

PHYSICAL CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER



STUDY MATERIAL

Behaviour of Gases

ENGLISH MEDIUM

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BEHAVIOUR OF GASES

INTRODUCTION :

Gaseous state is that state of matter where repulsive forces are dominating than 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.

(A) 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, $P_{\text{ext}} = \text{constant}$.

(b) Effusion :

- The property of the flow of gaseous molecules from high concentration to low concentration from a **pin hole** with external pressure.

or

- It is diffusion through **pin hole** which arises due to pressure difference.

In effusion, $P_{\text{ext}} = \text{variable}$

(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.

$$r = \frac{d_{\text{diffused gas}}}{t} = \frac{V_{\text{diffused gas}}}{t} = \frac{n_{\text{diffused gas}}}{t}$$

Graham'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 of the density.

$$r \propto \frac{1}{\sqrt{d}} \quad (\text{at constant } T \text{ and } P)$$

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

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

$$\frac{r_1}{r_2} = \frac{v_1}{t_1} \times \frac{t_2}{v_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

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

$$\frac{r_1}{r_2} = \frac{v_1}{t_1} \times \frac{t_2}{v_2} = \frac{P_1}{P_2} \sqrt{\frac{d_2}{d_1}} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

(B) REAL GASES : Those gases which do not follow ideal gas equation ($PV = nRT$) at all temperature and pressure.

• For real gases two assumptions of the kinetic theory do not hold good. These are

- (i) There is no force of attraction between the molecules of a gas.
- (ii) Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

(a) REAL GAS EQUATION OR VAN DER WAAL GAS EQUATION

$$PV = nRT \quad \dots(1) \text{ ideal gas equation}$$

Two major corrections are required for real gases

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

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

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

$$V_1 \neq 0 \text{ so } V_{\text{act}} = (V - nb)$$

$$b = \text{co-volume} = \text{excluded volume} = 4 \times \frac{4\pi r^3}{3} \times N_A$$

From equation (i)

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

- a and b are van der Waal's gas constant which depends on nature of gas but do not depend on the temperature and pressure.

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

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

$$\text{Pressure} = \frac{an^2}{V^2}$$

$$\text{unit of } a = \text{atm L}^2 \text{ mol}^{-2}$$

$$P_i = P_R + \frac{an^2}{V^2}$$

$$P_i > P_R$$

- $a \uparrow \Rightarrow F_{\text{att}} \uparrow \Rightarrow \text{liquefaction} \uparrow$.
- Order of a is 10^{-1} to $10^{-2} \text{ atm L}^2 \text{ mol}^{-2}$

(B) van der Waal gas constant (b)

It tells about molecular volume of gas molecules.

$$\text{Unit of } b = \text{L mol}^{-1}$$

$$b = \text{incompressible volume}$$

$$V_i > V_R$$

- If $b \uparrow \Rightarrow \text{effective size of molecule} \uparrow$
 $\Rightarrow \text{Incompressible volume} \uparrow$
 $\Rightarrow \text{compressible volume} \downarrow$
- Order of b is 10^{-2} to $10^{-4} \text{ L mol}^{-1}$

(b) DEVIATION OF REAL GASES FROM IDEAL GAS BEHAVIOUR :

"At very low pressure and high temperature real gases behave as ideal gas." Deviation of real gases from ideal gas behaviour is mathematically denoted by "Z" named as **compressibility factor**.

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

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

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

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

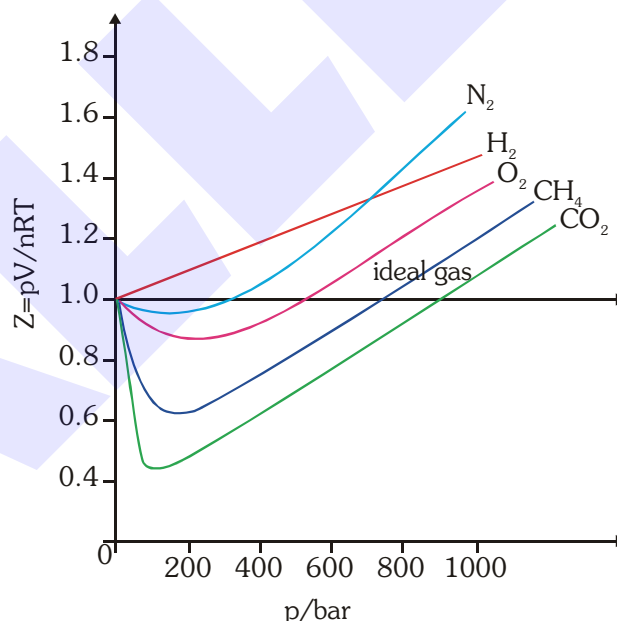
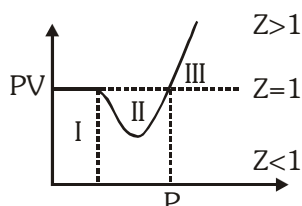
$$\frac{P(V_m)_{\text{obs}}}{RT} > 1 \Rightarrow P(V_m)_{\text{obs}} > RT$$

The gas shows the positive deviation generally at high pressure from ideal gas behaviour.

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

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

The gas show the negative deviation generally at low pressure from ideal gas behaviour.

**(c) Effect of pressure on van der Waal gas equation**

Case I At very-very low pressure

$$(Z = 1)$$

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

$$PV = nRT$$

$$\frac{PV}{nRT} = 1$$

$$\boxed{Z = 1}$$

Case II At low pressure/moderate pressure

$$(Z < 1)$$

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

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

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

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

Case III At very high pressure

$$(Z > 1)$$

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

$$PV - nPb = nRT$$

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

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

- At high temperature and low pressure, it acts as ideal gas equation.
- 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 L ² mol ⁻²)	b (L mol ⁻¹)
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.
- **Boyle's Temperature (T_b)** : Temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle's temperature.

$$T_b = \frac{a}{bR}$$

Illustrations

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) $\frac{\sqrt{P}}{d}$

Solution **Ans. (1)**

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{d}} \propto P \therefore \text{Rate of effusion} \propto \frac{P}{\sqrt{d}}$$

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

- (1) 16 g (2) 1 g (3) 1/4 g (4) 64 g

Solution **Ans. (2)**

$$\frac{r_{O_2}}{r_{H_2}} = \frac{V_{O_2}}{V_{H_2}} ; \frac{n_{O_2}}{n_{H_2}} = \sqrt{\frac{M_{wH_2}}{M_{wO_2}}} \Rightarrow \frac{4/32}{w/2} = \sqrt{\frac{2}{32}} \Rightarrow \frac{1}{4w} = \frac{1}{4} \Rightarrow w = 1$$

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

Solution **Ans. (4)**

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

Illustration 4

Van der Waal's constant 'a' and 'b' are related withrespectively –

- (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 rates 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 equation which will have highest value of 'a'.
 - (1) CH_4
 - (2) He
 - (3) NH_3
 - (4) H_2
3. The unit of the van der Waal's constant 'a' is :
 - (1) $\text{atm L}^2 \text{mol}^{-2}$
 - (2) $\text{atm L}^{-2} \text{mol}^{-2}$
 - (3) atm L mol^{-1}
 - (4) atm mol L^{-1}

ANSWER KEY
BEGINNER'S BOX-1

Que.	1	2	3
Ans.	1	3	1