CHAPTER - 05
STATES OF MATTER

- Matter - Anything which has mass and occupies space is called matter.

- ***Matter is mainly classified into three***

    1. Solid

    2. Liquid

    3. Gas

- This classification is mainly based on the intermolecular force.

- Intermolecular force is the force act between the constituent particle.

- There are mainly 2 types of intermolecular forces that are attractive and repulsive.

- Attractive intermolecular forces are known as van der Waal's forces.

Van der Waals forces

1.   Dispersion force of London force

Suppose we have two neutral symmetrical atoms 'A' and 'B' in the close vicinity of each other. It may so happen that momentarily electronic charge distribution in one of the atom say 'A' become unsymmetrical ie, the charge cloud is more on one side than the other. This result in the development of instantaneous dipole on the atom 'A' or a very short time. This instantaneous dipole cause to induce the dipole on B. Then the temporary dipoles on atom 'A' and 'B' attract each other.

2.   Dipole-Dipole force

This type of force act between the molecules possessing permanent dipole. (Eg : HCl). This interaction is stronger than London force but is weaker than ion-ion interaction. Dipole-dipole interaction energy between stationary polar molecule (as in solids) is proportional to $\dfrac{1}{r^3}$ and that between rotating polar molecule is proportional to $\dfrac{1}{r^6}$

3.   Dipole-Induced dipole force

This type of force operate between molecule having permanent dipole and the molecule lack of permanent dipole. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud. In this case also interaction energy is proportional to $\dfrac{1}{r^6}$.

4.   Hydrogen bond

This is special case of dipole-dipole interaction. This is found in the molecule in which highly polar N–H, O–H, H–F bonds are present

THE GASEOUS STATE

Properties of gas

1.   Highly compressible

2.   Extent pressure equally in all direction

3.   Much lower density than solid and liquid

4.   Volume and shape is not fixed

5.   If mix evenly and completely in all proportions.

In periodic table only eleven elements exist as gases under normal conditions.:-

H, N, O, F, Cl, He, Ne, Ar, Kr, Xe, Rn

The gas Laws

1.   Boyles law (P-V relationship)

At constant temperature, the pressure of a fixed amount of a gas varies inversely with its volume.
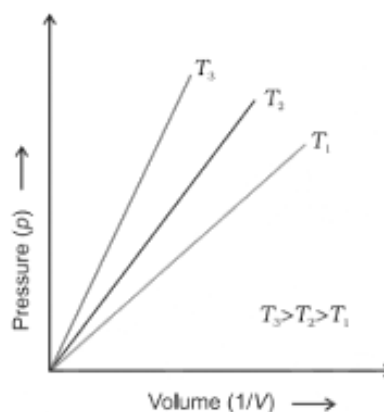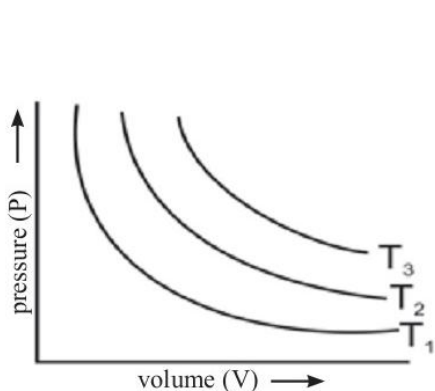
$$P \, \alpha \, \frac{1}{V}$$

$$P = K\frac{1}{V} \qquad K \rightarrow \text{proportionality } \cos \tan t$$
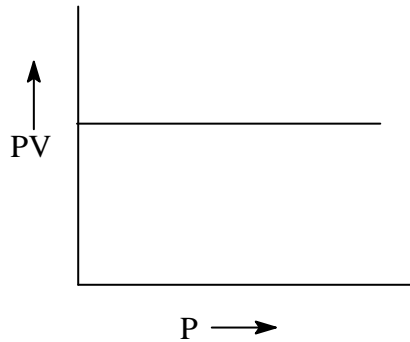
$$PV = K$$

It means at constant temperature the product of pressure and volume is constant for a fixed amount of gas.

If a fixed amount of gas at constant temperature T occupying volume V_1 at pressure P_1 undergoes expansion, so that volume become V_2 and pressure become P_2 then according to Boyle's law

$$P_1V_1 = P_2V_2$$

2.   Charles law (T–V relationship)

At constant pressure volume of a fixed amount of gas is directly proportional to the temperature.

$V \propto T$

$V = KT$

$K \rightarrow$ proportionality $\cos \tan t$

$\dfrac{V}{T} = K$

$\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$

Charles also found that for each degree rise in temperature, volume of a gas increases by $\dfrac{1}{273.15}$ of the original volume of the gas at 0°C. Thus if volume of the gas at 0°C and t°C are V_0 & V_t respectively then

$V_t = V_0 + \dfrac{1}{273.15} V_0$
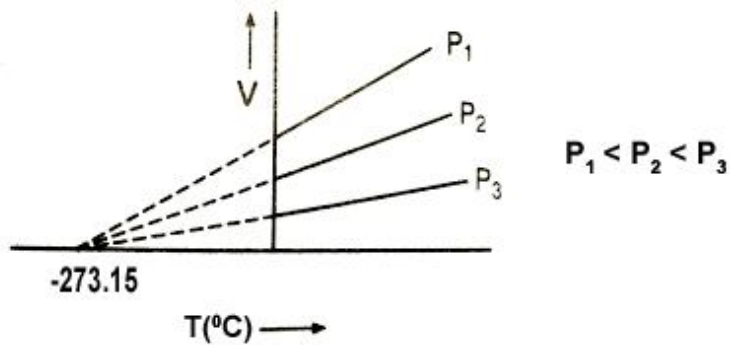
$V_t = V_0 \left(1 + \dfrac{t}{273.15} \right)$

$V_t = V_0 \left(\dfrac{273.15 + t}{273.15} \right)$

At this stage we define a new temperature scale called Kelvin temperature scale or absolute scale. Thus 0°C on the celsius scale is equal to 273.15 K at absolute scale. Thus we add 273.15 to the celsius temperature to obtain temperature at Kelvin scale.

If we write = $T_t = 273.15 + t$ and $T_0 = 273.15$ then modify the above equation.

$$V_t = V_0 \left(\frac{T_t}{T_0} \right)$$

$$\frac{V_t}{V_0} = \frac{T_t}{T_0}$$

Graph of V vs T is a straight line and on extenting to zero volume each line intercept the temperature axis at –273.15°C this temperature is called absolute zero. In fact all the gases get liquefied before this temperature is reached.

3. **Gay Lussac's Law (P–T relationship)**
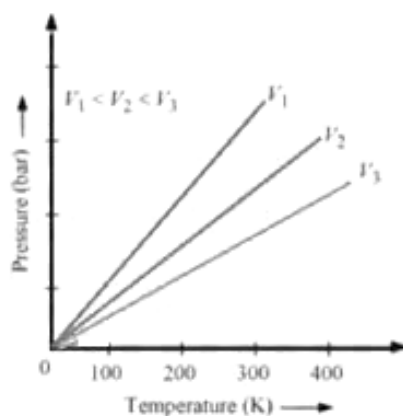
    At constant volume pressure of a fixed amount of gas varies directly with the temperature.

    $P \alpha\ T$

    $P = KT\ \ K \rightarrow$ proportionality constant

    $$\frac{P}{T} = K$$

    $$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

4.   Avogadro law (V - n relationship)

Equal volume of all gases under the same conditions of temperature and pressure contain equal number of molecule.

$V \alpha n$ $n \rightarrow$ number of moles of the gas

$V = Kn$

MOLAR VOLUME OF GAS

1.   When STP conditions taken are 0°C and 1 atm molar volume of a gas = 22.4 L

2.   When STP conditions are taken as 0°C and 1 bar molar volume of the gas = 22.7 L

3.   When SATP conditions are used 25°C and 1 bar molar volume = 24.8 L

Ideal gas equation

A gas that follows Boyles law, Charles law and Avogadro law strictly is called an ideal gas. Such a gas is hypothetical. This three laws combined together in a single equation which is known as ideal gas equation.

At constant T & n; $V \alpha \dfrac{1}{P} \left[\text{Boyles law}\right]$

At constant P & n; $V \alpha T$ [Charles law]

At constant P & T; $V \alpha n$ [Avogadro law]

$$V \alpha \frac{nT}{P}$$

$$V = R \frac{nT}{P}$$

where R is the proportionality constant called universal gas constant. $\boxed{PV = nRT}$

Unit of P	Unit of V	Value of R
atm	L (or) dm^3	0.0821 L atm K^{-1} mol^{-1}
atm	cm^3	82.1 cm^3 atm K^{-1} mol^{-1}
dynes cm^{-2}	cm^3	1.987 cal K^{-1} mol^{-1}
Nm^{-2} (or) Pa	m^3	8.314 JK^{-1} mol^{-1}
kPa	dm^3	8.314 kPa dm^3 K^{-1} mol^{-1}
bar	dm^3	0.083 bar dm^3 K^{-1} mol^{-1}

If, temperature, volume, pressure of a fixed amount of gas vary from T_1, V_1, P_1 to T_2, V_2, P_2 then we can write

$$\frac{P_1V_1}{T_1} = nR \quad \& \quad \frac{P_2V_2}{T_2} = nR$$

$$\therefore \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

DENSITY AND MOLAR MASS OF A GASEOUS SUBSTANCE

From the ideal gas equation PV = nRT

$$PV = \frac{W}{M}Rt \quad \left| n = \frac{W}{M} \right.$$

$$\frac{PM}{RT} = \frac{W}{V}$$

$$d = \frac{PM}{RT} \quad \left| d = \frac{W}{V} \right.$$

Dalton's law of partial pressure

The total pressure exerted by the mixture of non reactive gases is equal to the sum of the partial pressures of individual gases. In a mixture of gases the pressure exerted by the individual gases is called partial pressure. $P_{total} = P_1 + P_2 + P_3 + $ ....

Where P_{total} is the total pressure exerted by the mixture of gases and P_1, P_2, P_3 .... are the partial pressures of gases.

Partial pressure in terms of mole fraction

Suppose at the temperature T, three gases enclosed in the volume V, exert partial pressure P_1, P_2, P_3

respectively then, $P_1 = \dfrac{n_1RT}{V}$; $P_2 = \dfrac{n_2RT}{V}$; $P_3 = \dfrac{n_3RT}{V}$

n_1, n_2, n_3 are the number of moles of gases

$$P_{total} = P_1 + P_2 + P_3 = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} = \frac{RT}{V}\left(n_1 + n_2 + n_3\right)$$

On dividing P_1 by P_{total} we get $\dfrac{P_1}{P_{total}} = \dfrac{\dfrac{n_1RT}{V}}{\left(n_1 + n_2 + n_3\right)\dfrac{RT}{V}}$

$$\frac{P_1}{P_{total}} = \frac{n_1}{n_1 + n_2 + n_3} = x_1$$

$$\frac{P_1}{P_{total}} = x_1$$

$$P_1 = X_1 \ P_{total}$$
$$P_2 = X_2 \ P_{total}$$
$$P_3 = X_3 \ P_{total}$$

Partial pressure = mole fraction × total pressure

KINETIC MOLECULAR THEORY OF GASES

Postulates

1. Every gas is made up of large number of small particles called molecule all the molecules of a particular gas are identical in mass and size.

2. The molecules of a gas are separated from each other by large distance so that the actual volume of the molecule is negligible as compared to the total volume of the gas.

3. The force of attraction or repulsion between them are negligible.

4. The force of gravitation on the molecule is also supposed to be negligible.

5. The molecules are moving continuously in different direction with different velocity.

6. The pressure exerted on the walls of the containing vessel is due to the bombardment of the molecules on the walls.

7. Molecules are supposed to be perfectly elastic hard spheres so that no energy is wasted on collision.

8. Average KE is directly proportional to absolute temperature.

Kinetic gas equation

Based on the above postulates a mathematical equation has been derived. $PV = \dfrac{1}{3} mnc^2$

$P \rightarrow Pr\,essure$
$V \rightarrow Volume$
$M \rightarrow Mass \ of \ each \ molecule$
$n \rightarrow Total \ number \ of \ molecule$
$c \rightarrow Total \ mean \ square \ speed \ (RMS)$

Molecular speed

1. Average speed = $\sqrt{\dfrac{8RT}{\pi M}}$

2.   RMS = $\sqrt{\dfrac{3RT}{M}}$

3.   Most probable speed = $\sqrt{\dfrac{2RT}{M}}$

     $T \rightarrow$ Temperature

     $M \rightarrow$ Molecular mass

AVERAGE KINETIC ENERGY

From kinetic gas equation $PV = \dfrac{1}{3}mnc^2$ for 1 mole of gas $m \times n = M$, molar mass

$$\therefore PV = \frac{1}{3}Mc^2$$

$$PV = \frac{2}{3} \times \frac{1}{2}Mc^2$$

$$PV = \frac{2}{3}K.E. \qquad | K.E = \frac{1}{2}Mc^2$$

$$K.E. = \frac{3}{2}RT.............(1)$$

From ideal gas equation $PV = RT$

$$\therefore K.E. = \frac{3}{2}PV...........(2)$$

To calculate average K.E. per molecule

$$K.E. = \frac{3}{2}\frac{RT}{N_A}...........(3)$$

$$K.E. = \frac{3}{2}KT \qquad |\frac{R}{N_A} = K$$

$K \rightarrow$ Boltzmann $\cos \tan t = 1.38 \times 10^{-23} JK^{-1}$

MAXWELL-BOLTZMANN DISTRIBUTION CURVE

Fraction of the molecule possessing particular speed are plotted against their corresponding speed at particular temperature.
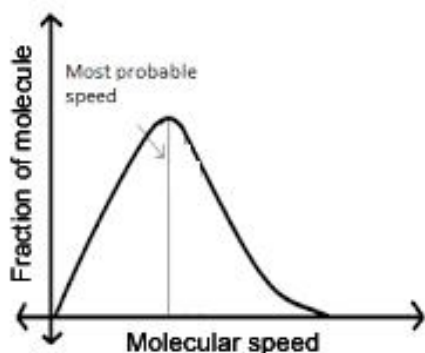
Observations

1.   Fraction of molecule having too low or too high speed are very small.

2.   The peak of the curve corresponds to the speed possessed by maximum fraction. This is called most probable speed.

Maxwell - Boltzmann curve at different temperature
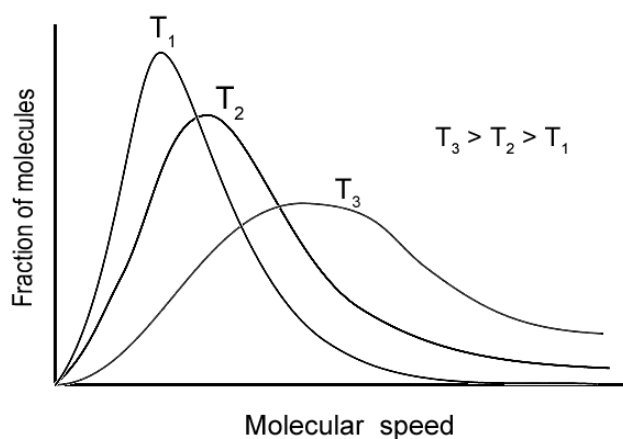

1.   Most probable speed increases on increase in temperature.

2.   Fraction of the molecule possessing most probable velocity decrease on increase in temperature.

3.   Fraction of the molecule having higher speed increase on increase in temperature.

4.   Fraction of the molecule having lower speed decreases on increasing temperature.

Ideal and Real gases

A gas which obey the ideal gas equation PV = nRT under all conditions of temperature and pressure is called ideal gas. The gases are found to obey gas laws fairly well if pressure is low or the temperature is high, such gases are real gases.

To study the deviation from ideal behaviour, let us study how real gases show deviation from Boyle's law. According to Boyles law pV = K at constant temperature. Hence the plot of PV vs P should be a straight line parallel to x-axis. However real gases do not show such a behaviour.
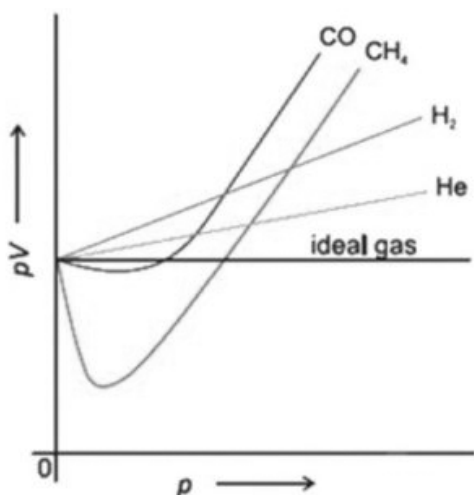
The extent to which a real gas deviates from ideal behaviour can be conveniently studied in terms of

'Z' called compressibility factor. $Z = \dfrac{PV}{nRT}$

1.   For ideal gas Z = 1

2.   For real gas Z $\neq$ 1

       a. Z > 1, gas show positive deviation

       b. Z < 1, gas show negative deviation

Vander Waals equation

To explain the behaviour of real gas van der Waals modified the ideal gas equation by applying corrections. That are volume correction and pressure correction.

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

a and b are van der Waals constants.

Significants

1. Greater the value of van der Waals constant 'a' larger are the intermolecular attraction.

2. Value of 'b' is a measure of effective size of the gas molecule. Its value is equal to four times the actual volume of the gas molecule. It is called excluded volume or co-volume.

    Units.

    'a' $\rightarrow$ atm L^2 mol^{-2} (or) bar dm^6 mol^{-2}

    'b' $\rightarrow$ L mol^{-1} (or) dm^3 mol^{-1}

Van der Waals equation at different conditions

1. At low pressure $\left(P + \dfrac{a}{V^2} \right) V = RT$

2. At high pressure $P(V - b) = RT$

CAUSE OF DEVIATION FROM IDEAL BEHAVIOUR

Two postulates of the kinetic theory of the gas not hold good in all cases.

1. Volume occupied by the gas molecule is negligible as compared to the total vol. of the gas.

2. The force of attraction or repulsion between the gas molecules are negligible.

    This assumptions true only if the pressure is low and temperature is high so that the distance between the molecule is large.

Liquefaction of gases and critical temperature

A gas can be liquefied by cooling or by application of pressure or the combined effect of both.

Critical temperature (TC) of a gas may be defined as that temperature above which it cannot be liquified however high pressure may be applied on the gas.

The pressure required to liquify the gas at the critical temperature is called critical pressure (P$_C$). Volume occupied by one mole of the gas at critical temperature and critical P is called critical volume (V$_c$). These three are called critical constant.

Critical constant in terms of van der Waals constant

$$P_C = \dfrac{a}{27b^2}$$

$$T_C = \dfrac{8a}{27Rb}$$

$$V_C = 3b$$

Boyle temperature (T$_B$)

The temperature at which real gases behave like an ideal gas called boyle temperature.

$$T_B = \dfrac{a}{Rb}$$

Relationship between critical constants

$$P_C V_C = \frac{3}{8} R T_C$$

Grahams law of diffusion/effusion

Spreading of the molecules of a gas throughout the available space is called diffusion. Gaseous molecules escaping through a small hole called effusion.

Under similar conditions of temperature and pressure, the values of diffusion/effusion of different gases are inversely proportional to the square root of their densities.

For two gases having densities d_1 and $_2$ and rate of diffusion r_1 and r_2

$$\therefore \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

$$\text{Rate of diffusion} = \frac{\text{Vol / Amount / no.of mole diffused}}{\text{Time taken}}$$

Molecular mass = 2 × density

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

If two gases taken at different pressure, then greater the pressure greater is the rate of diffusion.

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{d_2}{d_1}} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

If two gases diffuse at different temperature, $\dfrac{r_1}{r_2} = \sqrt{\dfrac{T_1 d_2}{T_2 d_1}} = \sqrt{\dfrac{T_1 M_2}{T_2 M_1}}$

LIQUID STATE

1. **Vapour pressure**

    Vapour pressure of a liquid at any temperature may be defined as the pressure exerted by the vapour present above the liquid in equilibrium with the liquid at that temperature.

    Vapour pressure and temperature are directly proportional.

2. **Boiling point**

    It is defined as the temperature at which the vapour pressure of the liquid become equal to the external pressure.

3.   Surface Tension

It is the force acting at right angles to the surface along one cm length of the surface.

$\text{Unit} \rightarrow \text{dynes per cm}$

$$(\text{OR})$$

$$\text{Nm}^{-1}$$

4.   Viscosity

It is the resistance to flow viscosity decreases on increasing the temperature.