BEHAVIOUR OF GASES

6.0 INTRODUCTION

Gaseous state is that state of matter where repulsive forces are dominating that attractive forces. For study of gases we require gas parameters like p, v, n and temperature. Gases having no interaction between gas molecules are known as ideal gases. They follow kinetic gas assumptions, kinetic gas equation, gas laws and ideal gas equation but certain gases which do not follow above conditions are known as real gases.

6.1 SOME IMPORTANT DEFINITIONS :

(a) **Diffusion :**

• The tendency of inter mixing of non-reacting gases spontaneously without external pressure.

Or

• The property of the spontaneous flow of gaseous molecules from high concentration to low concentration without external pressure. In diffusion, P_{ext} = constant

(b) **Effuison :**

• The property of the flow of gaseous molecules form high concentration to low concentration form a pin hole with external pressure.

• It is diffusion through pin hole which arises due to pressure difference. In effusion, $P_{ext} = variable$

(c) Rate of diffusion (r) :

At constant temperature and pressure, the distance travelled by diffused gas or volume of diffused gas or moles of diffused gas per unit time is called as rate of diffusion.

$$\mathbf{r} = \frac{\mathbf{l}_{\text{diffused gas}}}{\mathbf{t}_{(\text{taken})}} = \frac{\mathbf{V}_{\text{diffused gas}}}{\mathbf{t}_{(\text{taken})}} = \frac{\mathbf{n}_{\text{diffused gas}}}{\mathbf{t}_{(\text{taken})}}$$

Grahm's law of diffusion (Applicable for non-reacting gases) :-

• At constant temperature and pressure, the rate of diffusion is inversely proportional to the square root the density.

$$\mathbf{r} \propto \frac{1}{\sqrt{\mathbf{d}}}$$
 (at constant T and P)
 $\mathbf{r} \propto \frac{1}{\sqrt{\mathbf{VD}}}$
 $\mathbf{r} \propto \frac{1}{\sqrt{\mathbf{M}_{W}}}$
 $\frac{\mathbf{r}_{1}}{\mathbf{r}_{2}} = \frac{\mathbf{v}_{1}}{\mathbf{t}_{1}} \times \frac{\mathbf{t}_{2}}{\mathbf{v}_{2}} = \sqrt{\frac{\mathbf{d}_{2}}{\mathbf{d}_{1}}} = \sqrt{\frac{\mathbf{M}_{2}}{\mathbf{M}_{1}}}$

• At constant temperature rate of diffusion is proportional to $\frac{P}{\sqrt{d}}$.

| Power by: VISIONet Info Solution Pyt. Ltd | |
|---|--------------------------|
| Website : www.edubull.com | Mob no. : +91-9350679141 |
| | |

$$\frac{\mathbf{r}_{1}}{\mathbf{r}_{2}} = \frac{\mathbf{v}_{1}}{\mathbf{t}_{1}} \times \frac{\mathbf{t}_{2}}{\mathbf{v}_{2}} = \sqrt{\frac{\mathbf{d}_{2}}{\mathbf{d}_{1}}} = \frac{\mathbf{P}_{1}}{\mathbf{P}_{2}} \sqrt{\frac{\mathbf{M}_{2}}{\mathbf{M}_{1}}}$$

7.2 **REAL GASES :**

(i) Those gases which do not follow kinetic gas assumptions, kinetic gas equation, gas law's and ideal gas equation are known as real gases.

"At very low pressure and high temperature real gases behave as ideal gas."

(ii) Deviation of real gases from ideal gas behavior is mathematically denoted by "Z" named as compressibility factor.

$$Z = \frac{V_{real}}{V_{ideal}} \frac{V_{obs}P}{nRT} = \frac{P(V_m)_{obs}}{RT}$$

Case I If Z = 1; ideal gas; it signifies there is no interaction between gas molecules

$$\frac{P(V_m)_{obs}}{RT} = 1 \implies P(V_m)_{obs} = RT$$

Case II If Z > 1; positive deviation from ideal gas behavior ; signifies repulsive forces are greater than attractive forces so such gases can't be liquefied easily.

$$\frac{P(V_m)_{obs}}{RT} > 1 \Longrightarrow P(V_m)_{obs} > RT$$

Example H₂, He

Case III If Z < 1; Negative deviation from ideal gases behavior : it signifies attractive forces are higher than repulsive forces so gas can be liquefied easily.

$$\frac{P(V_m)_{obs}}{RT} < 1 \Longrightarrow P(V_m)_{obs} < RT$$

The gas show the negative deviation generally at low pressure from ideal gas behavior. Example SO₂, HCl, NH₃.

Figure

7.3 **REAL GAS EQUATION OR VAN DER WAAL GAS EQUATION :**

PV = nRT.....(1) ideal gas equation

Two major corrections are required for real gases

The intermolecular force of attraction between molecules is not negligible. (i)

$$F_{att} \neq 0$$
 so $P_{act.} = \left(P_{real} + \frac{n^2 a}{v^2}\right)$

(ii) The volume of a molecule is not negligible in comparison of total volume of gas. V_1

$$\neq 0$$
 so $V_{act} = (V - nb)$

B = covolume = exluded volume =
$$4 \times \frac{4\pi r^3}{3}$$

From equation (i)

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

- At high temperature and low pressure, it acts as ideal gas equation.
- a, b are van der Waal's gas constant depends on nature of gas

(A) van der Waal's gas constant (a) :-

| Power by: VISIONet Info Solution Pvt. Ltd | |
|---|--------------------------|
| Website : www.edubull.com | Mob no. : +91-9350679141 |

Where is a van der Waal gas constant which indicates the inter molecular force of attraction.

$$\begin{aligned} \text{Pressure} &= \frac{an^2}{V^2} \\ \text{Unit of } a &= \text{atm lit}^2/\text{mol}^2 \\ \text{P}_i &= \text{P} + \frac{an^2}{V^2} \\ \text{P}_i &> \text{P}_R \\ a^{\uparrow}, F_{\text{att}}^{\uparrow}, \text{ lique faction}^{\uparrow}. \\ \text{Order of } a \text{ is } 10^{-1} \text{ to } 10^{-2} \text{ L}^2 \text{ atm } / \text{ mol}^2 \end{aligned}$$

van der Waal gas constant (b) **(B)**

It tells about molecular volume of gas molecules.

Unit of $b = \frac{\text{lit.}}{\text{mol.}}$ B = correction volumeB = incompressible volume $V_i > V_R$

- If $b\uparrow$, effective size of molecule \uparrow In compressible volume¹ Order of b is 10^{-2} to 10^{-4} L / mol

Effect of pressure on van der Waal gas equation

Figure

Case I At very-very low pressure

$$(Z = 1)$$

 $\left(P\frac{n^2a}{V^2}\right)(V - nb) = nRT$
 $PV = nRT$
 $\frac{PV}{nRT} = 1$
 $Z = 1$

Case II At low pressure / moderate pressure

$$(Z < 1)$$

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

$$PV = \frac{n^{2}a}{V} = nRT$$

$$\frac{PV}{nRT} + \frac{na}{VRT} = 1$$

$$Z = 1 - \frac{na}{VRT}$$

Power by: VISIONet Info Solution Pvt. Ltd Website : www.edubull.com

Case III At very high pressure

$$(Z > 1)$$

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

$$PV - nPb = nRT$$

$$\frac{PV}{nRT} + \frac{Pb}{RT} = 1$$

$$Z = 1 + \frac{Pb}{RT}$$

GOLDEN KEY POINTS

- Critical temperature (T_C) : The temperature below which gas can be liquefied by application of pressure alone ; is called critical temperature $T_C = \frac{8a}{27bR}$
- **Critical pressure** (**P**_C) : The pressure required to liquefy a gas at critical temperature ; is called critical pressure $P_C = \frac{a}{27b^2}$
- Critical volume (V_C) : Volume occupied by 1 mol gas at critical temperature & pressure ; is called critical volume $V_C = 3b$
- Van Der waal gas constants : 📈

| Gas | $A(atm \times L^2/mol^2)$ | B(L/mol) |
|------------------|---------------------------|----------|
| H ₂ | 0.244 | 0.0266 |
| N_2 | 1.39 | 0.0391 |
| CH_4 | 2.25 | 0.0428 |
| CO_2 | 3.59 | 0.0427 |
| NH ₃ | 4.17 | 0.0371 |
| H ₂ O | 5.46 | 0.0305 |

• Higher value of "a" is more significant for liquefaction of a gas.

Illustrations

Ρ

Illustration 1. The rate of effusion of a gas is proportional to -

(1)
$$\frac{P}{\sqrt{d}}$$
 (2) $\frac{P}{d}$ (3) $\sqrt{\frac{P}{d}}$ (4) $\frac{N}{d}$
Solution Ans. (1)
Rate of effusion $\propto \frac{1}{\sqrt{d}} \propto P$ \therefore Rate of effusion $\propto \frac{P}{\sqrt{d}}$

Illustration 2. If 4g of oxygen diffuse through a very narrow hole, how much hydrogen would have diffused under identical conditions ?

$$\frac{\mathbf{r}_{O_2}}{\mathbf{r}_{H_2}} = \frac{\mathbf{V}_{O_2}}{\mathbf{V}_{H_2}} ; \frac{\mathbf{n}_{O_2}}{\mathbf{n}_{H_2}} = \sqrt{\frac{\mathbf{M}_{w_{O_2}}}{\mathbf{M}_{w_{O_2}}}} \implies \frac{4/32}{w/2} = \sqrt{\frac{2}{32}} \implies \frac{1}{4w} = \frac{1}{4} \implies w = 1$$

Illustration 3. Van der Waal's equation of state is obeyed by real gases. For n moles of a real gas, the expression will be -

$$(1) \left(\frac{P}{n} + \frac{na}{V^2}\right) \left(\frac{V}{n-b}\right) \qquad (2) \left(P + \frac{a}{V^2}\right) (V-b) = nRT$$
$$(3) \left(P + \frac{na}{V^2}\right) (nV-b) \qquad (4) \left(P + \frac{n^2a}{V^2}\right) (V-nb) = nRT$$

Solution Ans. (4)

Van der Waal's equation is $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

Illustration 4. Van der Waal's constant 'a' and 'b' are related with respectively -

(1) Attractive force and bond energy of molecules

- (2) Volume and repulsive force of molecules
- (3) Shape and repulsive forces of molecules
- (4) Attractive force and volume of the molecules

Solution Ans. (4)

'a' is related to attractive forces and 'b' to the volume of the molecules.

| BEGINNER'S BOX-1 | | | | | | | | | |
|------------------|---|---|--|--|--|--|--|--|--|
| 1. | The rate of diffusion of SO_2 and O_2 are in the ratio :- | | | | | | | | |
| | (1) 1 : $\sqrt{2}$ | (2) 1 : 32 | (3) 1 : 2 | (4) 1 : 4 | | | | | |
| 2. | In the van der Waal's (1) CH ₄ | equation which will h (2) He | ave highest value of 'a (3) NH ₃ | 2. (4) H ₂ | | | | | |
| 3. | The unit of the van de (1) atm $L^2 \text{ mol}^{-2}$ | er waal's constant 'a' i (2) atm L ⁻² mol ⁻² | s :- (3) atm L mol ⁻¹ | (4) atm L mol ^{-1} | | | | | |

ANSWER KEY



BEGINNER'S BOX-1