Assignment – 01

Chemistry 2nd Paper

1. Combination of gas laws

Let, absolute temperature, volume, pressure, number of molecules and mole number are T, V, P, N and n respectively.

Boyle's Law : At constant temperature, the volume of a definite mass of a given gas is inversely proportional to the pressure applied to that gas.

$$V \propto \frac{1}{P} \dots\dots (i) \text{ [when n and T constant]}$$

Charles' Law : At constant pressure, the volume of a definite mass of a given gas is proportional to absolute temperature.

$$V \propto T \dots\dots\dots (ii) \text{ [when n and P constant]}$$

Avogadro's Law : At constant temperature and pressure, the volume of a definite mass of a given gas is proportional to number of molecules. Again numbers of molecules are proportional to the mole number.

$$V \propto N \propto n$$
$$\therefore \quad V \propto n \dots\dots (iii) \qquad \text{[When P and T constant]}$$

From equation (i), (ii) and (iii)

$$V \propto \frac{1}{P}. \, T. \, n$$

$$\text{or, } V = k\frac{1}{P}.T.n \dots\dots (iv) \qquad \text{[K is proportional constant]}$$

For 1 mole gas PV = KT

$$\therefore \frac{PV}{T} = K \dots\dots\dots (v)$$

Hence, if temperature and pressure of a gas are variable then the ratio of product of pressure, volume and absolute temperature is always constant number.

Pressure P is changed into P_1, P_2, P_3 .... P_n and absolute temperature T is changed into T_1, T_2, T_3 .... T_n then the obtained volumes are changed from V to V_1, V_2, V_3 .... V_n.

From eq. (v)

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \dots\dots \frac{P_nV_n}{T_n} = K$$

$$\text{So, } \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Again from equation no (iv) we can write

$$PV = nKT$$

Moler gas constant 'R' is used instead of 'K' for all gases.

$$\text{So, } PV = nRT$$

2. **Description of the Conditions of real gases to behave ideally**

Ideal gas: The gas which follows 'gas Laws' such as Boyle's Law, Charles' Law and Avogadro's Law is known as ideal gas.
1. Intermolecular attraction force of ideal gas is negligible.
2. The volume of the molecules is negligible compared to the volume of the container.
3. Ideal gas follows gas lows at any temperature and pressure.
4. Ideal gas is an imaginary concept. There is no example of ideal gas.

Real gas: The gas which does not follow gas laws at any temperature and pressure is known as real gas.
1. Inter molecular attraction force of real gas is not negligible.
2. Volume of the gas molecule is considerable.
3. Real gas follows gas laws at high temperature and low pressure.
4. There is many examples of real gas such as H_2, N_2, CO_2 etc.

There are two causes of deviation of real gases from ideal nature. They are stated as below—
    i. Volume defect   ii. Pressure defect.

i. **Volume correction :** The volume of a gas is the free space in the container in which the molecules move about. Volume, V of an ideal gas is the same as the volume of the container. The dot molecules of ideal gas have zero-volume and the entire space in the container is available for their movement. However, Van der Waals assumed that molecules of a real gas are rigid spherical particles which possess a definite volume. The volume of a real gas is, therefore, ideal volume minus the volume occupied by gas molecules. If b is the effective volume of molecules per mole of the gas, the volume in the ideal gas equation is corrected as : $(V - b)$
For n moles of the gas, the corrected volume is : $(V - nb)$
'b' is termed the excluded volume which is a constant and characteristic for each gas.

ii. **Pressure correction:** According to the postulates of kinetic theory of gases, there exist no intermolecular forces in ideal gases, and as a result, all molecules exert same pressure, which is not true. Gases can be liquefied when the pressure is applied. It is clear from this observation that there exist intermolecular forces in real gas molecules. A molecule about to strike the wall of the vessel is attracted by molecules on one side only. Hence, it experiences an inward pull. Therefore, actual pressure of the gas, P, will be less than the ideal pressure:

∴ The actual pressure of real gas = ideal pressure + intermolecular force of attraction = $\left(P + \dfrac{n^2a}{V^2}\right)$

Van der Waals carried out several experiments and proved that the value of intermolecular force of attraction in real gases corresponds to $\left(\dfrac{n^2a}{V^2}\right)$

Hence, the equation of state for real gases becomes $- \left(P + \dfrac{n^2a}{V^2}\right)(V - nb) = nRT$

For 1 mole of gas, Van der Waals equation becomes $- \left(P + \dfrac{n^2a}{V^2}\right)(V - b) = RT$.

Real gases behave like ideal gas (i) at high temperature (ii) at low pressure.

(i) At high temperature : At high temperature the kinetic energy of gases is increased and the velocity of gas molecules is also increased. That time the intermolecular force among the gaseous molecules becomes negligible. So at high temperature $\dfrac{n^2a}{V^2}$ is negligible and 'P' can be written instead of $P + \dfrac{n^2a}{V^2}$.

Again at high temperature the volume of gas is increased (according Charls' Law). That time the volume

of each molecule of gas becomes negligible compared to volume of gas container. Then we can write the volume of gas 'V' instead of V−nb. So at high temperature the vander waals equation becomes PV = nRT, hence real gas behaves like ideal gas.

(ii) At low pressure : At low pressure the volume of gas is increased (according to the Boyle's low). Also the distance among the gaseous molecules is also increased. In this case, intermolecular force among the gaseous molecules is also decreased. So, at low pressure the value of $\frac{n^2a}{V^2}$ is negligible. Again at low pressure, the volume of gas is increased. That time the gaseous molecules exist as an individual molecule and their volume become negligible compared to the volume of gas container. Therefore at low pressure P $+ \frac{n^2a}{V^2} \approx P$ and V−nb $\approx$ V.

So at low pressure/high temperature—

$\left(P + \frac{n^2a}{V^2}\right)$ (V − nb) = nRT, it means vander waals equation becomes PV = nRt. That means real gas behaves like ideal gas.

3. Determination of the relation among pressure of gas mixture, partial pressure and mole fraction

Partial pressure : The pressure which is exerted by a component of a gaseous mixture if it would have occupied the whole volume of the gas mixture alone is called partial pressure.

Dalton's Law of partial pressure : At constant temperature, the pressure of non-reacting gaseous mixture would be the sum of the partial pressure of the constituent gases.
Let, P be the total pressure of a gaseous mixture containing 'n' component gases and $f_1, f_2, f_3 \ldots\ldots f_n$ be the partial pressure of the 'n' components respectively. Then from this law,

$\quad$ P = $f_1 + f_2 + f_3 \ldots\ldots\ldots + f_n$

Mole fraction : The ratio of mole number of any constituent of mixture and total mole number of the mixture is called mole fraction.

Mole fraction = $\dfrac{\text{Mole number of constituent of mixute}}{\text{Total mole number of mixture}}$

From ideal gas equation—
$$PV = nRT$$

$\therefore$ P = $\dfrac{n}{v}$ RT .... (i)

(i) no. equation is applicable in case of the gaseous mixture, if the components of the mixture would be individually ideal gas.
Let, the partial pressures of the component gases are P_1, P_2, P_3 and their mole number are n_1, n_2, n_3 respectively.
From equation (i)—

For, $\quad$ 1st gas, $P_1 = n_1 \dfrac{RT}{V}$ .... (ii)

$\qquad$ 2nd gas, $P_2 = n_2 \dfrac{RT}{V}$ .... (iii)

$\qquad$ 3rd gas, $P_3 = n_3 \dfrac{RT}{V}$ .... (iv)

eq. (ii) ÷ (i) —

$$\frac{P_1}{P} = \frac{\frac{n_1}{v} RT}{\frac{n}{v} RT}$$

or, $\frac{P_1}{P} = \frac{n_1}{n} = X_1$

∴ $P_1 = X_1.P$

Similarly, $P_2 = X_2.P$

$P_3 = X_3.P$ $\left[\text{Here, X = mole fraction Mole fraction} = \frac{\text{mole no. of a component}}{\text{mole no. of the mixture}} \right]$

So, $P = X.P$

Hence, Partial pressure = mole fraction X total pressure of the mixture.

21.0g nitrogen and 10.0g helium gas are mixed together. Calculate the mole fraction of each other of the gases.

Solution: Mole number of Nitrogen $= \frac{21.0}{28.0}$

$= 0.75$ mol

Mole number of Helium $= \frac{10.0}{4.0}$

$= 2.5$ mol

Mole fraction of Nitrogen gas $= \frac{0.75}{0.75 + 2.5}$

$= 0.23$

Mole fraction of Helium $= 1 - 0.23$

$= 0.77$

In 99.99 KPa and 13.33 KPa pressure H_2 and O_2 gas are taken in 1.50 m³ and 2.0 m³ volume of two containers respectively. If both containers are connected with one-another then what would be the total pressure of the mixture.

Solution: We know that,

Partial pressure of H_2, $f_1 = \frac{P_1 V_1}{V_1 + V_2}$

$= \frac{99.99 \times 1.50}{3.50}$

$= 42.85$ KPa

Partial pressure of O_2, $f_2 = \frac{P_2 V_2}{V_1 + V_2}$

$= \frac{13.33 \times 2}{3.50}$

$= 7.62$ KPa

Here, For H_2,

Pressure, $P_1 = 99.99$ KPa

Volume, $V_1 = 1.50$ m³

For O_2,

Pressure, $P_2 = 13.33$ KPa

Volume, $V_2 = 2.0$ m³

Volume of the mixture, $V = (1.50 + 2.0) = 3.50$ m³

Pressure of the mixture, $P = ?$

Total Pressure, $P = f_1 + f_2$

$= (42.85 + 7.62)$

$= 50.47$ KPa

Answer: 50.47 K.Pa

4. Mathematical Explanation of diffusion rate of two component gases in the gas mixture

Diffusion : Spontaneous dispersion of any substance through any medium is called diffusion. The cause of diffusion of due to the random movement of fine particles or gaseous molecules in available space.
At constant temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their densities.
If 'r' is the rate of diffusion and 'd' is the density of gas, then—

$$r \propto \frac{1}{\sqrt{d}}$$

$$\therefore r = k \frac{1}{\sqrt{d}} \text{ .... (i) [Here, K is constant]}$$

If at the same temperature and pressure the densities of two gases are d_1, d_2 and rates of diffusion are r_1, r_2 respectively, then from equation .... (i)

$$r_1 = K \frac{1}{\sqrt{d_1}} \text{ .... (ii) } r_2 = K \frac{1}{\sqrt{d_2}} \text{ .... (iii)}$$

eq. (ii) ÷ (iii)

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \text{ .... (iv)}$$

If molecular mass of gas is 'M' and molar volume is 'V' then $d_1 = \frac{M_1}{V_1}$ and $d_2 = \frac{M_2}{V_2}$

From eq. (iv)

$$\frac{r_1}{r_2} = \frac{\sqrt{\frac{M_2}{V_2}}}{\sqrt{\frac{M_1}{V_1}}}$$

At the same temperature and pressure, molar volume of all gases is equal. So, $V_1 = V_2$.

$$\therefore \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \text{ .... (v)}$$

Hence, at constant temperature and pressure the rates of diffusion of different gases are inversely proportional to the square roots of their molecular masses, which is the another statement of Graham's Law of diffusion. By using eq. (v) molecular mass of unknown gas can be calculated.

At constant temperature and pressure the rate of diffusion of O_2 gas is 30 m³/s. At the same condition what is the rate of diffusion of CO_2?

Solution: We know that,

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

or, $\dfrac{r_1^2}{r_2^2} = \dfrac{M_2}{M_1}$

or, $r_2^2 = \dfrac{M_1}{M_2} . r_1^2$

or, $r_2 = \sqrt{\dfrac{M_1 \times r_1^2}{M_2}}$

Given,
For O_2 gas,
Molecular mass, $M_1 = 32$
Rate of diffusion, $r_1 = 30$ m³/Sec.
For CO_2 gas,
Molecular mass, $M_2 = 44$
Rate of diffusion, $r_2 = ?$

or, $r_2 = \sqrt{\dfrac{32 \times (30)^2}{44}}$

∴ $r_2 = 25.58 \text{ m}^3/\text{s}$

Answer: $r_2 = 25.58 \text{ m}^3/\text{s}$