MORE ILLUSTRATIONS

Illustration - 17 *A mixture containing 1.12L of H_2 and 1.12L of D_2 (deuterium) at S.T.P., is taken inside a bulb connected to another bulb by a stop-cock with a small opening. The second bulb is fully evacuated. The stop-cock is opened for a certain time and then closed. The first bulb is found to contain 0.05 gm of H_2. Determine the percentage composition by weight of the gases in the second bulb.*

SOLUTION :

In the first bulb :

Initial moles of $H_2 = \dfrac{1.12}{22.4} = \dfrac{1}{20}$

Initial moles of $D_2 = \dfrac{1.12}{22.4} = \dfrac{1}{20}$

Now after opening of stop-cock, mass of H_2 left in the first bulb = 0.05

$\Rightarrow$ Moles of $H_2 = \dfrac{0.05}{2} = \dfrac{1}{40}$

$\Rightarrow$ Moles of H_2 effused into second bulb

$$= \frac{1}{20} - \frac{1}{40} = \frac{1}{40}$$

Let *n* be number of moles of D_2 effused.

From Graham's Law :

$$\frac{n}{1/40} = \sqrt{\frac{2}{4}}$$

$\Rightarrow$ $n = \dfrac{\sqrt{2}}{80}$ = moles of D_2 in second bulb.

In the second bulb:

The mass of H_2 gas $= \dfrac{1}{40} \times 2 = 0.05\,\text{gm}$

The mass of D_2 gas $= \dfrac{\sqrt{2}}{80} \times 4 = 0.07\,\text{gm}$

$\Rightarrow$ Total mass $= 0.05 + 0.07 = 0.12$ gm.

$\Rightarrow$ % of $H_2 = \dfrac{0.05}{0.12} \times 100 = 41.67\,\%$

and % of $D_2 = \dfrac{0.07}{0.12} \times 100 = 58.33\,\%$

Illustration - 18 *A mixture of ethane and ethene occupies 40 L at 1.0 atm and 400K. The mixture reacts completely with 130 gm of O_2 to produce CO_2 and H_2O, Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture.*

SOLUTION :

Let x = moles of C_2H_6 and y = moles of C_2H_4

$$C_2H_6 + 7/2\,O_2 \rightarrow 2CO_2 + 3H_2O$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

$\Rightarrow$ moles of O_2 used $= \left(\dfrac{7x}{2} + 3y\right)$

and moles of O_2 available $= \dfrac{130}{32}$

$\Rightarrow$ $\dfrac{7x}{2} + 3y = \dfrac{130}{32}$ $\Rightarrow$ $3.5x + 3y = 4.06$

Also, $x + y = \dfrac{PV}{RT} = \dfrac{1 \times 40}{0.0821 \times 400} = 1.218$

Solving for x and y, we get :

$\Rightarrow$ $x = 0.812$ and $y = 0.406$

$\Rightarrow$ $\chi_{C_2H_6} = \dfrac{0.812}{1.218} = 0.67$ and $\chi_{C_2H_4} = 0.33$

Illustration - 19 *1 mole of CCl_4 vapours at 77°C occupies a volume of 35.0 L. If van der Waal's constants are $a = 20.39\ L^2\ atm\ mol^{-2}$ and $b = 0.1383\ L\ mol^{-1}$, calculate compressibility factor Z under,*

(a) *low pressure region* **(b)** *high pressure region.*

SOLUTION :

(a) Under low pressure region, V_m is high $(V_m - b) \approx V_m$

$$\Rightarrow \quad \left(P + \frac{a}{V_m^2}\right) V_m = RT$$

$$\Rightarrow \quad PV_m + \frac{a}{V_m} = RT$$

$$Z = 1 - \frac{20.39}{0.0821 \times 350 \times 35} = 0.98$$

$$\left[\because \; Z = 1 - \frac{a}{RTV_m}\right]$$

(b) Under high pressure region P is high,

$$\left(P + \frac{a}{V_m^2}\right) \approx P$$

$$\therefore \quad P(V_m - b) = RT \quad \text{or} \quad PV_m - Pb = RT$$

$$\Rightarrow \quad P = \frac{RT}{V_m - b}$$

$$\Rightarrow \quad Z = \frac{PV_m}{RT} = \frac{V_m}{V_m - b} = \frac{1}{1 - \dfrac{b}{V_m}}$$

$$\Rightarrow \quad Z = \frac{1}{1 - \dfrac{0.138}{35}} = 1.004$$

Illustration - 20 *At 20°C, two balloons of equal volume and porosity are filled to a pressure of 2 atm, one with 14 kg N_2 and other with 1 kg of H_2. The N_2 balloon leaks to a pressure of 1/2 atm in 1 hr. How long will it take for H_2 balloon to reach a pressure of 1/2 atm ?*

SOLUTION :

Note : $\dfrac{r_1}{r_2} = \sqrt{\dfrac{M_2}{M_1}}$

$$\Rightarrow \quad \frac{n_1/t_1}{n_2/t_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\Rightarrow \quad \frac{(w_1/M_1)/t_1}{(w_2/M_2)/t_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\Rightarrow \quad \frac{w_1/t_1}{w_2/t_2} = \sqrt{\frac{M_1}{M_2}}$$

where w_1, w_2 are the weights of gas 1 and 2 effused in time t_1 and t_2 respectively.

At constant V and T for a gas $P \propto w$

Thus, for N_2: $P_1 = 2$ atm. $P_2 = \frac{1}{2}$ atm. at $t = 1$ hr

$w_1 = 14$ kg $\quad w_2 = ?$

$$\because \quad \frac{P_1}{P_2} = \frac{w_1}{w_2}$$

$$\Rightarrow \quad \frac{2}{1/2} = \frac{14}{w_2} \quad \Rightarrow \quad w_2 = \frac{14}{4}\ \text{kg}\ N_2$$

$$\text{Wt. of } N_2 \text{ diffused} = 14 - \frac{14}{4} = \frac{42}{4} = \frac{21}{2}\ \text{kg}$$

Similarly, for H_2: $P_1 = 2$ atm, $P_2 = \frac{1}{2}$ atm, at $t = t$ hr

$w_1 = 1$ kg $\quad w_2 = ?$

$$\Rightarrow \quad \frac{P_1}{P_2} = \frac{w_1}{w_2} \quad \Rightarrow \quad \frac{2}{1/2} = \frac{1}{w_2} \quad \Rightarrow \quad w_2 = \frac{1}{4}\ \text{kg}$$

$$\text{Wt. of } H_2 \text{ diffused} \quad \Rightarrow \quad 1 - \frac{1}{4} = \frac{3}{4}\ \text{kg}$$

Now $\dfrac{r_{N_2}}{r_{H_2}} = \sqrt{\left(\dfrac{M_{H_2}}{M_{N_2}}\right)}$ for diffusion of N_2 and H_2

or $\dfrac{w_{N_2}}{w_{H_2}} \times \dfrac{t_{H_2}}{t_{N_2}} = \sqrt{\dfrac{M_{N_2}}{M_{H_2}}}$

$$\Rightarrow \quad \frac{21/2}{3/4} \times \frac{t_{H_2}}{60} = \sqrt{\frac{28}{2}} \quad \Rightarrow \quad t_{H_2} = \frac{60}{\sqrt{14}}\ \text{min}$$

Alternative approach :

$$\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

$$\frac{\Delta P_1/t_1}{\Delta P_2/t_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

Here : $\Delta P_1 = \Delta P_2 = 2 - \frac{1}{2}$ atm and $P_1 = P_2 = 2$ atm

$$\Rightarrow \quad \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

$$\Rightarrow \quad t_{H_2} = t_{N_2}\sqrt{\frac{M_{H_2}}{M_{N_2}}} = \frac{60}{\sqrt{14}}\ \text{min}$$

Illustration - 21 *A gaseous mixture of helium and oxygen is found to have a density of 0.518 g dm^{-3} at 25 °C and 720 torr. What is the per cent by mass of helium in this mixture ?*

SOLUTION :

We know, $PM_o = dRT$

$$\Rightarrow \quad \frac{720}{760} \times M_o = 0.518 \times 0.0821 \times 298$$

$$\Rightarrow \quad M_o = 13.37 \text{ g/mol}$$

Let mole fraction of He in mixture be α.

$$\Rightarrow \quad \chi_{He} = \alpha, \qquad \chi_{O_2} = (1-\alpha)$$

Average molecular mass $= \alpha \times M_{He} + (1-\alpha)\ M_{O_2}$

$$\Rightarrow \quad 13.37 = \alpha \times 4 + (1-\alpha)\,32$$

$$\Rightarrow \quad \alpha = 0.666$$

$$\% \text{ by mass of He} = \frac{0.666 \times 4}{0.666 \times 4 + 0.334 \times 32} \times 100 = 19.95\%$$

THE LIQUID STATE Section - 5

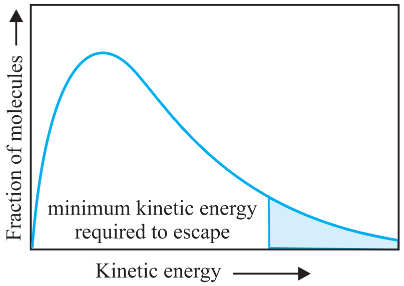
The liquid state is intermediate between gaseous and solid states. In the gaseous state the molecular interactions are very weak practically negligible and molecules are in random motion. Molecules continue to move unless they are reflected back by the walls of the vessel. Otherwise molecules would continue to move and the gas would expand to any volume. This is why gases do not have a definite volume.

In case of liquid, the molecular interactions are quite strong and a given quantity of liquid occupies a definite volume. Molecules of the liquid have so much freedom that they can flow readily and take up the shape of the container due to continuous breaking and making of weak van der Waal's bonds between the neighbouring molecules.

Molecules in solids completely lack in translation motion. The thermal motion of the molecules is so greatly reduced that they can only oscillate with respect to their fixed positions in the crystals. Each molecule in a solid has generally 6 to 12 nearest neighbours called coordination number. In the liquid state the coordination number of a molecule is not fixed but is only slightly less than in solid. The distance between the nearest neighbours in liquid is only slightly higher than that in solids. This is why there is very little expansion of solids on melting.

Vapour Pressure

The kinetic theory is the idea that there is distribution of kinetic energies and hence the molecular speeds, depending on the absolute temperature. Therefore, in any gas, liquid or solid at room temperature, a small fraction of molecules have relatively high kinetic energy. Some of these high energy molecules at the liquid surface become free resulting into its evaporation. With the departure of high energy molecules the average kinetic energy decreases leading to a fall in temperature of the liquid. This explains why evaporation causes cooling.



In a closed vessel, some free space above the liquid, the evaporated molecules cannot escape to the atmosphere. Initially the vapour pressure increases and then comes to a constant value. The volume of the liquid decreases initially and then becomes constant over a period of time. Increase in pressure means more number of collisions with the walls of the container.

Inside a closed vessel, the liquid and its vapours are in *dynamic equilibrium.* The pressure exerted by the vapours is then known as *equilibrium vapour pressure*. Since the vapour pressure is a kinetic phenomena, it is independent of the amount of a liquid .It only depends on the temperature. The temperature must, therefore, be specified with the vapour pressure of a liquid.