energy implies that gas molecules are moving with small speed in close range and therefore occupying small volume which in turn makes inappropriate to neglect the volume of individual gas molecules compared to the volume of the whole gas and thus making the volume deviation to be maximum too. Consequently the deviation of real gas from ideal behaviour is maximum at boiling point to the extent that the liquefaction of the gas start to take place.

At critical point the kinetic energy is high enough to break almost all intermolecular forces and therefore the pressure deviation is negligible. Also high kinetic energy implies that gas molecules are moving with very high speed with very large separation distance making them to occupy very large volume and therefore making possible to neglect the volume of individual gas molecules compared to the volume of the whole gas leading to almost zero volume deviation. Consequently the deviation of real gas from ideal behaviour is minimum at boiling point to the extent that the gas is almost ideal such that the liquefaction of the gas is extremely difficult.

Question 87

2.5g of calcium carbonate are placed in a globe of capacity 850cm³. The globe is evacuated and heated to a temperature of 800°C at which the temperature the carbon dioxide evolved exerts a pressure of 26660 Nm ⁻²(200mmHg). Calculate the percentage of the calcium carbonate which is decomposed.

Solution

From PV = nRT, n =
$$\frac{PV}{RT}$$

Thus
$$n_{CO_2}$$
 evolved = $\frac{200 \times 850}{760 \times 1000 \times 0.082 \times 1073}$ moles = 2.54227×10^{-3} moles

CaCO₃ Decompose according to the following equation:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

From which mole ratio of CO₂ to CaCO₃ is 1:1

Thus number of moles of $CaCO_3$ decomposed is also $2.54227~\times~10^{-3}$ moles

And mass of $CaCO_3$ decomposed is $2.54227 \times 10^{-3} \times 100g = 0.254227g$ (Using m = nM_r)

Hence the percentage of
$$CaCO_3$$
 decomposed = $\frac{0.254227}{2.5} \times 100\% = 10.17\%$

Hence 10.17% of CaCO₃ decomposed

Question 88

Define compressibility factor (Z) and explain its main significance.

Solution

Is the ratio of the real (actual) volume to the volume predicted by the ideal gas equation.

Significance

It is the measure of extent of deviation of real gas from ideal behaviour. If Z = 1; the gas is ideal. If $Z \neq 1$ the real gas shows deviation from ideal behaviour whereby Z < 1 implies that there is negative deviation of which the gas is more compressible than expected from ideal behaviour while Z > 1 implies that there is positive deviation of which the gas is less compressible than expected from ideal behaviour.

Question 89

1 cm³ of water measured at 4°C is heated until has attained a temperature of 2500°C; if steam of this temperature is 3.98% of mass dissociated into molecules of hydrogen and oxygen, Calculate the volume the gasses should occupy. Assume that the gas laws apply at the temperature given. Pressure is 760mmHg throughout.

Solution

Mass of water original present = $1 \text{cm}^3 \times 1 \text{g/cm}^3 = 1 \text{g (m=\rho V)}$

At 2500°C, 3.98% of water dissociated;

That is mass of water dissociated = $\frac{3.98}{100} \times 1g = 0.0398g$

Number of moles of water dissociated = $\frac{0.0398}{18 \text{gmol}^{-1}} = 2.2111 \times 10^{-3} \text{mole}$

Water vapour dissociated according to the following equation

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

From which mole ratio of H₂O to H₂ is 1:1

Thus number of moles of hydrogen produced was also 2.2111×10^{-3} moles

And also mole ratio of H_2O to O_2 is 2:1

Thus number of moles of O_2 produced is $\frac{2.2111 \times 10^{-3}}{2}$ moles = 1.10555×10^{-3} moles

Percentage by mass of water which remain undecomposed = (100% - 3.98)% or 96.02%

Thus mass of water vapour (gas) which remain undecomposed

$$=\frac{96.02}{100} \times 1g = 0.9602g$$

Number of moles of the vapour = $\frac{0.9602}{18}$ = 0.0533 moles

Total number of moles of gases

= Number of moles of water vapour + number of moles of $H_2(g)$ + number of moles of $O_2(g)$

$$= 2.2111 \times 10^{-3} + 1.10555 \times 10^{-3} + 0.0533 = 0.0566$$
 moles

Using PV = nRT

From which
$$V = \frac{nRT}{P} = \frac{0.0566 \times 0.082 \times 2773 \times 760}{760} = 12.87 dm^3$$

Hence the gases should occupy 12.87dm³

Question 90

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

Solution

Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The average velocity of all the molecules is constant at constant temperature.

Question 91

What volume of 0.165M sodium thiosulphate would be required to react with iodine from 3g of hydrogen iodine? If the latter were heated to a temperature where it is 16% dissociated; what mass of hydrogen would remain uncombined?

Solution

Mass of HI dissociated = $\frac{16}{100} \times 3g = 0.48g$

Number of moles of HI dissociated = $\frac{0.48}{128}$ moles = 3.75×10^{-3} moles

HI dissociated according to the following equation: 2HI (g) \Rightarrow H₂(g) + I₂(g)

From which mole ratio of HI to I₂ is 2:1

Thus number of mole of I_2 produced = $\frac{1}{2} \times 3.75 \times 10^{-3}$ moles = 1.875×10^{-3} moles

Iodine reacts with $Na_2S_2O_3$ 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 $Na_2S_2O_3$ 1:2

Thus number of moles of $Na_2S_2O_3$ required was $2 \times 1.875 \times 10^{-3}$ moles

Or 3.75×10^{-3} moles

But
$$[Na_2S_2O_3] = 0.165M$$

And
$$V = \frac{n}{n}$$

Thus volume of
$$Na_2S_2O_3 = \frac{3.75 \times 10^{-3}}{0.165} = 0.0227 \text{dm}^3 \text{ or } 22.7 \text{cm}^3$$

Hence volume of sodium thiosuphate required is 22.7cm³

Since mole ratio of H₂ to I₂ is 1:1; number of moles of H₂ produced was also

$$1.875 \times 10^{-3}$$
 moles

Using
$$m = nMr$$

So mass of hydrogen gas (H₂) which would remain uncombined

$$= 1.875 \times 10^{-3} \times 2g = 3.75 \times 10^{-3}g$$

Hence mass of uncombined hydrogen gas is $3.75 \times 10^{-3} g$

Question 92

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

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

Solution

Kinetic energy(K.E) of n moles of a gas with total mass, m, moving with velocity, c, in a container of volume, V, at temperature, T, and pressure, P, is given by one of the following equations:

K. E =
$$\frac{1}{2}$$
mc²----- (i)
K. E = $\frac{3}{2}$ PV---- (ii)
K. E = $\frac{3}{2}$ nRT---- (ii)

- (i) The decrease in volume and the increase in pressure occurs at the same proportion making the product PV (in (ii)) unchanged. Adding the fact that the temperature, T (in (iii)) was kept constant; no change in kinetic energy will occur and hence **the kinetic energy will remain the same**.
- (ii) Increasing T (in (iii)) clearly increases the kinetic energy. Analogously increasing P while V is kept constant, increases the value of the product PV (in (ii)) which in turn increases kinetic energy. Hence **the kinetic energy is increased** in this case.
- (iii) From (i) it is clearly understood that the increase of velocity (c) by factor of two, **increases the kinetic** energy by factor of 4.

Ouestion 93

At 27°C dinitrogen tetraoxide is 20% dissociated into nitrogen dioxide. 1dm³ of this mixture was heated to (a) 100°C and (b) 600°C. At 100°C the dinitrogen tetraoxide is 90% dissociated and at 600°C it is completely dissociated into nitrogen oxide and oxygen. Calculate the volume the gasses would occupy under condition (a) and (b). All measurements are made at 760 mmHg.

$$N_2O_4 \rightleftharpoons 2NO_2$$

Solution

For gases, volume ratio = moles ratio (Avogadro's law)

Thus we can treat volume in similar way as mole in stoichiometric ratio

N₂O₄ (Nitrogen tetraoxide) decompose partially into NO₂ according to the following equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

If initial volume of N_2O_4 (before its decomposition at 27°C) is V_1

Then after decomposition at 27°C

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$V_1 - \frac{20}{100}V_1 = 0.8V_1$$
 $\frac{2 \times 20V_I}{100} = 0.4V_1$

Total volume of gaseous mixture = $0.8V_1 + 0.4V_1 = 1.2V_1$

But it is given that, the volume of the gaseous mixture = $1 dm^3$

Then
$$1.2V_1 = 1$$
 or $V_1 = \frac{5}{6} \, dm^3$

Thus the initial volume of undecomposed N_2O_4 at 27°C was $\frac{5}{6}$ dm³

Since pressure is kept constant at 760mHg; Charles law is applicable.

That is from Charles law $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

From which $V_2 = \left(\frac{T_2}{T_1}\right) V_1$

Thus the volume of undecomposed N₂O₄ at (a) 100° C= $\frac{373}{300} \times \frac{5}{6}$ dm³ = $\frac{373}{360}$ dm³

So at 100°C (373K)

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

After Decomposition

$$\frac{373}{360} - x$$
 2x

Total volume of gaseous mixture = $\frac{373}{360} - x + 2x = \frac{373}{360} + x$

But $x = \frac{90}{100} \times \frac{373}{360}$ (At 100°C N₂O₄ is 90% decomposed); x = 0.9325

So total volume = $\frac{373}{360}$ + x = $\frac{373}{360}$ + 0.9325 = 1.969dm³

(a) Hence the gases will occupy 1.969dm³ at 100°C

Also from
$$V_2 = \left(\frac{T_2}{T_1}\right) V_1$$

The volume of undecomposed N_2O_4 at **(b)** $600^{\circ}C = \frac{873}{300} \times \frac{5}{6} \text{ dm}^3 = 2.425 \text{dm}^3$

But at 600° C, N_2O_4 is completely dissociated into nitrogen oxide and oxygen, so the equation for the reaction becomes: $N_2O_4(g) \rightarrow 2NO(g) + O_2(g)$

From which mole ratio of N_2O_4 to NO is 1:2

And mole ratio of N_2O_4 to O_2 is 1:1

Thus:

Volume of NO produced = $2 \times 2.425 = 4.85 \text{dm}^3$

Volume of O_2 produced = $2.425 dm^3$

So total volume of the gaseous mixture = (2.425 + 4.85)dm³ = 7.275dm³

(b) Hence the gases will occupy $7.275 dm^3$ at $600^{\circ}C$

Question 94

What is wrong with each of the following statement:

- (i) Dissociation of gas increases number of gas particles and therefore increasing its volume in accordance to Avogadro's law. According to Boyle's law the increase in volume as a result of dissociation leads to the decrease in pressure of the gas and hence it can be concluded that the dissociation of the gas decreases amount of the pressure exerted by the gas.
- (ii) One mole of an ideal gas at room temperature and pressure occupies a volume of 22.4L.

(iii) Collision between gas particles and walls of a container is completely elastic.

Solution

- (i) The Boyle's cannot be applied when the number of gas particles has been changed; that is reason of reaching the false conclusion which is "dissociation of the gas decreases amount of the pressure".
- (ii) For one mole of the gas to occupy the volume of 22.4L, the room pressure (1atm) must be accompanied with temperature of 0°C (and not the room temperature which is 25°C). At room temperature and pressure volume of one mole of the gas will be greater than 22.4L.
- (iii) That statement assumes that there is no intermolecular forces between gas particles. But in reality the intermolecular forces between gas particles they do exist and thus decreasing the speed of the particles and hence the collision becomes inelastic.

Question 95

At a certain temperature and under identical conditions, the volumes of oxygen and dinitrogen tetraoxide diffusing from an apparatus in a given time were in the ratio of 3 to 2. Calculate the degree of dissociation of dinitrogen tetraoxide of this temperature.

Solution

By Graham's law of diffusion:
$$\frac{V_{O_2}}{V_{N_2O_4}} = \sqrt{\frac{M_{N_2O_4}}{M_{O_2}}}$$

From which:
$$M_{N_2O_4} = M_{O_2} \left(\frac{V_{O_2}}{V_{N_2O_4}} \right)^2 = 32 \times \left(\frac{3}{2} \right)^2 = 72g/\text{mol}$$

Thus the observed molar mass of N_2O_4 is 72g/mol.

But the expected molar mass of N₂O₄ is 92g/mol. (as calculated from its molecular formula).

And N₂O₄ dissociated according to the following equation

$$N_2O_4(g) \rightleftharpoons 2NO_2(g); N = 2$$

Using i =
$$\frac{\text{Expocted molar mass}}{\text{Observed molar mass}} = \frac{92}{72} = 1.28$$

So from
$$\alpha = \frac{i-1}{N-1}$$

Degree of dissociation of
$$N_2O_4 = \frac{1.28 - 1}{2 - 1} = 0.28$$
 or 28%

Hence the degree of dissociation of N_2O_4 is 28%

Question 96

From kinetic equation of gases, derive the equation for root mean square speed (c) of a gas with molar mass, M_r , at absolute temperature, T, and hence deduce the mathematical equation which will enable you to calculate kinetic energy of 'n' moles of the gas.

Solution

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

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

And Nm =
$$N_A m = M_r (M_r \text{ is the molar mass of the gas})$$

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

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

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

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

The kinetic energy (K.E) can also be deduced from the above equation for the root mean square speed as follows:

From
$$c = \sqrt{\frac{3RT}{M_r}}$$

But kinetic energy (K. E) of the gas $=\frac{1}{2}$ mc² where m is the given mass of the gas.

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

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

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

Question 97

24cm³ of a mixture of methane and ethane were exploded with 90cm³ of oxygen. After cooling to room temperature, the volume of gas was noted. It was found to decrease by 32cm³ when treated with KOH solution (pressure is constant throughout). Calculate the composition of the mixture.

Solution

Let xcm³ of methane is mixed with ycm³ of ethane

Then
$$x + y = 24$$
.....(i)

Equation for combustion of methane: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_3$

From which mole of ratio and hence volume ratio of CH₄ to CO₂ is 1:1

Thus the volume of CO₂ produced by combustion of CH₄ was x cm³

Equation for combustion of ethane: $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O_3$

From which mole ratio and hence volume ratio of C₂H₆ to CO₂ is 1:2

Thus the volume of CO_2 produced from combustion of C_2H_6 was $2ycm^3$

So total volume of CO_2 produced from combustion = (x + 2y) cm³

When KOH is introduced into the gases, the strong alkaline solution absorb $CO_2(g)$ according to the following equation: $2KOH(aq) + CO_2(g) \rightarrow K_2CO_3 + H_2O$

So the decrease in volume after introduction of KOH; is the volume of ${\rm CO_2}$ which was formed from combustion of the two gases.

That is
$$x + 2y = 32$$
....(ii)

Solving (i) and (ii) simultaneously gives: x = 16 and y = 8

Hence there are 16cm³ of methane and 8cm³ of ethane in the mixture.

Question 98

How the following are related to the amount of pressure exerted by a gas in a container?

- (i) Collision frequency
- (ii) Collision intensity

Solution

- (i) The amount of pressure exerted by the gas increases as the amount of collision frequency increases.
- (ii) The amount of pressure exerted by the gas increases as the amount of collision intensity increases.

Question 99

How can these factors (mentioned in (a) above) be changed?

Solution

Collision frequency can be changed by one of the following ways:

- By changing temperature whereby increasing the temperature, increases the collision frequency.
- By changing pressure whereby increasing pressure by compression decreases volume of the gas and therefore increasing the collision frequency.
- By changing the volume of the container whereby using the container of smaller volume increases the collision frequency.
- By changing amount of the gas whereby adding the amount of the gas, increases the collision frequency.

Collision intensity can only be changed by changing pressure whereby increasing the temperature, increases the collision intensity.

Ouestion 100

32 cm³ of a mixture of carbon monoxide, methane and hydrogen were mixed with 50 cm³ of oxygen and exploded. After cooling to room temperature, the volume was noted. It was reduced by 22 cm³ when exposed to KOH solution, leaving 16 cm³ of excess oxygen. Calculate the composition of the mixture.

Solution

Let volume of carbon monoxide, methane and hydrogen be xcm³, ycm³ and zcm³ respectively

Then
$$x + y + z = 32$$
----(i)

Equation for combustion of carbon monoxide

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

 $xcm^3 \frac{x}{2}cm^3 xcm^3$

Equation for combustion of methane

$$CH_4(g)$$
 + $2O_2(g)$ \rightarrow $CO_2(g)$ + $2H_2O(i)$
 ycm^3 2 ycm^3 ycm^3

Equation for combustion of hydrogen

$$H_2(g)$$
 + $\frac{1}{2}O_2(g) \rightarrow H_2O(l)$
 zcm^3 $\frac{z}{2}cm^3$

Volume of CO_2 reduced volume after introducing KOH(aq) = $22cm^3$

Thus
$$x + y = 22$$
.....(ii)

Volume of oxygen reacted = (50 - 16)cm³ = 34cm³

Then
$$\frac{x}{2} + 2y + \frac{z}{2} = 34$$

or
$$x + 4y + z = 68$$
.....(iii)

Solving (i), (ii) and (iii) simultaneously gives: x = 10, y = 12 and z = 10

Hence the composition of the mixture was carbon monoxide, 10cm^3 , methane, 12cm^3 and hydrogen, 10cm^3 respectively

Question 101

Explain the following:

- (i) The concept of ideal gas is just ideal.
- (ii) Helium behave more as a gas than chlorine.

Solution

- (i) To be ideal the gas must obey ideal gas equation in all conditions of temperature and pressure. This requires the intermolecular forces between gas molecules and molecular size (volume) of gases to be neglected which is not possible especially at low temperature and high pressure and hence no gas is ideal making the whole concept just imaginary.
- (ii) Smaller molecular mass of helium means that helium has smaller molecular volume and weaker Vander-Waals intermolecular forces and therefore comparing to ideal behaviour of gases, helium has smaller volume deviation and smaller pressure deviation respectively and hence it is closer to ideal gas than chlorine.

Ouestion 102

65 cm³ of a mixture of hydrdogen, carbon monoxide and nitrogen are mixed with 50cm³ of oxygen at room temperature. The mixture is exploded and allowed to cool. The residual volume is 55 cm³. After absorption with KOH solution the final volume is 25 cm³, calculate the percentage by volume of each gas in the original mixture (Temperature and pressure constant room values).

Solution

Let volume of hydrogen, carbon monoxide and nitrogen be xcm³, ycm³ and zcm³ respectively

Then
$$x + y + z = 65$$
(i)

Equation for combustion of hydrogen

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$

 $xcm^3 + \frac{x}{2}cm^3$

Equation for combustion of carbon monoxide

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

$$ycm^3 \qquad \frac{y}{2}cm^3 \qquad ycm^3$$

Nitrogen does not combust easily in oxygen

Volume of
$$CO_2$$
 = Reduced volume after introducing KOH = $(55 - 25) = 30 \text{cm}^3$

Then
$$y = 30$$
.....(ii)

The gases which remain after introducing KOH are nitrogen and unreacted oxygen

Thus volume of unreacted oxygen + volume of nitrogen = 25cm^3

But volume of reacted oxygen = $\left(\frac{x}{2} + \frac{y}{2}\right)$ cm³

So the volume of unreacted oxygen = $50 - \left(\frac{x}{2} + \frac{y}{2}\right)$

And volume of nitrogen = $z cm^3$

If follows that: $50 - \left(\frac{x}{2} + \frac{y}{2}\right) + z = 25$

or
$$x + y - 2z = 50$$
....(iii)

Solving (i), (ii) and (iii) simultaneously gives

$$x = 30, y = 30 \text{ and } z = 5$$

$$%H_2 = \frac{30}{65} \times 100\% = 46.15\%$$

$$%CO = \frac{30}{65} \times 100\% = 46.15\%$$

$$\% N_2 = \frac{5}{65} \times 100\% = 7.7\%$$

Hence the percentage by volume of each gas in the original mixture was:

Hydrogen gas 46.15%

Carbon monoxide gas 46.15%

Nitrogen gas 7.7%

Question 103

The Van-der-Waals equation for 'n' moles of real gas can be written as follows:

$$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$$

- (i) Which single word can be used to represent the $\frac{n}{V}$?
- (ii) How does the larger value of the ratio $\frac{n}{v}$ affect the pressure of the real gas?
- (iii) Explain how would you make the value of the ratio, $\frac{n}{V}$ bigger?

Solution

- (i) Concentration
- (ii) Larger value of the ratio means greater pressure deviation and hence the real pressure will be much smaller compared to ideal pressure.
- (iii) The ratio can be increased by decreasing the volume of fixed amount of the gas by either using the container of smaller volume or compressing the gas through the application of higher external pressure.

 Another way of increasing the ratio is by adding amount of the gas to the fixed volume.

Question 104

100 cm³ of a sulphorous acid solution required 11.2 cm³ of 0.05M iodine solution for complete reaction. Calculate the volume of dissolved sulphur dioxide at 15°C and 742mmHg per dm³ of the acid

Solution

Number of moles of iodine in 11.2cm^3 of its solution = $\frac{11.2}{1000} \times 0.05 = 5.6 \times 10^{-4}$ moles

Iodine reacts with sulphorous acid according to the following equation:

$$I_2 + H_2 SO_3 + H_2O \rightarrow H_2SO_4 + 2HI$$

From which mole ratio of I₂ to H₂SO₃ is 1:1

Thus number of H_2SO_3 in $100cm^3$ of its solution is also 5.6×10^{-4} moles

H₂SO₃ is formed by mixing SO₂ and water according to the following equation

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

Thus number of moles of SO_2 in $100 cm^3$ of acid solution was also 5.6×10^{-4} moles

Hence number of moles of SO₂ per 1dm³ (1000cm³) of the acid solution

$$= 5.6 \times 10^{-4} \times 10 \text{ moles} = 5.6 \times 10^{-3} \text{moles}$$

Volume of the gas (dissolvedSO₂) can be found by using ideal gas equation as follows:

From PV = nRT

$$V = \frac{nRT}{p} = \frac{5.6 \times 10^{-3} \times 0.082 \times 288 \times 760 \text{dm}^3}{742}$$
$$= 0.1355 \text{dm}^3 \text{ or } 135.5 \text{cm}^3$$

Hence the volume of dissolved sulphur dioxide per dm³ of the acid was 135.5cm³

Question 105

The Van-der-Waals equation for 'n' moles of real gas can be written as follows:

$$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$$

- (i) The real gas becomes more ideal with smaller value or larger value of the ratio $\frac{n}{v}$? Explain.
- (ii) For given gas, is it possible to alter the value of constants 'a' and 'b'? Explain.

Solution

(i) Smaller value.

Explanation

The smaller value means less pressure deviation and therefore the real pressure will become closer to the ideal pressure.

(ii) Not possible.

Explanation

The given constants depend on the nature of the gas. While 'a' depends on the strength of intermolecular forces 'b' depends on the molecular size all of which depend on chemical nature of the gas and hence they cannot be altered.

Question 106

The carbon dioxide in the air of a room was estimated by drawing 200 dm³ of air at 14°C and 753mmHg through potassium hydroxide bulbs of known mass. The increase in mass of bulbs was 0.157g. Calculate the percentage by volume of carbon dioxide in the air.

Solution

Given that:

Volume of sample of air = $200 dm^3$

Mass of CO_2 in the air sample = 0.157g (potassium hydroxide bulb adsorbs CO_2 component only from the air components so the increase in mass of the bulb must be the mass of CO_2 in the air sample).

Temperature, $T = 14^{\circ}C = 287K$

$$P_{air} = 753 \text{ mmHg} = \frac{753}{760} \text{ atm}$$

From ideal gas equation: PV = nRT

So
$$n_{air} = \frac{P_{air} V}{RT} = \frac{753 \times 200}{760 \times 0.082 \times 287} = 8.42 \text{ moles}$$

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

Then
$$n_{CO_2} = \frac{m_{CO_2}}{M_{CO_2}} = \frac{0.157g}{44gmol^{-1}} = 3.5682 \times 10^{-3} \text{ moles}$$

But
$$\frac{n_{CO_2}}{n_{air}} = \frac{V_{CO_2}}{V_{air}}$$
 (From Avogadro's law)

So percentage by volume of CO_2 in the air = $\frac{n_{CO_2}}{n_{air}} \times 100\%$

$$=\frac{3.5682\times10^{-3}}{8.42}\times100\%=0.0424\%$$

Hence the percentage of CO_2 in the air is 0.0424% by volume.

Question 107

SO₂ used in the air manufacture of sulphuric acid, is obtained from sulphide ores (iron pyrites):

$$4\text{FeS}_2 \text{ (s)} + 110_2 \text{ (g)} \rightarrow 2\text{Fe}_2 \text{ 0}_3 + 8\text{SO}_2 \text{ (s)}$$

The SO_2 is then treated with suitable reagent to produce sulphorous acid and finally sulphuric such that one mole of SO_2 produces one mole of sulphuric acid

- a) How many kg of iron pyrites, FeS₂, would be required to produce 100kg of sulphuric acid containing 98 % H₂SO₄?
- b) How many m³ of air containing 21% of oxygen by volume and measured at 15°C and 750 mmHg, would be required for complete combustion of pyrites in (a) above?

Solution

Mass of
$$H_2SO_4$$
 in 100kg of 98% $H_2SO_4 = \frac{98}{100} \times 100$ kg = 98kg = 98000g

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

Number of moles of
$$H_2SO_4 = \frac{98000g}{98gmol^-} = 1000 moles$$

But 1 mole of SO₂ produce 1 mole of H₂SO₄

Thus 1000moles of H₂SO₄ are produced by 1000moles of SO₂

But from

$$4\text{FeS}_2(s) + 110_2(g) \rightarrow 2\text{Fe}_20_3(s) + 8\text{SO}_2(g)$$

Mole ratio of FeS₂ to SO₂ is 4:8 or 1:2

Thus number of moles of FeS₂ required to produce 1000moles of SO₂ is $\frac{1000}{2}$ moles = 500moles

Using m = nMr

Mass of iron pyrites, $FeS_2 = 500 \times 120g = 60000g$ or 60kg

(a) Hence 60kg of iron pyrites would be required

Form the given equation: Mole ratio of FeS_2 to O_2 is 4:11

So number of moles of O_2 required to complete combustion = $\frac{11}{4} \times 500$ moles = 1375 moles

If n_{air} is the number of moles of air containing 1375 moles of O_2

Then $\frac{21}{100}$ n_{air} = 1375 moles (For gases, percentage by volume is equal to the percentage by moles)

So
$$n_{air} = \frac{1375 \times 100}{21}$$
 moles $= \frac{137500}{21}$ moles

From PV = nRT

$$V_{air} = \frac{n_{air}RT}{P_{air}} = \frac{137500 \times 0.082 \times 288 \times 760}{21 \times 750} dm^3 = 156690 dm^3 \text{ or } 156.69 m^3$$

(b) Hence 156.69m³ of air would be required for complete combustion of the pyrites.

Question 108

Under what conditions real gases do fails to obey Charles's and Boyle's law?

Solution

Real gases fails to obey Charles's and Boyle's law at low temperature and high pressure.

Question 109

141.4cm³ of an inert gas diffused through a porous plug in the same time as it took 50 cm³ of oxygen to diffuse through the same plug under identical conditions. Calculate the relative atomic mass of inert gas.

Solution

By Grahm's law of diffusion:
$$\frac{V_{O_2}}{V_{inert}} = \sqrt{\frac{M_{inert}}{M_{O_2}}}$$

So
$$M_{inert} = M_{O_2} \left(\frac{V_{O_2}}{V_{inort}} \right)^2 = 32 \times \left(\frac{50}{141.4} \right)^2 = 4 \text{gmol}^{-1}$$

Hence the relative atomic mass of an inert gas is 4.

Question 110

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

- (a) Calculate the total pressure in the flask.
- (b) Calculate the mole fraction of H₂ in the flask.
- (c) Calculate the density (in gL^{-1}) of the mixture in the flask.
- (d) The mixture in the flask is ignited by a spark and the reaction represented below occurs until one of the reactants is entirely consumed.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

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

Solution

(a) From Dalton's law of partial pressure:

$$P_T = P_{H_2} + P_{O_2} + P_{Ar}$$

But from ideal gas equation; $P = \frac{nRT}{V}$

It follows that: $P_T = \frac{n_{H_2}RT}{V} + \frac{n_{O_2}RT}{V} + P_{Ar} = \frac{RT}{V} (n_{H_2} + n_{O_2}) + P_{Ar}$

$$P_T = \frac{0.082 \times 400}{8.2} (2.5 + 0.5) atm + 2 atm = 14 atm$$

The total pressure in the flask is 14atm.

(b)
$$X_{H_2} = \frac{P_{H_2}}{P_T} = \frac{n_{H_2}RT}{VP_T} = \frac{2.5 \times 0.082 \times 400}{8.2 \times 14} = 0.7$$

The mole fraction of hydrogen is 0.7.

(c) Density of the mixture $(\rho_m) = \frac{m_m}{V} = \frac{m_{O_2} + m_{H_2} + m_{Ar}}{V}$

Where: $m_{O_2} = 0.5 \text{mol} \times 32 \text{g/mol} = 16 \text{g}$

$$m_{H_2} = 2.5 \text{mol} \times 2 \text{g/mol} = 5 \text{g}$$

$$m_{Ar} = \frac{P_{Ar}VM_{Ar}}{RT} = \frac{2 \times 8.2 \times 40}{0.082 \times 400}g = 20g$$

$$\rho_{\rm m} = \frac{m_{\rm O_2} + m_{\rm H_2} + m_{\rm Ar}}{V} = \frac{(16 + 5 + 20)g}{8.2L} = 5g/L$$

Density of the mixture is 5g/L

(d) From the given reaction equation:

Mole ratio of oxygen to hydrogen is 1:2 while mole ratio of oxygen to gaseous water is also 1:2;

Thus 0.5mol of oxygen react with 1mol $(2 \times 0.5mol)$ of hydrogen to give 1mol $(2 \times 0.5mol)$ of gaseous water.

But number of moles of hydrogen gas was 2.5mol. Thus (2.5 - 1)mol = 1.5mol of hydrogen remained unreacted.

Whence after the reaction there are:

- 1.5mol of unreacted hydrogen gas,
- 1mol of produced gaseous water and
- $0.5 \text{mol } (20 \text{g}/40 \text{gmol}^{-1}) \text{ of argon.}$

Then using $X = \frac{n}{n_T}$;

$$X_{H_2} = \frac{1.5 \text{mol}}{(1.5 + 1 + 0.5) \text{mol}} = 0.5$$

$$X_{H_2O} = \frac{1 \text{mol}}{(1.5 + 1 + 0.5) \text{mol}} = 0.33$$

$$X_{Ar} = \frac{0.5 \text{mol}}{(1.5 + 1 + 0.5) \text{mol}} = 0.17$$

Question 111

Define the following terms:

- (i) Real gas
- (ii) Dimer

Solution

- (i) It is the gas whose molecules have volume and experience intermolecular forces so that it does not obey ideal gas law.
- (ii) Is the molecule that is formed after joining up two identical molecules.

Question 112

A quantity of 2.4g of a compound fills 934 cm³ as a vapour at 298K and 740 mmHg. It contains 37.21% carbon 7.8% hdygrogen and 55% chlorine. What is its molecular formula?

Solution

Composition by element	С	Н	Cl
Percentage by mass of each	37.21	7.8	55
Mass of each in 100g of the compound	37.21g	7.8g	55g
Number of moles of each using $n = \frac{m}{Mr}$	$\frac{37.21g}{12gmol^{-}} = 3.1mol$	$\frac{7.8g}{1gmol^{-1}} = 7.8mol$	$\frac{55g}{16g\text{mol}^{-1}} = 3.4375 \text{ mol}$
Divide by the smallest to get simpler ratio	$\frac{3.1 \text{ mol}}{3.1 \text{ mol}} = 1$	$\frac{7.8 \text{ mol}}{3.1 \text{ mol}} = 3$	$\frac{3.4375 \text{ mol}}{3.1 \text{ mol}}$

So empirical formula of the compound is CH₃Cl if the molecular formula of the compound is (CH₃Cl)_n

Then
$$12n + 3n + 35.5n = M_r \text{ or } 50.5n = M_r$$

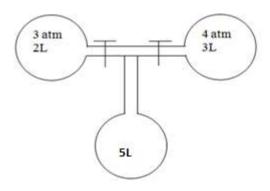
But
$$M_r = \frac{mRT}{PV} = \frac{2.4 \times 0.082 \times 298 \times 760 \times 1000}{740 \times 934} = 64$$

Then
$$50.5n = 64$$
 or $n = 1$

Hence the molecular formula of the compound is CH₃Cl

Ouestion 113

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



Solution

By using Boyle's law; $P_1V_1 = P_2V_2$

From which
$$P_2 = \frac{P_1 V_1}{V_2}$$

For the first gas with initial pressure of 3atm; $P_1 = 3$ atm, $V_1 = 2$ L, $V_2 = 10$ L

Then
$$P_2 = \frac{3atm \times 2L}{10L} = 0.6atm$$

For the second gas with initial pressure of 4atm; $P_1 = 4$ atm, $V_1 = 3$ L, $V_2 = 10$ L

Then
$$P_2 = \frac{4atm \times 3L}{10L} = 1.2atm$$

By Dalton's law of partial pressure:

Total pressure = P_2 of the first gas + P_2 of the second gas = (0.6 + 1.6)atm = 1.8atm

The total final pressure is 1.8atm

Question 114

Distinguish between diffusion and effusion of gas.

Solution

Diffusion is the spread up of gas molecules throughout the space form the side of higher concentration to that of lower concentration while effusion is the escaping of the gas from the container through very small hole.

Question 115

Give at least five differences between ideal gas and real gas.

	IDEAL GASES		REAL GASES
01	Obey all gas laws under all conditions of temperature and pressure	01	Obey gas laws only at low pressure and high temperature
02	The volume occupied by the gas molecules is negligible as compared to the total volume occupied by the gas	02	The volume occupied by the gas molecules is not negligible compared to the total volume of the gas
03	The force of attraction between gas molecules are negligible	03	The force of attraction between the gas molecules are not negligible
04	Obey ideal gas equation, PV = nRT	03	Obey Van der Waals equation $\left(P + a \left(\frac{n}{v}\right)^2\right) (V - nb) = nRT$
05	Collisions between gas molecules and walls of the container is elastic	05	Collisions between the gas molecules and walls of the container is not elastic

Question 116

Using Van-der-Waals equation, calculate the constant 'a' when two moles of a gas contained in a 4 litre flask exerts a pressure of 11 atmosphere at temperature of 300K. the values of b is 0.05 Lmol⁻¹

Solution

From Van – der – Waals equation:
$$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$$

Substituting given values:
$$\left(11 + a\left(\frac{2}{4}\right)^2\right) \left(4 - (2 \times 0.05)\right) = 2 \times 0.082 \times 300$$

$$a=6.46atmL^2mol^{-2} \\$$

Hence the value of 'a' for the gas is 6.46atmL2mol⁻²

Question 117

List down any three applications of Grahm's law of diffusion.

Solution

- 1. Separation of gases with different densities.
- 2. Determination of densities and molecular masses of unknown gases.
- 3. Separation of isotopes of some elements (e.g. uranium isotopes).

Question 119

For 10 minutes each, at 27°C, from two identical holes nitrogen and an unknown gas are leaked into a common vessel of 3L capacity. The resulting pressure is 4.18atm and the mixture contains 0.4 mole of nitrogen. What is the molar mass of unknown gas?

Solution

By Dalton's law of partial pressure total pressure (P_T) in the vessel is given by:

$$P_{T} = P_{N_{2}} + P_{u} = \frac{n_{N_{2}}RT}{V} + \frac{n_{u}RT}{V}$$

$$P_T = (n_{N_2} + n_u) \frac{RT}{V}$$
; From which $n_u = \frac{P_T V}{RT} - n_{N_2} = \frac{4.18 \times 3}{0.082 \times 300} - 0.4 = 0.1$ moles

From Grahm's law of diffusion:
$$\frac{V_{N_2}}{V_u} = \sqrt{\frac{M_u}{M_{N_2}}}$$

But from Avogadro's law it can be shown that: $\frac{V_{N_2}}{V_U} = \frac{n_{N_2}}{n_U}$

Thus
$$\frac{n_{N_2}}{V_u} = \sqrt{\frac{M_u}{M_{N_2}}}$$

$$M_u = M_{N_2} \left(\frac{n_{N_2}}{n_u}\right)^2 = \left(\frac{0.4}{0.1}\right)^2 \times 28g/mol = 448g/mol$$

Hence molar mass of unknown gas is 448g/mol

Question 120

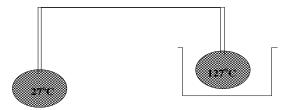
Distinguish between dissociation and association of gases.

Solution

Dissociation of gas is splitting of one larger gas molecule into smaller gas molecules while association is the combining of more than one smaller gas molecule into one larger molecule.

Question 121

Two flasks of equal volumes are connected by a narrow tube of negligible volume. Initially both flasks are at 27°C and each contains 0.35 moles of hydrogen gas at 0.5 atm. One of the flasks is then immersed in an oil bath at 127°C as shown below



Calculate:

- i) The number of moles of hydrogen gas in each flask
- ii) The final pressure of the system.

Solution

When another flask is immersed in the hot oil bath, the pressure in the hot flask will be greater than the pressure in the cold flask. So gas (hydrogen) molecules will start to move from the hot flask to the cold flask until the pressure in the two flasks balance; i.e. until Pressure in the cold flask = Pressure in the hot flask.

Let number of molecules moved from the hot flask be y.

Then number of moles of hydrogen molecules in the hot flask = 0.35 - y

And number of moles of hydrogen molecules in the cold flask = 0.35 + y

So when the pressure at the two flask are at equilibrium (balance each other)

$$\frac{(0.35-y)RT_2}{V} = \frac{(0.35+y)RT_1}{V}$$

Where T_1 is the temperature of the cold flask = $27^{\circ}C = 300K$

 T_2 is the temperature of the hot flask = $127^{\circ}C = 400K$

(It should be noted that: In this calculation; the expansion of volume of the flask due to rise in temperature has been neglected, that is why the volume of the two flasks, V remains the same).

Substituting the given values: (0.35 - y) 400 = (0.35 + y) 300

From which, y = 0.05 moles

- (i) Hence
 - Number of hydrogen gas in the hot flask is (0.35 y) moles = (0.35 0.05) moles = 0.3 moles.
 - Number of moles of hydrogen gas in the cold flask is (0.35 + y) moles = (0.35 + 0.05) moles = 0.4 moles

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

Where
$$n = 0.35$$
, $R = 0.082$, $T = 300K (27^{\circ}C)$, $P = 0.5atm$

So volume of each flask =
$$\frac{0.35 \times 0.082 \times 300}{0.5}$$
 dm³ = 17.22dm³

Then the final pressure in each flask can be found from either cold or cold flask and will give the same result by using;

$$P = \frac{nRT}{V}$$

So for cold flask:
$$P = \frac{0.4 \times 0.082 \times 300}{1.722}$$
 atm = 5.7atm

Hence the final pressure of the system is 5.7atm in each flask

Question 122

Mention main variables of gaseous state.

Solution

Pressure, volume, number of gas particles and temperature.

Ouestion 123

Pyridine contains 75.92% C, 6.37% H and the rest being N. At 110°C and 630mmHg the density of gaseous pyridine was 2.12gdm⁻³. Determine the empirical formula and molecular formula of pyridine.

Solution

(a) $\%$ N =	100 -	(% C + % H)	= 100 -	(75.92 + 6.37)) = 17.71%
(u) /UII —	100	(/0 0 1 /011	, — 100	(/ 5.7 - 6.5/	, — , , , _ ,

Composition by element	С	Н	N
Percentage by mass of each	75.92	6.37	17.71
Mass of each in 100g of the compound	75.92g	6.37g	17.71g
Number of moles of each using, n $= \frac{m}{M_r}$	$\frac{75.92g}{12gmol^{-1}} = 6.33mol$	$\frac{6.37g}{1g\text{mol}^{-1}} = 6.37 \text{ mol}$	$\frac{17.71g}{14gmol^{-1}} = 1.265mol$
Divide by smallest to get simpler ratio	$\frac{6.33 \text{mol}}{1.265 \text{ mol}} = 5$	$\frac{6.37 \text{ mol}}{1.265 \text{ mol}} = 5$	$\frac{1.265 \text{ mol}}{1.265 \text{ mol}} = 1$

The empirical formula of the compound is C₅H₅N

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

But
$$\frac{m}{v}$$
 = density, ρ

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

Let molecular formula of the compound be $(C_5H_5N)_n$

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

Hence the molecular formula of the compound is C₅H₅N

Question 124

Explain the following:

- (i) The experimentally determined molar mass of a substance is not always the same as that suggested by its molecular formula.
- (ii) Victor's Meyer method is not suitable for determination of molar mass of glucose.

Solution

- (i) Abnormal results on experimentally determined molar mass are obtained when the substance undergoes dissociation or association. Dissociation splits one molecule into smaller molecules and therefore making experimental molar mass smaller than that suggested by the molecular formula while association join smaller molecules into one molecule and therefore making experimental molar mass larger than that suggested by the molecular formula.
- (ii) Victor's Meyer method is compatible with volatile substances whose boiling points are below 100°C so that they can be vapourised by steam. Glucose being non-volatile substance cannot be vapourised by Victor's Meyer apparatus and hence its molar mass cannot be determined by this method.

Question 125

A gaseous compound X has 46.1%C and 53.9% H; in 20 seconds, 50cm^3 of X diffused through a porous plug and the same volume of 0_2 diffused in 15.7 seconds.

- (i) Determine the molecular mass of X.
- (ii) What volume of CO₂ would diffuse in 20 seconds under the same conditions as before?

Solution

Composition by element	С	Н
Percentage by mass of each	46.1	53.9
Mass of each in 100g of the compound	46.1g	53.9g
Number of moles of each, $n = \frac{m}{M_r}$	$\frac{46.1g}{12gmol^{-1}} = 3.84mol$	$\frac{53.9g}{1g\text{mol}^{-1}} = 53.9 \text{ mol}$
Divide by smallest to get simpler ratio	$\frac{3.84}{3.84} = 1$	$\frac{53.9}{3.84} = 14$

So the empirical formula of the compound is CH₁₄

By Graham's law of diffusion:
$$\frac{t_X}{t_{O_2}} = \sqrt{\frac{M_X}{M_{O_2}}}$$

$$M_X = M_{O_2} \left(\frac{t_X}{t_{O_2}}\right)^2 = 32 \left(\frac{20}{15.7}\right)^2 = 52g/\text{mol}$$

If the molecular formula of the compound is $(CH_{14})_n$

Then
$$12n + 14n = M_r = 52$$

$$26n = 52 \text{ or } n = 2$$

Hence molecular formula of the compound is C₂H₂₈

$$\frac{V_{CO_2}}{V_X} = \sqrt{\frac{M_X}{M_{CO_2}}} \text{ or } V_{CO_2} = V_X \sqrt{\frac{M_X}{M_{CO_2}}}$$

$$V_{CO_2} = 50 \sqrt{\frac{52}{44}} = 54.4 \text{cm}^3$$

Hence $54.4 \, \text{cm}^3$ of CO_2 would diffuse in 20 seconds

Question 126

Identify the postulate of the kinetic molecular theory most closely identified with the Van - der - Waals constant 'a' and explain the relationship. Repeat the procedure for the constant 'b'

Solution

The postulate related to the constant 'a':

Intermolecular forces of attraction are negligible in the motion of gas molecules.

Relationship: Weaker intermolecular forces means smaller value of the constant and whence the postulate becomes valid while stronger intermolecular forces leads to larger value of the constant and thus the postulate becomes invalid.

The postulate related to the constant 'b':

Volume of a gas molecule (particle) is negligible compared to the volume of the whole gas or the volume of the container.

Relationship: Smaller molecular size (volume) means smaller value of the constant and whence the postulate becomes valid while larger molecular size leads to larger value of the constant and thus the postulate becomes invalid.

Question 127

- (i) Under what set of experimental condition is the Van der Waals equation more applicable than the ideal gas equations?
- (ii) Use the Van der Waals equation: Calculate the pressure of 10moles of NH₃ gas in 10L vessel at 0° C. 'a' = 4.2L2atm/moL², 'b' = 0.037 L/mol

Solution

- (i) Low temperature and high pressure
- (ii) From Van-der-Waals equation: $\left(P + a\left(\frac{n}{V}\right)^2\right)(V nb) = nRT$

Substituting given value:
$$\left(P + 4.2 \left(\frac{10}{10}\right)^2\right) \left(10 - (10 \times 0.037)\right) = 10 \times 0.082 \times 273$$

From which P = 19.0461atm

Hence the pressure of ammonia gas is 19.0461atm

Question 128

State Dalton's law of partial pressure

Solution

"The total pressure exerted in the container of the mixture of two or more gases is equal to the summation of their partial pressures provided that the gases do not react."

Question 129

(a) A reaction mixture for combustion of SO_2 was prepared by opening a stop cock connecting two separate chambers, one having volume of 2.125L, filled at 0.75 atm with SO_2 and other having a 1.5L volume filled at a pressure of 0.5 atm with O_2 , both gases at 80° C

What were the:

- i) Mole fraction of SO_2 in the mixture
- ii) The total pressure
- iii) The partial pressure of SO₂
- (b) If the mixture was passed over a catalyst that promote the formulation of SO_3 and then was returned to the original connected vessels. What were the:
- (i) The mole fraction of SO_3 in the final mixture
- (ii) The final total pressure.

Solution

(a) Using
$$n = \frac{PV}{RT}$$

Before opening the cock:

Number of moles of
$$SO_2 = \frac{0.75 \times 2.125}{0.082 \times 353}$$
 moles = 0.055 moles

Number of moles of
$$O_2 = \frac{0.5 \times 1.5}{0.082 \times 353}$$
 moles = 0.02591moles

After opening the cock:

The two gases mix together then:

- Total number of moles of gaseous mixture, $n_T = (0.055 + 0.02591)$ moles = 0.08091moles
- Total volume of the gaseous mixture = total volume of the two chambers = (2.125+1.5)L = 3.625L

$$X_{SO_2} = \frac{n_{SO_2}}{n_T} = \frac{0.055}{0.08091} = 0.68$$

Thus mole fraction of SO₂ was 0.68

$$P_T = \frac{n_T RT}{V} = \frac{0.08091 \times 0.082 \times 353}{3.625} = 0.646atm$$

The total pressure is 0.646atm

Partial pressure of SO_2 , $P_{SO_2} = X_{SO_2}P_T = 0.68 \times 0.646$ atm = 0.43928atm

(b) If the mixture is allowed to react after passing through catalyst:

 SO_2 reacts with O_2 according to the following equation (Assuming reaction reach to completion i.e. it is irreversible): $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

From which mole ratio of SO_2 to O_2 is 2:1

Thus 0.02591 moles of O_2 reacts with $0.02591 \times 2 = 0.05182$ moles of SO_2

So SO_2 present in excess and (0.055 - 0.05182)moles = 0.00318moles of it remain unreacted at the end of the reaction

Also from the above reaction equation; mole ratio of O₂ (limited reactant) to SO₃ is 1:2

Thus number of moles of SO_3 produced was $0.02591 \times 2 = 0.05182$ moles

So at the end of the reaction there are 0.00318moles and 0.05182moles of SO₂ and SO₃ respectively.

Therefore; the total number of moles of the final gaseous mixture = (0.05182 + 0.00318) moles = 0.055moles

Then
$$X_{SO_3} = \frac{n_{SO_3}}{n_T} = \frac{0.05182}{0.055} = 0.9422$$

Thus mole fraction of SO_3 in the final mixture was 0.3813

$$P_T = \frac{n_T RT}{V} = \frac{0.055 \times 0.082 \times 353}{3.625} atm = 0.4392 atm$$

The total pressure in the final mixture is 0.4392atm

Question 130

From the equation , $PV = \frac{1}{3} Nmc^2$; deduce :

- (i) Grahm's law of diffusion
- (ii) Avogadro's law

Solution

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

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

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

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

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

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

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

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

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

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

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

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

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

For two gases, say 1 and 2

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

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

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

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

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

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

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

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

The last two equations are then become:

$$PV_1 = \frac{2}{3} N_1 kT (vii)$$

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

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

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

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

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

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

Question 131

At the start of an experiment one end of the U tube of 6mm glass is immersed in a concentrated ammonia solution and other end is immersed in concentrated acid solution. At the point in the tube where the vapours of NH₃ and HCl meet a white cloud of NH₄Cl forms. At what fraction of distance along the tube from the ammonia the white clouds first forms?

Solution

By Grahm's law of diffusion:
$$\frac{V_{NH_3}}{V_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}}$$

(Time taken for diffusion of each solution is constant because the two ends of the tube were immersed in the solutions at the same time)

But volume of solution diffused varies directly proportional to the distance travelled by the solution.

It follows that:
$$\frac{l_{NH_3}}{l_{HCl}} = \sqrt{\frac{36.5}{17}} = 1.465$$

$$l_{NH_3}$$
: $l_{HCl} = 1.465$: 1

If total length of the tube is l, then the distance traveled by NH₃ before forming a white cloud of

$$NH_4Cl = \left(\frac{1.465}{1 + 1.465}\right)l = \frac{293}{493}l$$

Hence a white cloud of NH_4Cl (s) forms at $\frac{293}{493}$ of the total length of the tube from the ammonia.

Question 132

Write the formula of Van't Hoff's factor in terms of the following:

- (i) Number of particles
- (ii) Volume of the gas
- (iii) Pressure of the gas
- (iv) Molar mass

Solution

- (i)
- $i = \frac{\text{Observed number of particles}}{\text{Expected number of particles}} :$ Since number of gas particles varies directly proportional to its volume, then : (ii)

$$i = \frac{\text{Observed(measured)volume of the gas}}{\text{Expected volume of the gas}}$$

(iii) As number of gas particles varies directly proportional to the pressure exerted by the gas, then:

$$i = \frac{Observed(measured) pressure of the gas}{Expected pressure of the gas}$$

(iv) Since number of gas particles varies directly proportional to the volume of the gas which in turn varies inversely proportional to the molar mass of the gas, then:

$$i = \frac{Expected \ molar \ mass}{Measured(observed) \ molar \ mass}$$

Question 133

At the top of mountain the thermometer reads 0°C and barometer reads 710mmHg. At the bottom of the mountain the temperature is 30°C and the pressure is 760 mmHg. Compare density of the air at the top with that at the bottom.

Solution

From
$$PV = \frac{m}{Mr}RT$$
 then $P = \left(\frac{m}{V}\right)\frac{RT}{Mr}$ but $\frac{m}{V} = \rho$

$$P = \frac{\rho RT}{Mr}$$
 or $\rho = \frac{PM_r}{RT}$

If P_B and P_T are density of air at the bottom and the top of the mountain respectively

Then
$$\rho_T = \frac{P_T M_r}{R T_T}$$
 and $\rho_B = \frac{P_B M r}{R T_B}$ So $\frac{\rho_T}{\rho_B} = \frac{P_T T_B}{P_B T_T} = \frac{710 \times 303}{760 \times 273} = 1.0369$

Hence $\rho_T = 1.0369 \rho_B$

Where ρ_T is the density of air at the top of the mountain and ρ_B is the density of air at the bottom of the mountain

Question 134

Explain the following:

- (i) It easier to liquefy ammonia gas than fluorine gas.
- (ii) Duma's method is useless in the experimental determination of molar mass of table salt.

Solution

- (i) Liquefaction of a gas involves strengthening intermolecular forces potentially present in the gas. Ammonia having intermolecular hydrogen bonding in additional to Van-der-Waals dispersion forces has stronger intermolecular forces than fluorine which has Van-der-Waals dispersion forces only.
- (ii) Duma's method works with volatile substances only. Table salt being non-volatile substance cannot be vapourised by Duma's apparatus and hence the method is not suitable in determining its molar mass.

Question 135

A 15L vessel containing 5.65g of Nitrogen (N_2) is connected by means of valve to a 6L vessel containing 5g oxygen (O_2) . After the valve is opened and the gases were allowed to mix, what would be partial pressure of each gas and the total pressure at 27°C?

Solution

$$P_{N_2} = \frac{n_{N_2}RT}{V} = \frac{m_{N_2}RT}{M_{N_2}V}$$

Where
$$m_{N_2} = 5.65g$$
, $R = 0.082$, $T = 300k$

$$M_{N_2} = 28g/mol, V = (15L + 6L) = 21L$$

$$P_{N_2} = \frac{5.65 \times 0.082 \times 300}{28 \times 21} = 0.2364 \text{ atm}$$

Partial pressure of nitrogen gas is 0.2364atm

$$P_{O_2} = \frac{n_{O_2}RT}{V} = \frac{m_{O_2}RT}{M_{O_2}V}$$

Where $m_{O_2} = 5g$ and $M_{O_2} = 32g/mol$

$$P_{O_2} = \frac{5 \times 0.082 \times 300}{32 \times 21} = 0.183 \text{ atm}$$

Partial pressure of oxygen gas 0.183atm

By Dalton's law of partial pressure: $P_T = P_{O_2} + P_{N_2} = (0.2364 + 0.183)$ atm = 0.4194 atm

The total pressure is 0.4194atm

Question 136

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

Solution

The combination of Boyle's law and Charles's law is the combined gas law which can be represented as follows;

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$
, where n is constant.

When volume is constant, $V_1 = V_2 = V$

Then $\frac{P_1V}{T_1} = \frac{P_2V}{T_2}$ or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ which is equivalent to Gay-Lussac's pressure law.

Hence the Gay-Lussac's law is contained in Gay-Lussac's law as shown above.

Question 137

The pressure in a vessel that contained pure oxygen dropped from 2000 torr to 1500torr in 55 minutes as the oxygen leaks through a small hole into a vacuum. When the vessel was filled with another gas, the pressure dropped from 2000 torr to 1500 torr in 85 minutes. What is the molecular weight of the second gas?

Solution

By Grahm's law of diffusion:
$$\frac{\text{Rate of diffusion of oxygen gas}}{\text{Rate of diffusion of second gas}} = \sqrt{\frac{M_S}{M_{O_2}}}$$

But rate of diffusion varies directly proportional to the rate of pressure change then $\frac{\frac{\Delta P_{O_2}}{t_{O_2}}}{\frac{\Delta P_S}{t_S}} = \sqrt{\frac{M_S}{M_{O_2}}}$

$$\frac{\Delta P_{O_2} t_S}{\Delta P_U t_{O_2}} = \sqrt{\frac{M_S}{M_{O_2}}} \quad \text{or } \frac{(2000 \times 1500)85}{(2000 \times 1500)55} = \sqrt{\frac{M_S}{32}} \quad \text{or } M_S = 76 \text{ g/mol}$$

Hence the molecular weight of second gas is 76g/mol

Question 138

From the fundamental gas equation derive:

- (i) Gay-Lussac's law.
- (ii) Combined gas law.

Solution

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

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

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

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

Therefore; PV =
$$\frac{2}{3}$$
kT or P = $\frac{2k}{3V}$ T - - - - - - - (*i*)

If V is constant:

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

Hence $P \propto T$

The result is the mathematical form of the Gay-Lussac's law.

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

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

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

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

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

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

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

Hence
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3} = \cdots \dots \dots = \frac{P_nV_n}{T_n}$$
 which is the mathematical form of the combined law.

Question 139

Calculate the kinetic energy of 1mol of an ideal gas at 25°C.

Solution

K.
$$E = \frac{3}{2}$$
 RT for one mole of a gas

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

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

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

Question 140

What are the shortcomings of kinetic theory for gases?

Solution

Kinetic theory does not recognise that; at low temperature and high pressure:

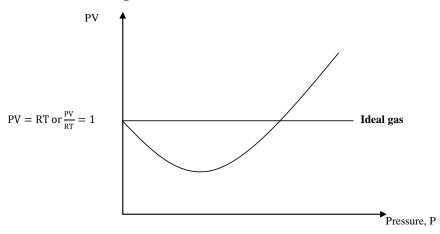
- Intermolecular forces of attraction cannot be neglected.
- Volume of gas molecules cannot be neglected compared to the volume of whole gas (container).

Question 141

With the help of Amagat's curves, show how CO₂ deviates from ideal gas behaviour.

Solution

Amagat's curve to show deviation of CO₂ from ideal has behaviour is shown below:



Question 142

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

Solution

K. E = $\frac{3}{2}$ RT for one mole of a gas

$$K.E = \frac{3}{2} \times 8.314 \times 300 = 3741.3J$$

Hence kinetic energy for one mole of the gas is 3.7413kJ

Question 143

A mixture of gases ethane, ethene and helium is contained in a container of unknown volume at 300K and 680 mmHg. The mixture is burned with excess oxygen and all the carbon is converted into carbon dioxide and hydrogen into water. The carbon dioxide is collected in a container of volume 0.25dm³ and found to exert a pressure of 561.3mmHg at 300K. The Helium is also collected in a separate container of volume 0.25 dm³ and exerts a pressure of 187.1 mmHg at 300K

$$C_2H_6(g) + 7/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

 $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

- i) How many moles of Helium are in the original vessel?
- ii) How many moles of carbon dioxide are produced?
- iii) What is the partial pressure of Helium in the original vessel?
- iv) What is the volume of original vessel?

Solution

$$n_{He} = \frac{P_{He}V}{RT} = \frac{187.1 \times 0.25}{0.082 \times 300 \times 760} = 2.5 \times 10^{-3} \text{moles}$$

(i) There were 2.5×10^{-3} moles of Helium in the original vessel.

$$n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{561.3 \times 0.25}{0.082 \times 300 \times 760} = 7.5 \times 10^{-3} moles$$

- (ii) Thus 7.5×10^{-3} moles of carbon dioxide gas was produced
- (iii) If n_{ea} and n_{ee} represent number of moles of ethane and ethene respectively (which are originally present in the vessel)

Then from given equation for combustion:

Number of moles of CO_2 produced by combustion of ethane = $2n_{ea}$

And number of moles of CO_2 produced by combustion of ethene = $2n_{ee}$

It follows that: $2n_{ea} + 2n_{ee} = 7.5 \times 10^{-3}$ moles

From which: $n_{ea} + n_{ee} = 3.75 \times 10^{-3}$ moles

So total number of moles of gases present in the original vessel is:

$$n_{ea} + n_{ee} + n_{He} = (3.75 + 7.5) \times 10^{-3} \text{ moles} = 6.25 \times 10^{-3} \text{moles}$$

But total pressure present in the original vessel, $P_T = 680 \text{mmHg}$

And
$$P_{He} = P_{He} = \left(\frac{n_{He}}{n_T}\right) \times P_T = \frac{2.5 \times 10^{-3}}{6.25 \times 10^{-3}} \times 680 \text{mmHg} = 272 \text{mmHg}$$

Hence the partial pressure of Helium in the original vessel was 272mmHg

(iv) Using
$$V = \frac{nRT}{P}$$

Substituting the value of partial pressure of Helium obtained in (iii) above;

$$V = \frac{2.5 \times 10^{-3} \times 0.082 \times 300 \times 760}{272} = 0.11718 dm^3 \text{ or } 171.8 cm^3$$

Hence the volume of the original vessel was 0.11718dm³ or 171.8cm³

Question 144

Define Amagat's curve and give its main significance.

Amagat's curve is the plot of compression factor (Z) against pressure of gases.

Significance:

It shows deviation of real gases from ideal behaviour at different pressures.

Question 145

Calculate the pressure of real gases of 0.02mol occupied in 1.6L bulb at 20°C.

Given that: a = 1.34 atm L^2 mol⁻² and b = 0.32 L moL⁻¹

Solution

From Van der Waals equation for real gases:
$$\left(P + a\left(\frac{n}{v}\right)^2\right)(v - nb) = nRT$$

Substituting given values
$$\left(P + 1.34 \left(\frac{0.02}{1.6}\right)^2\right) \left(1.6 - (0.02 \times 0.32)\right) = 0.02 \times 0.082 \times 293$$

$$P = 0.3atm$$

Hence the pressure of real gas is 0.3atm

Ouestion 146

a) At 110°C and 454mmHg, 0.11g of ethanoic acid vapour occupies 63.7cm³. At 156°C and 458mmHg, 0.081g of ethanoic acid vapour occupies 66.4cm³. Calculate the molar mass of ethanoic acid in the vapour phase at each temperature.

b) Give the interpretation of the results in 146(b) above.

Solution

Using
$$M_r = \frac{mRT}{PV}$$

At 110°C (383K)

$$M_r = \frac{0.11 \times 0.082 \times 383 \times 760 \times 1000}{454 \times 63.7} = 91g/mol$$

Molar mass of ethanoic acid at 100°C is 91g/mol

At 156°C (429K)

$$\rm M_r = \frac{0.081 \times 0.082 \times 429 \times 760 \times 1000}{458 \times 66.4} = 71 \rm g/mol$$

Molar mass of ethanoic acid at 110°C is 71g/mol

Interpretation of the results:

Measured molar mass of CH₃COOH is greater than its expected molar mass of 60g/mol, because molecules of the acid are capable of undergoing association as result of strong hydrogen bonding formed between its molecules. Degree of association of the acid decrease with an increase in temperature as the high temperature weakens the strength of hydrogen bonding and hence molar mass of CH₃COOH at 156°C become smaller than that measured at 110°C.

Question 147

The Van-der-Waals equation for 'n' moles of real gas can be written as follows:

$$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$$

- (i) Which constant (a or b) is related to the gas's ability to undergo liquefaction? Give a reason to support your answer.
- (ii) Does the ability of the gas to be liquefied favoured with large value or small value of the constant mentioned in (i) above? Explain.

Solution

(i) Both constants 'a' and 'b'.

Explanation

During gas liquefaction both strengthening of intermolecular forces between gas molecules and decreasing of volume of empty space (occupied by gas molecules) to zero are done simultaneously. Since the intermolecular forces is related to 'a' and the volume of empty space is related to 'b', both constants are related to the liquefaction.

(ii) Both constants 'a' and 'b'.

Explanation

Large value of 'a' means stronger intermolecular forces while large value of 'b' implies large molecular volume which means less of the empty space is left and hence easier liquefaction for gases with large value of constants, 'a' and 'b'.

Question 148

A 3.2m³ vessel contains a mixture of 86.2g of oxygen and 1.5 g of hydrogen at 88°C. Calculate the total pressure in the vessel.

Solution

By Dalton's law of partial pressure: $P_T = (n_{O_2} + n_{H_2}) \frac{RT}{V} = (\frac{m_{O_2}}{M_{O_2}} + \frac{m_{H_2}}{M_{H_2}}) \frac{RT}{V}$

$$P_T = \left(\frac{86.2}{32} + \frac{1.5}{2}\right) \frac{0.082 \times 361}{3.2 \times 10^3} \text{ atm} = 0.032 \text{ atm}$$

Hence the total pressure in the vessel is 0.032atm

Question 149

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

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

Solution

(i) Yes, the total pressure changes.

Explanation

Increasing the amount of gases, increases collision frequency between gas particles and walls of the flask and therefore increasing pressure. So adding the neon will increase pressure in the flask.

(ii) No effect.

Explanation

Neon is incapable of reacting with any gas present in the flask, so adding it in the flask will do both increase the total pressure in the flask and decrease the mole fraction of the gases by the same proportion and hence the partial pressures will remain the same.

Question 150

Gas A of a certain volume diffuses for 580.8s while the same volume of gas J diffuses for 300s under identical experimental conditions. Calculate the relative molecular mass of J if the relative molecular mass of gas A is 120.

Solution

$$\frac{t_{J}}{t_{A}} = \sqrt{\frac{M_{J}}{M_{A}}}$$
 or $M_{J} = M_{A} \left(\frac{t_{J}}{t_{A}}\right)^{2} = 120 \times \left(\frac{300}{580.8}\right)^{2} \text{g/mol} = 32\text{g/mol}$

Hence relative molecular mass of J is 32g/mol

Question 151

Write Van-der-Waals equation for one mole of the gas.

Solution

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Question 152

A certain compound has an approximate RMM of 207. At 80°C and in a 3 litres vessel, the vapour of this compound exerts a pressure of about 0.12atmosphere. What is the mass in grams of the vapour of this compound?

Solution

From PV =
$$\frac{m}{Mr}$$
 RT or $m = \frac{PVMr}{RT} = \frac{0.12 \times 3 \times 207}{0.082 \times 353} = 2.57g$

Hence mass of the vapour is 2.57g

Question 153

Outline the two assumptions of kinetic theory of gases that are not considered to be negligible under real gas behaviour.

Solution

- (i) Intermolecular forces of attraction between gas molecules in motion is negligible i.e. when gas molecules are moving there is neither attraction force nor repulsion force between them.
- The volume of the gas molecule is negligible compared to the volume of the whole gas.

Ouestion 154

At what conditions does real gas obey the ideal gas equation?

Solution

At:

- High temperature and
- Low pressure

Question 155

Under what conditions (s), does Dalton's law of partial pressure apply?

Solution

- Temperature must be kept constant
- If there is no chemical reaction between gases

Ouestion 156

KClO₃ is decomposed by the following reaction:

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

The O₂ produced was collected by the displacement of water at 22°C at a total pressure of 760torr. The volume of gas collected was 1.2L and the vapour pressure of water at 22°C is 21torr. Calculate:

- (i) The partial pressure of O_2 in the gas collected and
- (ii) The mass of KClO₃ in the sample that was decomposed.

Solution

(i) By Dalton's law of partial pressure;

$$P_T = P_{O_2} + P_{H_2O}$$

Substituting 760torr = P_{0_2} + 21torr; P_{0_2} = 739torr

The partial pressure of oxygen gas is 739torr

(ii) From ideal gas equation;

$$n_{0_2} = \frac{P_{0_2}V}{RT} = \frac{739 \times 1.2}{760 \times 0.082 \times 295} \text{ mol} = 0.04824 \text{mol}$$
From the reaction equation, male ratio of VCIO, to O, is

From the reaction equation, mole ratio of $KClO_3$ to O_2 is 2:3;

Thus number of moles of KClO₃ required is $\frac{2}{3} \times 0.04824$ mol = 0.03216mol

Using $m = nM_r$ where M_r of $KClO_3 = 122.5g/mol$

Thus mass of KClO₃ decomposed is 0.03216mol $\times 122.5$ g/mol = 3.94g

Question 157

Define (i) Molar gas volume (ii) Relative molecular mass (RMM)

Solution

- (i) The molar gas volume is the volume occupied at s.t.p by one mole of molecules of a gas and is 22.4dm³
- (ii) The relative molecular mass is the mass of one molecule of an element or a compound compared with the mass of an atom of ${}^{12}_{6}$ C which is arbitrarily assigned as 12.00

Question 158

Some compounds are said to have 'abnormal' relatives densities when determination is carried out experimentally.

Result can either be higher or lower than the expected from their molecular formulae.

- i) What factor(s) lead to such abnormalities.
- ii) For each factor, give two examples of compounds whose vapour shows such abnormalities, illustration your answer with equations or structures.

Solution

- (i) Dissociation and association
- (ii) **Dissociation** makes the observed relative density of the compound to be lower than the expected from its molecular formula
 - 1. N_2O_4 (g) dissociate into NO_2 according to the following equation

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

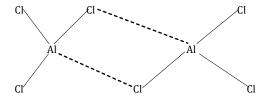
2. PCl₅ dissociated into PCl₃ and Cl₂ according to the following equation:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Association makes the measured (observed) relative density of the compound to be greater than the expected from its molecular formula

Examples:

(i) Two molecules of AlCl₃ can associate according to the following structure;



(ii) Two molecules of ethanoic acid can associate according to the following structure



Question 159

Define the following as applied in gases:

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

Solution

- (i) Normal density of a gas is the mass per unit volume of the gas at given conditions of temperature and pressure.
- (ii) Relative density of a gas is the ratio of the normal density of the gas to the normal density of hydrogen gas at the given conditions of temperature and pressure.

Question 160

267cm³ of a certain gas at 18°C and 100400Pa pressure has a mass of 0.162g calculate:

- (i) Normal density of the gas at s.t.p
- (ii) Relative density of the gas at s.t.p

Solution

$$At = s.t.p. T = 273K, P = 103100Pa$$

So taking:
$$T_1 = 18^{\circ}C = 291K$$
, $V_1 = 267cm^3$, $P_1 = 100400Pa$, $T_2 = 273K$,

$$P_2 = 101300 Pa, V_2 = ?$$

From general gas equation: $\frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1}$

$$V_2 = \left(\frac{T_2}{T_1}\right) \left(\frac{P_1}{P_2}\right) V_1 = \frac{273 \times 100400 \times 267}{291 \times 101300} \, cm^3 = 248 cm^3$$

Thus volume of the gas at s.t.p = $248cm^3$

Normal density,
$$\rho = \frac{m}{v} = \frac{0.162}{248} = 6.532 \times 10^{-4} \text{g/cm}^3$$

(i) Normal density of the gas is $6.532 \times 10^{-4} \text{g/cm}^3$ or 0.6532g/dm^3

Using Mr =
$$\frac{mRT}{PV} = \frac{\rho RT}{P} = \frac{0.6532 \times 0.082 \times 273 \times 101300}{101300} = 14.6g/mol$$

Relative density of the gas
$$=\frac{M_r}{2g/mol} = \frac{14.6}{2} = 7.3$$

(ii) Relative density of the gas is 7.3

Question 161

Gas laws comprise of number of laws which attempt to explain behaviour of gases. But among those laws, only three laws are considered to be primary gas laws.

- (i) Mention the three fundamental gas laws.
- (ii) Why the laws mentioned in (i) above are considered fundamental?

Solution

- (i) The three fundamental laws are:
 - ✓ Boyle's law,
 - ✓ Charles's law and
 - ✓ Avogadro's law
- (ii) They all express relationship between main variables of gaseous state with volume as the common changing variable in all of them.

Question 162

200cm³ of oxygen gas takes 250 seconds to diffuse through a porous diaphragm. Under identical conditions, 200cm³ of an unknown gas T takes 177 seconds to diffuse. Calculate the relative molecular mass for unknown gas.

Solution

From Grahm's law of diffusion:
$$\frac{t_u}{t_{0_2}} = \sqrt{\frac{M_u}{M_{0_2}}}$$
 or $M_u = \frac{32g}{mol} \times \left(\frac{177}{250}\right)^2 = 16g/mol$

The relative molecular mass of unknown gas is 16

Question 163

Define the following:

- (i) Boyle's law
- (ii) Charles's law
- (iii) Gay-Lussac's law
- (iv) Avogadro's law

Solution

- (i) Boyle's law is the law which express relationship between pressure and volume of ideal gas when temperature and amount of the gas are kept constant.
- (ii) Charles's law is the law which express relationship between volume and temperature of ideal gas when pressure and amount of the gas are kept constant.
- (iii) Gay-Lussac's law is the law which express relationship between pressure and temperature of ideal gas when volume and amount of the gas are kept constant.
- (iv) Avogadro's law is the law which express relationship between amount of ideal gas and its volume when pressure and temperature are kept constant.

Ouestion 164

The mass for 243cm³ of a gas at 273K and an atmospheric pressure of 1 atmosphere is 0.162g. Calculate the normal density and relative density of the gas.

Solution

Normal density,
$$\rho = \frac{m}{v} = \frac{0.162}{0.243} = 0.6667 g/dm^3$$

Normal density of the gas is 0.6667g/dm³

Using
$$M_r = \frac{\rho RT}{P} = \frac{0.6667 \times 0.082 \times 273}{1} = 15g/mol$$

Relative density of the gas
$$=\frac{M_r}{2g/mol} = \frac{15}{2} = 7.5$$

The relative density of the gas is 7.5

Question 165

Define the following terms

- i) Mole
- ii) Avogadro's constant

Solution

- (i) Mole is the amount of substance which contains as many elementary entities as there are carbon atoms in 12 grams of the ¹²_cC isotope.
 - (ii) Avogadro's number is the number of particles (atoms, ions, electrons, protons, neutrons or molecules etc) amounted to 6.02×10^{23} present in one mole of the substance.

How many atoms would be present in:

- (i) 11.5g of sodium
- (ii) 11.2dm³ of gas Q at s.t.p

Solution

Atomic mass of sodium = 23

Number of moles of sodium atom $\frac{m}{M_r} = \frac{11.5}{23} = 0.5$

Number of sodium atoms = $nN_A = 0.5 \times 6.02 \times 10^{23}$ atoms = 3.01×10^{23} atoms

There are 3.01×10^{23} atoms of sodium

Number of moles of atoms of gas $Q = \frac{Given volume}{Gas molar volume}$

But gas molar volume at s.t.p = $22.4 dm^3$

Number of moles = $\frac{11.2}{22.4}$ = 0.5 moles

Number of atoms of gas Q = $nN_A = 0.5 \times 6.02 \times 10^{23}$ atoms = 3.01×10^{23} atoms

There are 3.01 \times 10²³ atoms of gas Q

Question 167

From ideal gas equation, derive the relationship between density of a gas in grams per dm^3 , the gas pressure in atmospheres, the temperature T in kelvin, the relative molecular mass of a gas (M_r) and the as constant, R.

Solution

From ideal gas equation: PV = nRT

But $n = \frac{m}{M_r}$; where m is the mass of the gas in grams

Then PV = $\left(\frac{m}{M_r}\right)$ RT)

Or $\frac{PM_r}{RT} = \frac{m}{v}$

But $\frac{m}{v}$ = Density of the gas in gdm⁻³, ρ

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

Question 168

1 mole of hydrogen gas was reacted with 1 mole of iodine vapour. Calculate the number of moles of hydrogen iodide formed at t seconds. After t seconds; 0.8moles for hydrogen remained.

Solution

Number of moles of H_2 reacted after t seconds = (1 - 0.8)moles = 0.2moles

 H_2 and I_2 React according to the following equation: $H_2 + I_2 \rightarrow 2HI$

From which mole ratio of H₂ to HI is 1:2

Hence number of moles of HI formed after t seconds was 2×0.2 moles = 0.4 moles

Question 169

"A gas consists of very small molecules in a random motion of which there is a collision between gas molecules and walls of the container"

- (i) What is the characteristics feature of that collision? (Assume the gas is ideal)
- (ii) The collision will result into important property of the gas: mention it.
- (iii) Explain clearly how, the presence of intermolecular forces in real gas, will affect facts mentioned in (i) and (ii) above.

Solution

- (i) It is completely **elastic.**
- (ii) Pressure
- (iii) Under presence of intermolecular forces, the collision will not be elastic. This is because, the intermolecular forces lowers speed as well as kinetic energy making the collision inelastic as some kinetic energy are transformed into intermolecular energy.

Also the intermolecular forces, lowers the observed pressure. This is because as result of decrease in speed, both collision frequency and collision force (intensity) are decreased resulting to decrease in pressure of the gas.

Question 170

Two porous containers are filled with hydrogen and neon respectively. Under identical conditions, $\frac{2}{3}$ of hydrogen escapes in 6 hours. How long will it take for half the neon to escape? (You may use the following molar masses: $H_2 = 2.02g/mol$, Ne = 20.18g/mol).

Solution

From Grahm's law of diffusion:
$$\frac{R_{H_2}}{R_{Ne}} = \sqrt{\frac{M_{Ne}}{M_{H_2}}} = \sqrt{\frac{20.18}{2.02}} = 3.16$$

If $t_{\rm H_2}$ represents the time for $^2/_3$ of H_2 to diffuse and $t_{\rm Ne}$ represents the time for $^2/_3$ of Ne (the same amount as that of H_2) to diffuse: and because rate of diffusion varies inversely proportional to the time taken for the diffusion to take place, it follows that: $\frac{R_{\rm H_2}}{R_{\rm Ne}} = \frac{t_{\rm Ne}}{t_{\rm H_2}} = 3.16$

Substituting
$$\frac{t_{Ne}}{6hr} = 3.16$$
: $t_{Ne} = 3.16 \times 6hr = 18.96 \text{ hr}$

Thus 18.96 hours is required for $\frac{2}{3}$ of Ne to diffuse

Then (by cross-multiplication) $\frac{1/2 \times 18.96}{2/3}$ hours or 14.22hours is required for 1/2 of Ne to diffuse

Hence the time taken for half the neon to diffuse is 14.22 hours

Question 171

State the following gas laws. In each case give their corresponding mathematical equation.

- (i) Gay-Lussac's law
- (ii) Combined gas law

Solution

(i) Pressure of given mass of a gas varies directly proportional to its absolute temperature provided that the volume of the gas is constant.

Mathematical equation:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

(ii) Volume of fixed mass of a gas varies directly proportional to absolute temperature and inversely proportional to its pressure.

Mathematical equation:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Question 172

A container has two gases in it and one of them weighs 64g/mol. Given the following information; calculate the molecular mass of the other component.

- \checkmark The mole fraction of unknown gas is 0.35
- ✓ The total pressure inside the 1litre container is 1.6atm
- ✓ The density of the gaseous mixture is 3.45g/L at 25°C

Solution

Substituting
$$n = \frac{m}{M_r}$$
 in PV = nRT gives PV = $\frac{mRT}{M_r}$

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

If M_m is the average molar mass of the mixture and m_m is the mass of the mixture.

It follows that: $M_m = \frac{m_m RT}{PV}$

But
$$\frac{m_m}{V} = \rho_m$$
 where ρ_m is the density of the mixture

Then
$$M_m = \frac{\rho_m RT}{P} = \frac{3.45 \times 0.082 \times 298}{1.6} \text{g/mol} = 52.69 \text{ g/mol}$$

If:

X_u is the mole fraction of unknown gas

M_u is the molecular mass of unknown gas

 X_k is the mole fraction of known gas and

 $\ensuremath{M_k}$ is the molecular mass of known gas.

It follows that: $M_m = X_u M_u + X_k M_k$

Where
$$X_u = 0.35$$
: $X_k = 1 - X_u = 1 - 0.35 = 0.65$ and $M_k = 64g/mol$

Substituting
$$52.69 = 0.35M_u + 0.65 \times 64$$

From which
$$M_u = 31.69g/mol$$

Hence molecular mass of the other component is 31.69g/mol

Question 173

From the ideal gas equation derive the relationship between pressure (P) and number of moles (n) and hence state the result in words as the P-n law.

Solution

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

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

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

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

In words: For fixed volume of a gas at constant temperature, pressure of the gas varies directly proportional to the number of moles of the gas.

Question 174

When an open flask containing air is heated from 27°C to 87°C, what percentage of the air in the flask is expelled? Assume that the volume of the flask and atmospheric pressure are constant.

Solution

From
$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

If:
$$P_1 = P_2 = P$$
 and $V_1 = V_2 = V(P \text{ and } V \text{ are constant})$

$$\frac{PV}{n_1T_1} = \frac{PV}{n_2T_2} \ \ \, \text{or} \; n_1T_1 = \; n_2T_2$$

Substituting $n_1 \times 300 = n_2 \times 360$

$$\frac{n_1}{n_2} = \frac{360}{300} = \frac{6}{5}$$

Thus n_1 : $n_2 = 6$: 5 where n_1 is the number of moles of air before heating and n_2 is the number of moles of air after heating.

Then number of moles of air decreased (expelled)= (6-5)mol = 1mol

And percentage of air expelled =
$$\frac{\text{number of moles expelled}}{\text{original number of moles before heating}} = \frac{1}{6} \times 100\% = 16.67\%$$

Hence the percentage of air expelled is 16.67%

Question 175

Define the following:

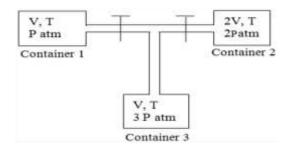
- (i) Ideal volume of gas
- (ii) Ideal pressure of gas

Solution

- (i) The ideal volume is the amount of empty space that can be occupied freely by gas molecules under assumption that individual gas molecules have zero volume.
- (ii) The ideal pressure is the pressure exerted by gas molecules under assumption that the gas molecules experience no intermolecular forces.

Question 176

When we open the taps given in the picture below, find the final pressure exerted by gases.



Solution

Final volume, $V_{\text{final}} = V + 2V + V = 4V = V_2$

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

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

For container 1: $P_1 = P$, $V_1 = V$

Then
$$P_2 = \frac{P \times V}{4V} = \frac{1}{4} p \text{ atm}$$

For container 2: $P_1 = 2 p atm$, $V_1 = 2V$

Then
$$P_2 = \frac{2P \times 2V}{4V} = 1 P atm$$

For container 3: $P_1 = 3p$ atm, $V_1 = V$

Then
$$P_2 = \frac{3P \times V}{4V} = \frac{3}{4}P$$
 atm

By Dalton's law of partial pressure: $P_{\text{final}} = \left(\frac{P}{4} + P + \frac{3P}{4}\right) \text{ atm} = 2P \text{ atm}$

Hence the total final pressure is 2P atm

Question 177

State the following gas laws. In each case give their corresponding mathematical equation.

- (i) Ideal gas law
- (ii) Avogadro's law

Solution

(i) Volume of all gases varies directly proportional to their number of moles and absolute temperature and inversely proportional to their pressure.

$$PV = nRT$$
 (Mathematical equation)

(ii) Volume of all gases varies directly proportional to their number of moles at constant temperature and pressure.

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$
 (Mathematical equation)

Question 178

0.964g sample of mixture of sodium methanoate and sodium chloride is analysed by adding sulphuric acid. The equation for the reaction for sodium methanoate with sulphuric acid is shown below.

$$2HCOONa + H_2SO_4 \rightarrow 2CO + 2H_2O + Na_2SO_4$$

The carbon monoxide formed measures 242mL when collected over water at 752mmHg and 22°C. Calculate the percentage of sodium methanoate in the original mixture. Given that: vapour pressure of water at 22°C is 19.8mmHg.

Solution

By Dalton's law of partial pressure: $P_T = P_{H_2O} + P_{CO}$

From which
$$P_{CO} = P_T - P_{H_2O} = (752 - 19.8) \text{mmHg} = 732.2 \text{mmHg}$$

From ideal gas equation PV = nRT, $n = \frac{PV}{RT}$

Thus
$$n_{CO} = \frac{732.2 \times 0.242}{760 \times 0.082 \times 295} \text{mol} = 0.00964 \text{mol}$$

But from the equation for the reaction, mole ratio of CO to HCOONa is 1:1

Thus $n_{CO} = n_{HCOONa} = 0.00964$ mol

Using m = nMr; $M_{HCOONa} = 0.00964 mol \times 68 g/mol = 0.65552 g$

Then %HCOONa =
$$\frac{M_{HCOONa}}{M_T} \times 100\% = \frac{0.65552}{0.964} \times 100\% = 68\%$$

Ouestion 179

A mixture of hydrogen gas, oxygen gas and 2mL of liquid water is present in a 0.5L rigid container at 25°C. The number of moles of hydrogen gas and the number of moles of oxygen gas is equal. The total pressure is 1146mmHg.

The mixture is sparked, and H₂ and O₂ react until one reactant is completely consumed.

- a) Identify the reactant remaining and calculate the number of moles of the reactant remaining
- b) Calculate the total pressure in the container at the conclusion of the reaction if the final temperature is 90°C.
- c) Calculate the number of moles of water present as vapour in the container at 90°C

Given that:

- ✓ The vapour pressure of water at 25°C is 24mmHg
- ✓ The vapour pressure of water 90°C is 526mmHg

Solution

a) Equation for the reaction: $2H_2 + O_2 \rightarrow H_2O$

From which mole ratio of H_2 to O_2 is 2:1; that is for each one mole of O_2 two moles of H_2 is required?

But it is given that $n_{H_2} = n_{O_2}$ and whence O_2 present in excess.

Thus the reactant remaining is oxygen gas

Calculation of the amount remaining:

By Dalton's law of partial pressure; total pressure exerted by gases before the sparking (reaction) is given by: $P_T = P_{O_2} + P_{H_2} + P_{H_2O}$

Substituting $1146 = P_{O_2} + P_{H_2} + 24$ From which $P_{O_2} + P_{H_2} = 1122$ mmHg

Because $n_{O_2} = n_{H_2}$; $P_{O_2} = P_{H_2}$

Thus
$$P_{O_2} + P_{O_2} = 2P_{O_2} = 1122$$
mmHg

Or $P_{O_2} = 561$ mmHg

But from the equation of the reaction:

Number of moles of O_2 reacted = $\frac{1}{2}n_{H_2}$

Thus number of moles of O_2 remained = $n_{O_2} - \frac{1}{2} n_{H_2}$

But
$$n_{O_2} = n_{H_2}$$

Then number of moles of O_2 remained = $n_{O_2} - \frac{1}{2}n_{O_2} = \frac{1}{2}n_{O_2}$

And because pressure varies directly proportional to the number of moles, pressure exerted by the remained oxygen gas $=\frac{P_{O_2}}{2}=\frac{561 \text{mmHg}}{2}=280.5 \text{mmHg}$

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

Number of moles of O₂ gas remained = $\frac{280.5 \times 0.5}{760 \times 0.082 \times 298}$ mol = 0.00755mol

Hence the number of reactant remaining is 0.00755mol of O₂

b) From pressure law:
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$
 From which $P_2 = \left(\frac{T_2}{T_1}\right) P_1$

Partial of
$$O_2$$
 at $90^{\circ}C = \frac{363}{298} \times 280.5$ or 341.68 mmHg

And by Dalton's law of partial pressure:

$$P_T = P_{H_2O} + P_{O_2} = (526 + 341.68) \text{mmHg} = 867.68 \text{mmHg}$$

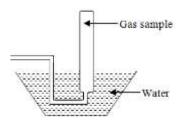
Hence the total pressure at 90°C is 867.68mmHg

c)
$$n_{H_2O} = \frac{P_{H_2O}V}{RT} = \frac{526 \times 0.5}{760 \times 0.082 \times 363} \text{mol} = 0.0116 \text{mol}$$

Hence number of moles of H₂O at 90°C is 0.0116mol

Question 180

A student collected a sample of hydrogen gas by the displacement of water as shown by the diagram below



The relevant data are given in the following table

GAS SAMPLE DATA		
Volume of sample	90mL	
Temperature	25°C	
Atmosphere pressure	745mmHg	

Vapour	pressure	of	23.8mmHg
H ₂ O(25°C)			

- a) Calculate the number of moles of hydrogen gas collected
- b) Calculate the number of molecules of water vapour in the sample gas
- c) Calculate the ratio of average speed of the hydrogen molecules to the average speed of the water vapour molecules in the sample.
- d) Which of the two gases, H₂ or H₂O, deviate more from ideal behaviour? Explain your answer.

Solution

a) From Dalton's law of partial pressure: $P_T = P_{H_2} + P_{H_2O}$

From which
$$P_{H_2} = P_T - P_{H_2O} = (745 - 23.8) \text{mmHg} = 721.2 \text{mmHg}$$

Then
$$n_{H_2} = \frac{P_{H_2}V}{RT} = \frac{721 \times 0.09}{760 \times 0.082 \times 298} \text{mol} = 0.00349 \text{mol}$$

Hence number of moles of hydrogen gas collected is 0.00349mol

b) Using $n_{H_2O} = \frac{P_{H_2O}V}{RT} = \frac{23.8 \times 0.09}{760 \times 0.082 \times 298} \text{mol} = 0.00012 \text{mol}$

Then number of molecules, $N = nN_A = 0.00012 \times 6.02 \times 10^{23}$ molecule

$$= 7.2 \times 10^{19}$$
 Molecule

Hence the number of molecules of water is 7.2×10^{19} Molecule

c)Using;

$$C = \sqrt{\frac{3RT}{M_r}}$$

$$C_{\rm H_2} = \sqrt{\frac{3RT}{M_{\rm H_2}}} \ ; \quad C_{\rm H_2O} = \sqrt{\frac{3RT}{M_{\rm H_2O}}} \label{eq:chi2O}$$

Then
$$\frac{C_{H_2}}{C_{H_2O}} = \sqrt{\frac{M_{H_2O}}{M_{H_2}}} = \sqrt{\frac{18}{2}} = 3$$

Thus the ratio of speed of H_2 to H_2O vapour is 3

d) H₂O deviate more from ideal behaviour

Explanation

- H₂O molecules exhibit stronger intermolecular forces of attraction due to its greater molecular weight and therefore stronger Van der Waals dispersion forces. It is also has hydrogen bonds which is very strong intermolecular forces of attraction.
- H₂O molecule has greater volume because it has greater size. Thus H₂O molecule occupies greater space and its volume cannot be neglected compared to the whole volume of the water vapour (gas).

Question 181











Represented above are five identical balloons, each filled to the same volume at 25°C and 1 atmosphere pressure with the pure gases indicated.

- a) Which balloon contains the greatest mass of gas? Explain
- b) Compare the average kinetic energies of the gas molecules in the balloons? Explain
- c) Which balloon contains the gas that would be expected to deviate most from the behaviour of an ideal gas? Explain
- d) Twelve hours after being filled, all the balloons have decreased in size. Predict which balloon will be the smallest. Explain your reasoning.

Solution

- a) CO₂: according to Avogadro's law, they all contain the same number of particles, therefore, the heaviest molecule, CO₂ with molar mass of 44g/mol will have the greatest mass.
- b) All the same according to kinetic theory of gases: at the same temperature all gases have the same kinetic energy.
- c) CO₂: Since it (CO₂) has greater molecular weight, it has strongest Van der Waals dispersion forces and therefore strongest intermolecular forces of attraction. Furthermore having greatest molecular weight and therefore largest molecular size its molecules occupy greater space (volume).
- d) He: it has the smallest molar mass and therefore greatest rate of effusion

Question 182

- (i) State the law which governs the total pressure in the container of mixture of two or more gases.
- (ii) From kinetic equation of gases, derive the law stated in (i) above.

Solution

(i) The law is Dalton's law of partial pressure.

It states that: The total pressure exerted in the container of the mixture of two or more gases is equal to the summation of their partial pressure provided that the gases do not react.

(ii) From kinetic equation of gases:

$$PV = \frac{Nmc^2}{3}$$
 or $P = \frac{Nmc^2}{3V}$

For mixture of gases, say three gases A,B and C with their respective number of molecules N_A , N_B and N_C and the total pressure excited by gaseous mixture, P_T :

$$\begin{split} &P_T = \left(\frac{N_A + N_B + N_C}{3V}\right) mc^2 \\ &= \frac{N_A mc^2}{3V} + \frac{N_B mc^2}{3V} + \frac{N_C mc^2}{3V} \\ &But \frac{N_A mc^2}{3V} = P_A, \frac{N_B mc^2}{3V} = P_B \text{ and } \frac{N_C mc^2}{3V} = P_C \end{split}$$

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

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

Question 183

- (i) Under what conditions does the behaviour of real gas begin to differ significantly from the ideal gas law?
- (ii) What is the physical meaning of the 'a' and 'b' constants in the Van der Waals equation?

Solution

(i) Low temperature and high pressure

(ii) **a** is the coefficient of attraction reflecting the strength of intermolecular force of attraction between gas particles (molecules).

b is the effective volume reflecting the molecular size of the gas.

Question 184

It takes 22 hours for neon-filled balloon to shrink to half its original volume at s.t.p. If the same balloon is filled with helium, then how long it have taken for the balloon to shrink to one third of its original volume at s.t.p?

Solution

From Grahm's law:
$$\frac{R_{Ne}}{R_{He}} = \sqrt{\frac{M_{He}}{M_{Ne}}}$$

But
$$R_{Ne} = \frac{V_{Ne \text{ diffused}}}{t_{Ne}} = \frac{\frac{1}{2}V_{Ne}}{t_{Ne}}$$
 (Volume of Ne diffused is half of its original volume)

And
$$R_{He} = \frac{V_{He} \text{ diffused}}{t_{He}} = \frac{\frac{2}{3}V_{He}}{t_{He}}$$
 (Volume of He shrinked to $\frac{1}{3}$ of original volume meaning $\frac{2}{3}$ of the original volume effused).

Then
$$\frac{\frac{\frac{1}{2}V_{\text{Ne}}}{t_{\text{Ne}}}}{\frac{2}{3}V_{\text{He}}} = \sqrt{\frac{M_{\text{He}}}{M_{\text{Ne}}}}$$

But $V_{Ne} = V_{He}$ (balloon was the same)

Substituting:
$$\frac{3 \times t_{He}}{4 \times 22 hr} = \sqrt{\frac{4}{20}}$$
; $t_{He} = 13.12$ hours

Hence the time is 13.12 hours

Question 185

Traditionally, high-flying aircraft and Formula 1 racing cars have had their tyres inflated with nitrogen gas instead of air. Recently, this practice has been extended to some other cars.

A car tyre is filled with nitrogen gas to a volume of 8.98dm³ and a pressure of 207kPa at 20°C.

- (i) Using the ideal gas equation, calculate the mass of nitrogen gas, in grams, present in the car tyre under these conditions. Show your work clearly.
- (ii) During a car journey, the tyres become warm. Use the ideal gas equation to deduce the effect of that this has on the pressure in the tyres.
- (iii) One reason for the use of nitrogen gas in car tyres is that less gas is lost from the tyres during use because nitrogen molecules are larger than oxygen molecules. A suggested explanation for this is that nitrogen atoms are larger than oxygen atoms. Explain why a nitrogen atom is larger than an oxygen atom.

Solution

(i) From ideal gas equation; PV = nRT; where
$$n = \frac{m}{M_P}$$

$$PV = \frac{m}{M_r} RT$$
; From which $m = \frac{PVM_r}{RT}$

$$\begin{split} m = & \frac{_{207000Nm^{-2}\times8.98\times10^{-3}m^{3}\times28gmol^{-1}}}{_{8.31Nmmol^{-1}K^{-1}\times293K}} (1Pa = 1Nm^{-2}\text{, 1J} = 1Nm \text{ and } 1dm^{3} = 10^{-3}m^{3}) \\ & = 21.4g \end{split}$$

Mass of nitrogen gas is 21.4g

(ii) From ideal gas equation; PV = nRT; $P = \frac{nRT}{V}$; $P \propto T$ (When V and n are constant)

Thus the increase in temperature will result in an increase in pressure of the tyres.

(iii) Nitrogen having fewer number of protons while shielding (screening) effect is the same for both; (both N and O have the same number of shells) experiences weaker effective nuclear attractive force.

Question 186

Which of the following gases would be nearly impossible to collect over water? Why?

Solution

HCl and NH₃

Explanation

HCl and NH₃ being polar, they are highly soluble in water; so they will dissolve in it to make a solution and hence they would not come out the other end.

Question 187

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

Solution

Carbon monoxide gas reacts with oxygen gas according to the following equation:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

Since the CO was in excess, after reaction the gaseous mixture consisted of unreacted CO and produced CO₂.

Then from Grahm's law of diffusion:

$$\frac{t_{mixture}}{t_{Br_2}} = \sqrt{\frac{M_{mixture}}{M_{Br_2}}}$$

But
$$t_{\text{mixture}} = \frac{1}{2} t_{\text{Br}_2}$$

Then
$$\frac{\frac{1}{2}t_{Br_2}}{t_{Br_2}}=\sqrt{\frac{M_{mixture}}{M_{Br_2}}}=\sqrt{\frac{M_{mixture}}{160}}$$

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

$$= 40g/mol$$

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

Then let the percentage by volume of CO be x and thus the percentage of CO_2 will be 100 - x;

Where molar mass of CO and CO₂ are 28g/mol and 44g/mol respectively.

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

From which x = 0.25 and 100 - x = 75

Hence:

The percentage of CO is 25%

The percentage of CO₂ is 75%

A certain dry gas is composed of 21% by volume of oxygen, 1% of argon and 78% of nitrogen. Find its density in grams per dm³ at 20°C and 98.65kNm⁻² pressure.

Solution

Density of the mixture (ρ) is given by $\rho = \frac{PM_r}{RT}$

Where M_r is the average molar mass of the gaseous mixture and $P = \frac{98.65}{101.325}$ atm = 0.9736 atm

But
$$M_r = \frac{P_1 M_1 + P_2 M_2 + P_3 M_3}{P_1 + P_2 + P_3}$$

Where
$$P_1 = 21\%$$
 $M_1 = 32g/mol$ $P_2 = 1\%$

$$M_2 = 40g/mol P_3 = 78\% M_3 = 28g/mol$$

$$M_r = \frac{(21\times32)+(1\times40)+(78\times28)}{21+1+78} = 28.96 \text{ g/mol}$$

The substituting
$$\rho = \frac{0.9736 \times 28.96}{0.082 \times 293} = 1.17 g/dm^3$$

Hence the density is 1.17g/dm³

Ouestion 189

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

Solution

Boyle's law: $P \propto \frac{1}{V}$ at constant T and n

Justification:

A decrease in V leads to an **increased gas molecules concentration** and thus an **increase in the number of collisions per second** with the walls of the container. More frequent collisions leads to greater pressure exerted by the gases in the container.

Charles's law: V ∝ T at constant P and n

Justification:

Initially an increase in T leads to an increase in kinetic energy and thus speed of gas molecules and frequency of collision is increased too. As result pressure (P) appears to increase at initial stages. The only way to prevent P from increasing under such conditions is to increase V, which will decrease collision frequency despite the increased speed.

Avogadro's law: $V \propto n$ at constant P and T

Justification:

Initially, an increase in n leads to an increased gas molecules concentration and thus an increase in frequency of collision with the walls and thus pressure. The only way to prevent P from increasing under such conditions is to increase volume proportionally, which will keep concentration constant.

Question 190

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

Solution

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

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

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

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

It will take 0.06498seconds

Question 191

- (a) Define the following:
 - (i) Molar volume of a gas at s.t.p.
 - (ii) Dalton's law of partial pressure.

Solution

- (i) Is the volume of one mole of a gas at temperature of 0°C (273K) and pressure of 1atm (760 mmHg).
- (ii) Is the law which express the total pressure exerted by mixture of two or more gases in terms of their partial pressures.

Question 192

From the fundamental gas equation derive ideal gas equation.

Solution

From the fundamental gas equation; $PV = \frac{N}{3}mc^2$

But $mc^2 = 2K$. E

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

But from one of assumptions of kinetic theory of gases;

$$K.E \propto T$$
 or $K.E = kT$

Then
$$PV = \frac{2}{3}NkT$$

But from
$$n = \frac{N}{N_A}$$
; $N = nN_A$

Then
$$PV = \frac{2}{3}nN_AkT$$

But $\frac{2N_Ak}{3}$ gives another constant, R (universal molar gas constant)

Hence PV = nRT (Ideal gas equation)

Question 193

Two gas burettes, one containing 10cm^3 of sulphur dioxide (SO₂) and the other containing 30cm^3 of hydrogen sulphide (H₂S) both at 1 atmosphere and at 0°C are initially separated by a stop cork. The stop cork is then opened and the two gases are allowed to mix according to the reaction:

$$SO_2(g) + 2H_2S(g) \rightarrow 3S(s) + 2H_2O(l)$$

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

Solution

Equation for the reaction:

$$SO_2(g) + 2H_2S \rightarrow 3S(s) + 2H_2O(l)$$

From which mole ratio of SO₂ to H₂S is 1:2

Since mole ratio = Volume ratio (Avogadro's law), volume of H₂S reacted twice the volume of SO₂

That is
$$V_{H_2S}$$
 reacted = $2V_{SO_2} = 2 \times 10$ cm³ = 20 cm³

But total volume of H₂S was 30 cm³

Then
$$V_{H_2S}$$
 unreacted = $(30 - 20) \text{ cm}^3 = 10 \text{cm}^3$

So after the reaction, 10 cm³ of H₂S will determine the final pressure in the vessel.

But at s.t.p:
$$n = \frac{V \ln cm^3}{22400 \text{ cm}^3/\text{mol}}$$

Then
$$n_{H_2S}$$
 unreacted = $\frac{10 \text{ cm}^3}{22400 \text{ cm}^3/\text{mol}} = \frac{1}{2240} \text{mol}$

Also from
$$P = \frac{nRT}{V}$$
;

If V represents final volume (of container),

$$V_f = (10 + 30) \text{cm}^3 = 40 \text{ cm}^3 = 0.04 \text{ dm}^3$$

Then final pressure,
$$P_f = \frac{n_{H_2S} \text{ unreacted} \times RT}{V_f} = \frac{1 \times 0.082 \times 273}{2240 \times 0.04} \text{atm} = 0.25 \text{ atm}$$

Hence the final pressure after the reaction has ended is 0.25atm.

Question 194

State the following:

- (i) Boyle's law
- (ii) Grahm's law of diffusion

Solution

- (i) Volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature.
- (ii) The rate of diffusion of gases at given temperature and pressure varies inversely proportional to the square root of their densities.

Ouestion 195

State the postulates of kinetic theory of gases.

Solution

- 1. A gas consists of very small particles in a random motion of which there is a collision between gas molecules (particles) themselves and the collision between gas molecules and the walls of the container thus exerting a pressure.
- 2. Force of gravity has no effect on the motion of gas molecules.
- 3. Intermolecular forces of attraction are negligible in the motion of gas molecules.
- 4. Kinetic energy of gas molecules varies directly proportional to the absolute temperature.
- 5. The collision between gas molecules and walls of the container is completely elastic.
- 6. Volume of a gas molecules is negligible compared to the volume of the whole gas or the volume of the container.

When carbon dioxide gas is put in a sealed container at 701K and pressure of 10 atm and is heated to 1401K, some of the CO_2 decomposes to carbon monoxide and oxygen gas and the pressure rises to 22.5 atm. Calculate the mole percent of CO_2 that decomposes.

Solution

Using Gay-Lussac's law to calculate the expected pressure of CO₂ at 1401K.

That is
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$
 or $P_2 = \left(\frac{T_2}{T_1}\right) P_1$

Where
$$P_1 = 10$$
 atm, $T_1 = 701$ K, $T_2 = 1401$ K

Then
$$P_2 = \frac{1401 \times 10}{701}$$
 atm = 19.9857 atm

Using
$$i = \frac{Observed pressure}{Expected pressure} = \frac{22.5 \text{ atm}}{19.9857 \text{ atm}} = 1.1258$$

CO₂ decompose according to the following equation:

$$CO_2(g) \rightleftharpoons CO(g) + \frac{1}{2}O_2(g); N = 1.5$$

Then using
$$\alpha = \frac{i-1}{N-1} = \frac{1.1258-1}{1.5-1} = 0.2516$$
 or 25.16%

Hence the percent of CO_2 that decomposes was 25.16%.

Question 197

Compressibility factor, **Z**, is used to test ideality and non-ideality of real gases:

- (i) Derive an expression for **Z**
- (ii) At what value of Z a real gas shows ideal behaviour, positive and negative deviation from ideality?

Solution

(i) From its definition, compressibility factor (Z) is given by;

$$Z = \frac{Real\ volume}{Ideal\ volume}$$

If V represents real volume, the formula becomes:
$$Z = \frac{V}{Ideal \, volume}$$

But ideal volume can be calculated from ideal gas equation with measured (actual) P, T and n

That is
$$V = \frac{nRT}{P}$$
 (From $PV = nRT$)

Where V is the ideal volume.

Then the formula
$$Z = \frac{V}{ideal \ volume}$$
 becomes $Z = \frac{V}{\frac{nRT}{P}} = \frac{PV}{nRT}$

Thus the compressibility factor, $Z = \frac{PV}{nRT}$

Where:

P is the measured (real) pressure

V is the measured (real) volume

n is the measured number of moles

(ii) For ideal behaviour, Z = 1For the positive deviation, Z > 1

The atomic radius of sodium is 1.86×10^{-8} cm, and the molar volume of sodium is 23.68 cm³. If 68.52% of this volume is the actual volume occupied by sodium atoms, calculate the Avogadro's constant. (Volume of one sodium atom $\frac{4}{3}\pi r^3$).

Solution

Actual molar volume of sodium atoms = $\frac{68.52}{100} \times 23.68$ cm³ = 16.2255cm³/mol

Volume of one sodium atom = $\frac{4}{3}\pi r^3 = \frac{4}{3} \times 3.14 \times (1.86 \times 10^{-8} \text{cm})^3 = 2.6941 \times 10^{-23} \text{ cm}^3/\text{atom}$

Then actual molar volume = Volume of one atom × Avogadro's constant, NA

From which;

$$NA = \frac{Actual\ molar\ volume}{Volume\ of\ onee\ atom} = \frac{16.2255cm^3/mol}{2.6941\times10^{-23}\ cm^3/atom} = 6.02\times10^{23}\ atom/mol$$

Hence the Avogadro's constant is 6.02×10^{23} .

Question 199

- (i) State the meaning of an ideal gas.
- (ii) Derive an ideal gas equation.

Solution

- (i) Is the gas which obeys ideal gas equation (PV=nRT) in all conditions of temperature and pressure.
- (ii) Ideal gas equation can be derived by combining Boyle's law, Charles's law and Avogadro's law as shown below:

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

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

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

Combining the three laws: $V \propto \frac{nT}{P}$ or $V = \frac{nRT}{P}$

Where R is the proportionality constant; and the constant is known as universal molar gas constant Hence PV = nRT and the result is known as ideal gas equation.

Question 200

A compound of phosphorous (P) and Fluorine (F) was analysed as follows:

Heating 0.2324g of the compound in a $378cm^3$ container turn all of it to gas, which had a pressure of 97.3 mmHg at 77° C. Then the gas was mixed with calcium chloride solution which turned all of the F to 0.2631g of CaF_2 . Determine the molecular formula of the compound.

Solution

Molar mass of CaF_2 is 78 g/mol. Thus mass of F in 78g of $CaF_2 = 38$ g

And mass of F in 0.2631g of
$$CaF_2 = \frac{38 \times 0.2631g}{78} = 0.1282g$$

If P_xF_y represent the molecular formula of the compound (of phosphorous and fluorine).

Then 0.1282 g will also be the mass of F in 0.2324 g of P_xF_y

And mass of P in 0.2324 of $P_x F_y$ will be (0.2324 - 0.1282)g = 0.1042 g

Using
$$n = \frac{PV}{RT}$$
 (From $PV = nRT$)

Number of moles of $P_x F_y = \frac{97.3 \times 378 \times 10^{-3}}{760 \times 0.082 \times 350}$ moles = 1.6862×10^{-3} mol

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

Number of moles of P atoms in 1.6862×10^{-3} mol of $P_x F_y = \frac{0.1042g}{31g/mol} = 3.3613 \times 10^{-3}$ mol

Thus number of moles of P atoms in 1 mole of $P_x F_y = \frac{3.3613 \times 10^{-3}}{1.6862 \times 10^{-3}} \text{mol} = 2 \text{ mol of P atoms}$

Whence x = 2 (x is the number of moles of P atoms in 1 mol of $P_x F_y$).

Question 201

Comment on the following statements:

- (i) The molecular attraction between gas molecules is high at low temperature.
- (ii) In Van der Waals equation for real gases, the value of constant, 'a' is larger for NH_3 gas than for N_2 gas but that of 'b' is larger for N_2 gas.

Solution

- (i) At low temperature, kinetic energy is not enough to break intermolecular forces and therefore making the molecular attraction high.
- (ii) Ammonia having intermolecular hydrogen bonding which is stronger than the Van-der-Waals dispersion forces present in the nitrogen, has stronger intermolecular forces and hence larger value of 'a' for ammonia. But larger molecular mass of nitrogen implies that nitrogen molecule has larger molecular volume and hence larger value of 'b' for nitrogen.

Question 202

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

Solution

If P₁ and P₂ represents partial pressure in each of the given bulb.

Then by Dalton's law of partial pressure;

$$P_1 + P_2 = P_T = 760 \text{ mmHg} \text{ (At s.t.p, pressure} = 1 \text{ atm} = 760 \text{ mmHg)}$$

But since temperature is constant and the two bulbs have equal volume; $P_1 = P_2 = P$.

Thus P + P = 2P = 760 mmHg

From which P = 380 mmHg

Thence pressure exerted by the gas at each of the two Bulbs at 273K is 380 mmHg.

When one of the bulb is lowered into the melting ice and another into hot water, the partial pressure of the gas in the melting ice (273K) will remain 380 mmHg while that in hot water will rise in accordance to P-T law.

 $P_T = 380 + pressure of the gas in the hot bulb (P₂) = 877.6 mmHg$

From which $P_2 = 497.6 \text{ mmHg}$

Then by using P-T law;

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{or } T_2 = \left(\frac{P_2}{P_1}\right) T_1$$

Where $P_1 = 380 \text{ mmHg}$ $T_1 = 273 \text{K}$ $P_2 = 497.6 \text{ mmHg}$ $T_2 = ?$

Substituting
$$\frac{497.6}{380} \times 273 \text{K} = 357.5 \text{K}$$

Hence the temperature of hot water is 357.5K or 84.5°C.

Question 203

State at least one application of each of the following:

- (i) Grahm's law of diffusion
- (ii) Dalton's law of partial pressures
- (iii) Avogadro's hypothesis

Solution

- (i) Separation of gases having different densities by diffusion.
 - 1. In determination of densities and molar masses of unknown gases by comparing the rates of diffusion with known gases.
 - 2. In separation of isotopes of some of the elements.
- (ii) During the preparation of gases by downward displacement of water
- (iii)In determination of molecular formula of gases.
 - 1. In determination of atomicity of gases.
 - 2. In establishing the relationship between relative molecular mass and vapour density.

Question 204

Then Van der Waals equation for real gases is: $\left(P + \frac{n^2 a}{v^2}\right)(V - nb) = nRT$

Where all symbols carry their usual meaning:

- (i) Explain briefly the significance of the term $\frac{n^2a}{v^2}$ and nb in the equation.
- (ii) The compressibility factor for one mole of a real gas at 273K and 100 atm pressure is found to be 0.5. Assuming that the volume of gas molecules is negligible, calculate Van der Waals constant. Show your work clearly including manipulation of units.

Solution

(i) $\frac{n^2a}{v^2}$ is the pressure deviation of real pressure from ideal pressure and therefore it corrects the real pressure (P) to be ideal pressure (P + $\frac{n^2a}{v^2}$).

nb is the volume deviation of real gas from ideal gas and therefore it corrects the real volume (V) to be ideal volume (V - nb).

(ii) Compressibility factor, $z = \frac{PV}{nRT}$

From which;
$$V = \frac{ZnRT}{P} = \frac{0.5 \times 1 mol \times 0.082 atm dm^3 mol^{-1} K^{-1} \times 273 K}{100 atm} = 0.11193 \ dm^3$$

But the volume of gas molecules is negligible, b=0 and the given Van der Waals equation becomes:

$$\left(P + \frac{n^2 a}{v^2}\right) V = nRT$$

Then substituting;

$$\left(100 \text{atm} + \frac{1 \text{mol}^2 \times \text{a}}{0.11193^2 \text{dm}^6}\right) \times 0.11193 \text{dm}^3 = 1 \text{mol} \times 0.082 \text{atmdm}^3 \text{mol}^{-1} \text{K}^{-1} \times 273 \text{K}$$

From which $a = 1.252 \text{ dm}^6 \text{atmmol}^{-2}$

Hence Van der Waals constants are;

 $a = 1.252 \text{ dm}^6 \text{atmmol}^{-2} \text{ and } b = 0$