STATE OF MATTER

❑ INTRODUCTION :

Matter is made up of atoms or molecules. The arrangement of these molecules determines the state of matter. There are three recognised state of matter : Solid, Liquid and Gas. Matter can change between states when the temperature or pressure is changed. State changes of matter are physical rather than chemical.

DIFFERENCE BETWEEN STATES OF MATTER :

	Gas	Liquid	Solid
i.	Assumes the shape and volume of its container.	Assumes the shape of the part of the container which it occupies	Retains a fixed volume and shape.
ii.	Particles can move past one another.	Particles can move/slide past one another.	Rigid-particles locked into place.
iii.	Compressible, lots of free space between particles	Not easily compressible, little space between particles.	Not easily compressible, little free space between particles.
iv.	Flows easily, particles can move past one another.	Flows easily, particles can move/slide past one another	Does not flow easily, rigid-particles cannot move/slide one past another
v.	Low density.	Intermediate density.	High density.
vi.	Very small intermolecular attraction but high kinetic energies.	Considerable intermolecular attraction, kinetic energy is less.	Intermolecular forces are high, vibrational motion only.

❑ GASEOUS STATE

1. Important properties of gases :

(i) **Mass** : Mass in gm = Moles Ч Molecular mass.

(ii) **Volume** : Volume of the gas is the volume of container in which they are filled in.

(iii) **Temperature** : Temperature of a gas is the measure of kinetic energy of gas.

$$\text{Kinetic energy} \propto \text{Temperature}$$

(iv) **Pressure** : Pressure of gas is defined as the force exerted by the gas on the walls of its container. It is often assumed that pressure is isotropic, i.e. it is the same in all the three directions.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}},$$

$$P = \frac{Mg}{A} = \frac{v \times d \times g}{A}$$

$$= \frac{A \times h \times d \times g}{A}$$

$$P = hdg$$

Where.... h = height of the mercury column supported by the barometer.

d = density of mercury.

g = acceleration due to gravity.

2. Units and determination of pressure of gas :

(a) In SI unit the unit of pressure is the pascal (N/m^2) instead, the unit bar, kPa or MPa is used.

$$1 \text{ bar} = 10^5 \text{ N/m}^2 = 100 \text{ kN/m}^2 = 100 \text{ kPa}$$

(b) Pressure are also stated in mm or cm of mercury.

$1 \text{ atm} = 760 \text{ mm Hg} = 1.01325 \text{ bar} = 1.01325 \text{ Ч } 10^5 \text{ Pa} = 101.325 \text{ KN/m}^2 = 1.0332 \text{ Kgf/cm}^2$

$1 \text{ Pa} = 1 \text{ Nm}^{-2} = 1 \text{ Kgm}^{-1} \text{ S}^{-1}$

$1\text{L} = 1\text{dm}^3 = 10^{-3} \text{ m}^3$ (SI unit)

$1\text{L atm} = 101.325 \text{ J}$

$$1 \frac{\text{KN}}{\text{m}^2} = 1 \text{ Ч } 10^3 \frac{\text{N}}{\text{m}^2} = \frac{1 \times 10^3 \times \text{kg}}{9.8 \times 10^4 \text{cm}^2} = \frac{1}{98} \text{ kgf/cm}^2$$

$$1\text{Torr} = \frac{101325}{760} \text{Pa} = 133.322 \text{ Pa}$$

(d) The pressure relative to the atmosphere is called gauge pressure. The pressure relative to the perfect vacuum is called absolute pressure.

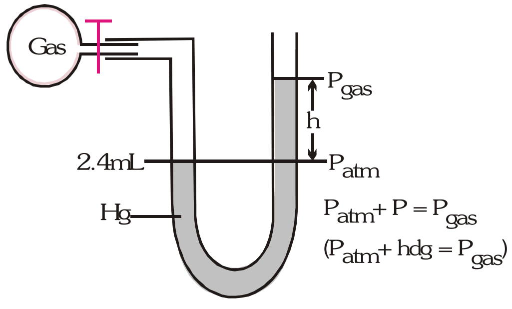
Absolute pressure = Gauge pressure + Atmosphere pressure

(e) When the pressure in a system is less than atmospheric pressure, the gauge pressure becomes negative, but is frequently designated and called vacuum.

For example, 16 cm vacuum will be -

$$\frac{76-16}{76} \text{ Ч } 1.013 = 0.80 \text{ bar}$$

(f) Pressure is measured using a manometer which is a simple device with a horizontal arm and a U-tube carrying mercury or any other suitable liquid.



An open arm manometer

Ex.4 Calculate the mass of mercury in a uniform column 760 mm high and 1.00 cm^2 in cross-sectional area. Is there any change in.

(a) mass and

(b) pressure of column of same height but with 2.00cm^2 cross sectional area is taken ?

(density of Hg = 13.6 g/cm^3)

Sol. 760 mm = 76 cm

$\therefore$ $V = 76 \text{ Ч } 1 = 76 \text{ cm}^3$

$\therefore$ $\text{Mass} = V \text{ Ч } d = 76 \text{ Ч } 13.6 = 1033.6 \text{ g}$

(a) If area of cross-section is 2cm^2 (doubled) then volume is also doubled hence,

$\therefore$ $\text{Mass} = 76 \text{ Ч } 2 \text{ Ч } 13.6 = 2067.2 \text{ g}$

(b) This mass would rest on twice the area and so exert the same pressure.

☐ GAS LAWS

The gas laws are a set of laws that describe the relationship between thermodynamic temperature (T), pressure (P) and volume (V) of gases.

1. Boyle's law

It states "at a constant temperature (T), the pressure (P) of a given mass (or moles, n) of any gas varies inversely with the volume (V)". Pressure (P) and volume (V) of gases.

i.e. $P \propto \frac{1}{V}$ (for given n and T)

or, $PV = K =$ constant

For two or more gases at constant temperature

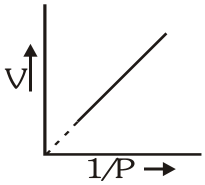
$$P_1V_1 = P_2V_2 = \ldots\ldots = K$$

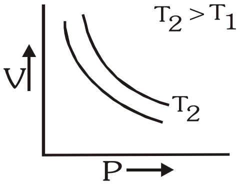
Also, density $d \propto \dfrac{1}{V}$

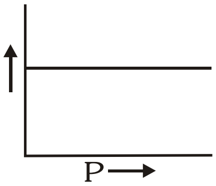
Hence $P \propto d$

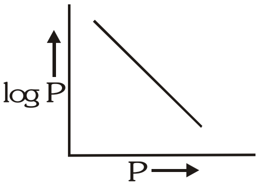
or $\dfrac{P_1}{d_1} = \dfrac{P_2}{d_2} = \ldots\ldots\ldots = K$

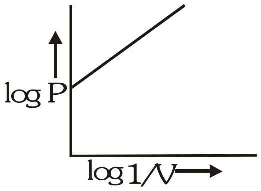
◆ **Graphical representation :**











These plots drawn at constant temperature for a gas are called Isotherms.

Ex.3 The diameters of a bubble at the surface of a lake is 4 mm and at the bottom of the lake is 1 mm. If atmospheric pressure is 1 atm and the temperature of the lake-water and the atmosphere are equal, what is the depth of the lake ? (The density of lake-water and Hg are 1 gm/ml and 13.6 gm/ml respectively. Also neglect the contribution of pressure due to surface tension).

Sol. The pressure on the bubble = 1 atm (when it is at the surface)

The pressure on the bubble = P atm (say) (when it is at the bottom)

The volume of the bubble = $\dfrac{1}{6}\pi\,(0.1)^3$

$$P \text{ Ч } \frac{1}{6}\pi \text{ Ч } (0.1)^3 = 1 \text{ Ч } \frac{1}{6}\pi\,(0.4)^3$$

or $P = 64$ atm. Thus the pressure due to water is 63 atm ($\therefore$ atmospheric pressure = 1 atm)

Now, consider the depth of lake is h cm

$\therefore$ $63 \text{ Ч } 76 \text{ Ч } 13.6 \text{ Ч } g = h \text{ Ч } 1 \text{ Ч } g$

or $h = 63 \text{ Ч } 76 \text{ Ч } 13.6$ cm = 65116.8 cm.

Ex.4 A 10 cm volume of air is trapped by a column of Hg, 8 cm long in capillary tube horizontally fixed as shown below at 1 atm pressure. Calculate the length of air column when the tube is fixed at same temperature.

(a) Vertically with open end up

(b) Vertically with open end down

(c) At 45°C from with open end up

(fig. 1)

Sol. (a) When the capillary tube is held as vertically open end up (fig.2),

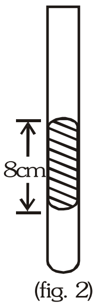
The pressure on the air column = atmospheric pressure + pressure of 8 cm Hg column

= 76 + 8 = 84 cm of Hg.

Let, at this condition the length of the air column = ℓ_2

and the length of air column when capillary is horizontally fixed = ℓ_1 = 10 cm and pressure on air column = 1atm.

Let the cross section of the capillary = a cm^2



(fig. 2)

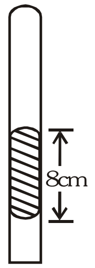
$\therefore$ $76\ \text{Ч}\ 10\ \text{Ч}\ a = 84\ \text{Ч}\ \ell_2\ \text{Ч}\ a$

or $\ell_2 = \dfrac{76 \times 10}{84} = 9.04$ cm

(b) When the capillary tube is held as vertically open end down (fig.3), the pressure on the air column

= atmospheric pressure – pressure of 8 cm Hg column

= 76 – 8 = 68 cm of Hg.



(fig. 3)

Let at this condition the length of air column = ℓ_3.

$\therefore$ $68\ \text{Ч}\ \ell_3\ \text{Ч}\ a = 76\ \text{Ч}\ 10\ \text{Ч}\ a$

or $\ell_3 = \dfrac{76 \times 10}{68} = 11.17$ cm

(c) When the capillary is held at 45° with open end up, the weight of Hg is partially borne by, the gas and partially by the Hg. The pressure on the gas due to Hg column

$= 8\ \text{Ч}\ \cos 45°$

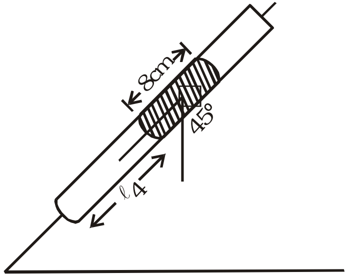
$= 8\ \text{Ч}\ \dfrac{1}{\sqrt{2}} = \dfrac{8}{\sqrt{2}} =$ cm of Hg

$\therefore$ total pressure on the gas = $\left(76 + \dfrac{8}{\sqrt{2}}\right)$ cm of Hg.

Let length of air column at this pressure = ℓ_4.

$\therefore$ $\ell_4\ \text{Ч}\ a\ \text{Ч}\ \left(76 + \dfrac{8}{\sqrt{2}}\right) = 10\ \text{Ч}\ a\ \text{Ч}\ 76$

$\therefore$ $\ell_4 = \left(\dfrac{10 \times 76}{76 + 8/\sqrt{2}}\right) = 9.3$ cm



(fig. 4)

Ex. An iron tank contains helium at a pressure of 3.0 atm at 27°C. The tank can withstand a maximum pressure of 10 atm. The building in which tank has been placed catches fire predict whether the tank will blow up first or melt. (melting point of iron is 1535°C)

Sol. $P_1 = 3.0,\qquad T_1 = 300$ K

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \qquad \Rightarrow \qquad \frac{3.0}{300} = \frac{P_2}{1808}$$

$$P_2 = \frac{3.0 \times 1808}{300} = 18.08 \text{ atm}$$

Since at melting point it is greater than the maximum pressure, therefore it will blow up.

2. Charles' law :

It states "at constant pressure, the volume of a given mass of a gas, increases or decreases by $\dfrac{1}{273.15}$ th of its volume at 0°C for every rise or fall of one degree in temperature".

$$\frac{V_t}{V_0} = 1 + \frac{1}{273.15}t \text{(at constant n and P)}$$

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

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

0°C on the Celsius scale is equal to 273.15 K at the Kelvin or absolute scale.

i.e. T_t (Temperature in Kelvin scale) = 273.15 + t

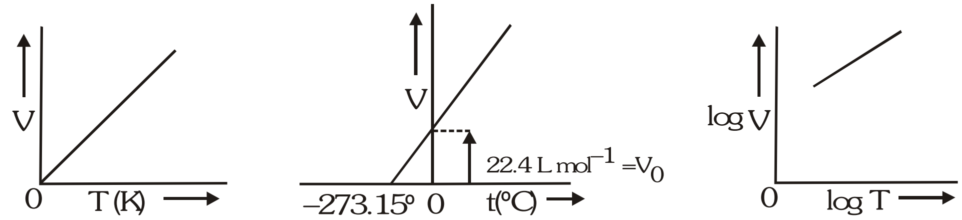
$\therefore$ From the above equation we get $\frac{V_t}{V_0} = \frac{T_t}{T_0}$

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

i.e. The volume of a given gas is proportional to the absolute temperature.

$\frac{V_1}{T_1} = \frac{V_2}{T_2}$ (at constant P)

◆ **Graphical representation :**



Graphs between V and T at constant pressure are called Isobars.

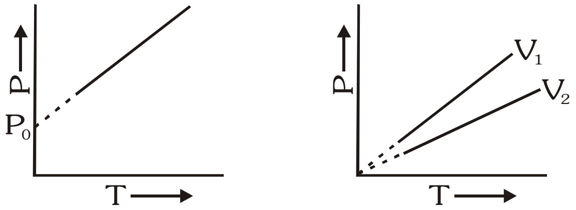
3. Gay-Lussac's law : Dependence of Pressure on Temperature :

It states "at constant volume, the pressure of a given mass of a gas is directly proportional to the absolute temperature of the gas".

$P \propto T$ or $P = KT$

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

◆ **Graphical representation :**



The plots drawn at constant volume for a gas is called as Isochore.

◆ **The combined gas Law :**

It states "for a fixed mass of gas, the volume is directly proportional to absolute temperature and inversely proportional to the pressure".

Boyle's Law, $V \propto \frac{1}{P}$ (at constant n, T)

Charle's Law, $V \propto T$ (at constant n, P)

Therefore, $V \propto \frac{T}{P}$ or $V = K\frac{T}{P}$ or $\frac{PV}{T} = K$ or $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

◆ **Volume coefficient (α_v) of a gas :**

The ratio of increase in volume of a gas at constant pressure per degree rise of temperature to its volume at 0°C is the volume coefficient of the gas.

$\alpha_v = \frac{V_t - V_0}{V_0 \times t}$ or $V_t = V_0(1 + \alpha_v t)$

For all gases, $\alpha_v = \frac{1}{273}$

◆

Pressure coefficient (α_p) of a gas :

The ratio of increase in pressure of the gas at constant volume per degree rise of temperature to its pressure at 0°C is the pressure coefficient of the gas.

$$\alpha_p = \frac{P_t - P_0}{P_0 \times t} \qquad \text{or} \qquad P_t = P_0(1 + \alpha_p t)$$

For all gases, $\alpha_p = \dfrac{1}{273}$

4. Avogadro's Law :

It states "equal volumes of any two gases at the same temperature and pressure contain the same number of molecules".

$V \propto n$ (At constant P and T)

or, $\dfrac{V_1}{n_1} = \dfrac{V_2}{n_2}$

THE IDEAL GAS EQUATION

An ideal gas is defined to be a system in which there are no inter molecular/interatomic forces. Such a system can only exist as a gas. Any real system will approach ideal gas behaviour in the limit that the pressure is extremely low and the temperature is high enough to overcome attractive intermolecular forces.

An ideal gas is a gas to go which the laws of Boyle and Charles are strictly applicable under all conditions of temperatures and pressures.

From Boyle's law we get,

$V \propto 1/P$ (at constant n and T)

From charles law we get,

$V \propto T$ (at constant n and P)

From Avogadro's law we get,

$V \propto n$ (at constant T and P)

Combining the above three equations we get

$$V \propto \frac{nT}{P} \qquad \text{or} \quad V = R\frac{nT}{P}$$ [Where R = ideal gas constant]

or $PV = nRT$

Ideal gas equation is a relation between four variables and it describes the state of any gas. For this reason, it is also called Equation of State.

◆

Dimension of R :

$$R = \frac{PV}{nT} = \frac{\text{Pressure} \times \text{Volume}}{\text{Mole} \times \text{Temperature}}$$

$$= \frac{(\text{Force} / \text{Area}) \times (\text{Area} \times \text{Length})}{\text{Mole} \times \text{Degree(K)}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Mole} \times \text{Degree(K)}} = \frac{\text{Work or energy}}{\text{Mole} \times \text{Degree (K)}}$$

◆

Physical significance of R :

The dimentions of R are energy per mole per kelvin and hence it represents the amount of work (or energy) that can be obtained from one mole of a gas when its temperature is raised by 1K.

◆ Units of R :

(i) In lit-atm $R = \frac{1\text{ atm} \times 22.4\text{lit}}{273\text{ K}} = 0.0821$ lit-atm $\text{mol}^{-1}\text{K}^{-1}$

(ii) In C.G.S system $R = \frac{1 \times 76 \times 13.6 \times 980\text{ dyne cm}^{-2} \times 22400\text{cm}^3}{273\text{ K}}$

$= 8.314 \text{ Ч } 10^7$ erg $\text{mole}^{-1}\text{K}^{-1}$.

(iii) In M.K.S. system $R = 8.314$ Joule $\text{mole}^{-1}\text{K}^{-1}$. [$10^7$ erg = 1 joule]

(iv) In calories $R = \frac{8.314 \times 10^7\text{ erg mole}^{-1}\text{K}^{-1}}{4.184 \times 10^7\text{erg}}$

$= 1.987 \approx 2$ calorie $\text{mol}^{-1}\text{K}^{-1}$.

Ex.2 At room temperature following reaction goes to completion

$$2NO + O_2 \longrightarrow 2NO_2 \longrightarrow N_2O_4$$

Dimer N_2O_4 at 262 K is solid. A 250 ml flask and a 100 ml flask are separated by a stop cock. At 300 K, the nitric oxide in the large flask exerts a pressure of 1.053 atm and the smaller on contains O_2 at 0.789 atm. The gases are mixed by opening the stop cock and after the end of the reaction, the flasks are cooled to 220 K. Neglecting the vapour pressure of dimer. Find out the pressure and composition of gas remaining at 220 K (Assume gases behave ideally).

Sol. For NO gas :-

$$n_{NO} = \frac{PV}{RT} = \frac{1.053 \times 250}{0.0821 \times 300 \times 1000} = 1.069 \text{ Ч } 10^{-2}$$

For O_2 gas :- $n_{O_2} = \frac{0.789 \times 100}{0.0821 \times 300 \times 1000} = 0.32 \text{ Ч } 10^{-2}$

Now,	$2NO$	+	O_2	$\longrightarrow$	N_2O_4
Mole before reaction	$1.069 \text{ Ч } 10^{-2}$		$0.32 \text{ Ч } 10^{-2}$		0
Mole after reaction	$1.069 \text{ Ч } 10^{-2} - 2 \text{ Ч } 0.32 \text{ Ч } 10^{-2}$		0		$0.32 \text{ Ч } 10^{-2}$

$= 0.429 \text{ Ч } 10^{-2}$

Moles of NO left = $4.29 \text{ Ч } 10^{-3}$

$P_{NO} \text{ Ч } V = nRT$ Given T = 220 K

$$V = \frac{250 + 100}{1000} = \frac{350}{1000} \text{ litre}$$

$$P_{NO} \text{ Ч } \frac{350}{1000} = 4.29 \text{ Ч } 10^{-3} \text{ Ч } 0.821 \text{ Ч } 220$$

P_{NO} (left) = 0.221 atm.

❑ DALTON'S LAW OF PARTIAL PRESSURES

Dalton's law of partial pressure states "at a given temperature, the total pressure exerted by two or more non-reacting gases occupying a definite volume in equal to the sum of the partial pressures of the component gases."

$$P_{Total} = p_1 + p_2 + p_3 + \ldots\ldots \text{ (At constant V and T)}$$

$$= \left(\frac{n_1}{V} + \frac{n_2}{V} + \frac{n_3}{V} + \ldots..\right)RT = (n_1 + n_2 + n_3 + \ldots\ldots)\frac{RT}{V} = \frac{nRT}{V}$$

Where $n = n_1 + n_2 + n_3 + \ldots\ldots$ = Total moles, V = Total volume

$$P_{Total} = \sum p_i = \frac{RT}{V}\sum n_i$$

Dalton's law of partial pressure is applicable only to non-reacting gases.

If the two non-reacting gases A and B having n_A and n_B number of moles respectively are filled in a vessels of volume V at temperature T, Then

$$PV = (n_A + n_B)\,RT \qquad \text{....(i)}$$

Partial pressure may be calculated as

$$p_AV = n_ART, \quad p_BV = n_BRT$$

Total pressure $(p_A + p_B)\,V = (n_A + n_B)RT$ .....(ii)

from (i) and (ii)

$P = p_A + p_B$

$$\frac{p_A}{P} = \frac{n_ART/V}{(n_A+n_B)RT/V} = \frac{n_A}{n_A+n_B} = x_A \text{ (mole fraction of A)}$$

$p_A = x_A$ Ч P, similarly $p_B = x_B$ Ч P

Partial pressure of a component = Mole fraction Ч total pressure.

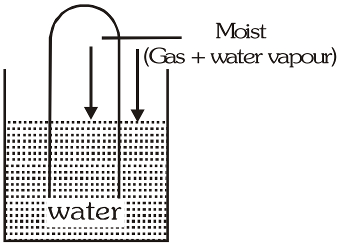
It has been observed that gases are generally collected over water and therefore are moist.

$P_{dry\ gas} = P_{moist\ gas} - P_{water\ vapour}$

The pressure exerted by water vapour is constant with water at a particular temperature is called as aqueous tension, which varies directly with the temperature and becomes 760 mm at 100°C.

$$\text{Relative Humidity (RH)} = \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}$$

Pressure of dry gas = Pressure of moist gas – aqueous tension.



❑ AMAGAT'S LAW OF PARTIAL VOLUME

According to this law at constant temperature and pressure, the total volume of mixture of gases which don't react is equal to the sum of partial volumes of each component present in mixture.

$$V_T = V_1 + V_2 + V_3 + \ldots\ldots.$$

◆ **Partial Volume :**

Partial volume of any component is defined as the volume occupied by that particular component measured under the given condition of pressure and temperature.

$$PV = nRT$$

$$V \propto n$$

◆ **Partial volume :**

Let us consider a three non-reacting gases A, B and C are present in a container which have no. of moles n_A,n_B and n_C respectively. For each gas partial volume is

$$V_A = n_A\left(\frac{RT}{P}\right), \qquad V_B = n_B\left(\frac{RT}{P}\right) \qquad \text{and} \qquad V_C = n_C\left(\frac{RT}{P}\right)$$

◆ **Total volume :**

$$V_T = V_A + V_B + V_C = (n_A + n_A + n_A)\left(\frac{RT}{P}\right) = n_T\left(\frac{RT}{P}\right)$$

Ex. A vessel of 2 lit capacity contains hydrogen at 380 mm pressure at 27°C. 16gm of O_2 is added to the container then find the total pressure and partial pressure where R = 0.0821 L atm mol^{-1} k^{-1}.

Sol. For H_2 gas :

Given V = 2L and $p_{H_2} = \frac{380}{760} = \frac{1}{2}$atm

$$p_{H_2}V = n_{H_2}RT$$

$1 = n_{H_2}$ Ч 0.0821 Ч 300

$$n_{H_2} = \frac{10000}{821\times300} = \frac{1}{24.6}$$

Moles of $O_2 = \frac{16}{32} = \frac{1}{2}$

Partial pressure of H_2 gas $(p_{H_2}) = \frac{1}{2} = \frac{n_{H_2}}{n_{H_2}+n_{o_2}}$ Ч P

$$\frac{1}{2} = \frac{\frac{1}{24.6}}{\frac{1}{24.6}+\frac{1}{2}}\times P \qquad \text{or} \qquad P = 6.65 \text{ atm}$$

Ex. 1 mole of N_2 and 3 moles of H_2 are mixed in 8.21 lit container at 300 K to form NH_3. If equilibrium average molecular mass was found to be 34/3 gram then find partial pressure of each component.

Sol.

	N_2 +	$3H_2$ $\rightleftharpoons$	$2NH_3$
Initially	1	3	0
at equilibrium	(1 − x)	3 (1 − x)	2x

Total moles = 1 − x + 3 − 3x + 2x = (4 − 2x) moles

Given Average molecular mass = $\frac{34}{3}$

$$\frac{34}{3} = \frac{28(1-x)+2(3-3x)+17(2x)}{(4-2x)}$$

$$\frac{34}{3}(4-2x) = 34 \Rightarrow 4-2x = 3 \Rightarrow x = 1/2$$

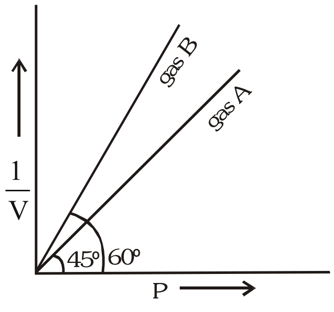
So total no. of moles = 3

$$PV = nRT \Rightarrow P = \frac{nRT}{V} = \frac{3\times0.821\times300}{8.21} = 9 \text{ atm}$$

$$p_{N_2} = \frac{1-x}{3}\times P = \frac{0.5}{3}\times 9 = 1.5 \text{ atm}$$

$$p_{H_2} = \frac{3-3x}{3}\times P = \frac{1.5}{3}\times 9 = 4.5 \text{ atm}$$

Ex. At constant temperature of 273K, $\frac{1}{V}$ Vs P are plotted for 2 ideal gases A and B as shown. Find out the number of moles of gas A and B.



Sol. PV = nRT, $P = \frac{1}{V}nRT$

$$\frac{1}{V} = \frac{1}{nRT}P$$

Comparing by equation :

$y = mx + C$

$C = 0$

$$m = \frac{1}{nRT} \qquad (m = \tan\theta)$$

$$\tan\theta = \frac{1}{nRT} \qquad n_A = \frac{1}{RT\tan\theta}$$

$$n_A = \frac{1}{0.0821 \times 273 \times \tan 45^\circ} \quad \Rightarrow \quad n_A = \frac{1}{22.4}$$

$$n_B = \frac{1}{RT\tan 60^\circ} = \frac{1}{22.4\sqrt{3}}$$

Ex. One litre flask contains air, water vapour and a small amount of liquid water at a pressure of 200 mmHg. If this is connected to another one litre evacuated flask, what will be the final pressure of the gas mixture at equilibrium ? Assume the temperature to be 50°C. Aqueous tension at 50°C = 93 mmHg.

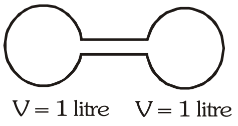
Sol. The aqueous tension remains same in both the flask. Also flask are at same temperature

$\therefore$ $P_1V_1 = P_2V_2$

where $P_1 = 200 - 93 = 107$ mm

$V_1 = 1$ litre

$V_2 = 2$ litre



$\therefore$ 107 Ч $1 = P$ Ч 2

$P = 53.5$ mm

Since aqueous tension is also present in flask, equivalent to 93 mm.

$\therefore$ pressure of gaseous mixture = 93 + 53.5 = 146.5 mmHg.

Ex. A 500 ml bulb is filled with CH_4 at a pressure of 1 atm and oxygen at a pressure of 4 atm at 27°C. The mixture is then exploded, when the reaction $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O\ (\ell)$ occurs. Calculate the pressure if the final temperature is 27°C. Aqueous tension at 27°C is 26.7 mm.

Sol. Partial pressure of CH_4, $(p_{CH_4}) = 1$ atm

Partial pressure of O_2, $(p_{O_2}) = 4$ atm

$\therefore$ moles of CH_4 present, $(n_{CH_4}) = \frac{1 \times 0.5}{RT} = \frac{0.5}{RT}$

$\therefore$ moles of O_2 present $(n_{O_2}) = \frac{4 \times 0.5}{RT} = \frac{2}{RT}$

	$CH_4(g)$ +	$2O_2(g)$ =	$CO_2(g)$ +	$2H_2O(\ell)$
Initially	$\frac{0.5}{RT}$	$\frac{2}{RT}$		
Finally	–	$\frac{1}{RT}$	$\frac{0.5}{RT}$	

After the reaction, moles of residual $O_2 = \frac{2}{RT} - \frac{1}{RT} = \frac{1}{RT}$

After the reaction, moles of CO_2 produced $= \frac{0.5}{RT}$

Hence total no. of moles of O_2 and $CO_2 = \frac{1.5}{RT}$

$\therefore$ total pressure due to O_2 and $CO_2 = \frac{1.5}{RT}$ Ч $\frac{RT}{0.5} = 3$ atm

$\therefore$ pressure exerted by the entire gaseous components

$$= 3 + \frac{26.7}{760} = 3 + 0.03513 = 3.0513 \text{ atm}$$

Ex.4.27 What is the difference in the density of dry air at 1 atm and 25°C and moist air with 50% relative humidity under the same condition. The vapour pressure of water at 25°C is 23.7 Torr and dry air has 75.5% N_2 and 24.5% O_2.

Sol. $$\text{M (dry air)} = \frac{M_1(O_2)X_1(\%\,\text{of}\,O_2) + M_2(N_2)X_2(\%\,\text{of}\,N_2)}{X_1 + X_2}$$

$$= \frac{32 \times 24.5 + 28 \times 75.5}{100} = 28.98\ \text{g mol}^{-1}$$

$$\text{d (dry air)} = \frac{\text{PM(air)}}{\text{RT}} = \frac{1 \times 28.98}{0.0821 \times 298} = 1.184\ \text{g L}^{-1} = 1.184\ \text{kg m}^{-3}$$

$$\left(\because 1\text{g}\,\text{L}^{-1} = \frac{10^{-3}\text{kg}}{10^{-3}\text{m}^3} = 1\text{kg m}^{-3}\right)$$

$$\text{relative humidity (50\%)} = \frac{\text{partial pressure of } H_2O \text{ in air}}{\text{vapour pressure of } H_2O}$$

∴ P (H_2O) = 0.50 Ч 23.7 Torr

$$= 11.85\ \text{torr} = \frac{11.85}{760}\text{atm} = 0.0156\ \text{atm}$$

$$\%\ \text{of}\ H_2O\ \text{vapour in air} = \frac{0.0156 \times 100}{1} = 1.56\%$$

% of N_2 and O_2 in air = 98.44%

$$\text{M (wet air)} = \frac{28.98 \times 98.44(\text{air}) + 18 \times 1.56(\text{water vapour})}{100} = 28.81\ \text{g mol}^{-1}$$

$$\text{d (wet air)} = \frac{\text{PM(wet air)}}{\text{RT}} = \frac{1 \times 28.81}{0.0821 \times 298} = 1.177\ \text{g L}^{-1} = 1.177\ \text{kg m}^{-3}$$

difference = 1.184 – 1.177 = 0.007 kg m^{-3}

III.4 A sample of butane gas C_4H_{10} of unknown mass is contained in a vessel of unknown volume V at 25°C and a pressure of 760 mmHg. To this vessel 8.6787 g of neon gas is added in such a way that no butane is lost from the vessel. The final pressure in the vessel is 1920 mm Hg at the same temperature. Calculate the volume of the vessel and the mass of butane.

Sol. Partial pressure of C_4H_{10} (p_1) = 760 mm Hg

By Dalton's law of partial pressure, $P_{total} = p_1 + p_2$

1920 = 760 + p_2 or p_2 = 1160 mm Hg

p_2 = x_2 Ч p_{total}

where x_2 = mole fraction of Ne

$$x_2 = \frac{p_2}{P_{total}} = \frac{1160}{1920} = 0.60\ ;\ \text{Moles of Ne} = \frac{8.6787}{20.2} = 0.43$$

$$x_2 = \frac{n_2}{n_1 + n_2}\ ;\ 0.60 = \frac{0.43}{0.43 + n_1} \Rightarrow n_1 = 0.28$$

Molecular weight of C_4H_{10} = 48 + 10 = 58

so, amount of C_4H_{10} = n_1 Ч 58 = 16.24 g

again for C_4H_{10}

$$PV = n_1RT\ ;\ T = 273 + 25 = 298\ \text{K},\ P = \frac{760}{760}\text{atm} = 1\ \text{atm}$$

$$V = \frac{n_1RT}{P} = \frac{0.28 \times 0.0821 \times 298}{1} = 6.85\ \text{L}$$

Ex. A mixture of CO and CO_2 is found to have a density of 1.50 g/litre at 30°C and 730 mm. Calculate the composition of mixture.

Sol. For mixture, $P = (730/760)$ atm,

$T = 303$ K, $\quad d = 150$ g litre^{-1}

$\therefore \quad PV = nRT = (w/M)\,RT \Rightarrow P(w/VM)\,RT \Rightarrow P = \frac{d}{M}RT$

$\therefore \quad \frac{730}{760} = \frac{1.50}{M} \times 0.0821 \times 303$

$\therefore \quad M = 38.85$

Let n_1 moles of CO and $(100 - n_1)$ moles of CO_2 are present in 100 moles.

$\therefore \quad$ Average molecular weight (M) = $\frac{n_1 \times 28 + (100 - n_1) \times 44}{100} = 38.85 \Rightarrow n_1 = 32.19$

$\therefore \quad$ mole % of CO = 32.19, and mole % of CO_2 = 67.81.

Ex. An open vessel at 27°C is heated until 3/5th of the air in it has been expelled. Assuming that the volume of the vessel remains constant. Find

(a) the temperature at which vessel was heated ?

(b) the air escaped out if vessel is heated to 900 K ?

(c) temperature at which half of the air escapes out ?

Sol. One should clearly note the fact that on heating a gas in a vessel there are the number of moles of gas which go out, the volume of vessel remains constant.

Let initial moles of air at 300 K be 'n'. On heating 3/5 moles of air are escaped out at temperature T.

$\therefore \quad$ Moles of air left at temperature T $= \left(n - \frac{3}{5}n\right) = \frac{2n}{5}$

(a) Under simillar conditions of P and V

$n_1T_1 = n_2T_2$

$n \times 300 = \frac{2n}{5} \times T \quad \Rightarrow \quad T = 750$ K

(b) On heating vessel to 900 K, let n_1 moles be left again $n_1T_1 = n_2T_2$

$n_1 \times 900 = 300 \times n \quad \Rightarrow n_1 = \frac{1}{3}n$

$\therefore$ moles escaped out $= n - \frac{n}{3} = \frac{2}{3}n$ moles

(c) Let n/2 moles are escaped out at temperature T then

$n_1T_1 = n_2T_2$

$n/2 \times T = n \times 300$

$T = 600$ K

GRAHAM'S LAW OF DIFFUSION AND EFFUSION

Diffusion :

The process of mixing of gases by random motion of the molecules is called diffusion.

Effusion :

When gas is confined to a container at high pressure than in the surrounding atmosphere it will escape from a small hole which is opened in the container until the pressure outside and inside have been equalised. This process is called effusion.

The difference between diffusion and effusion is that in the former case, the gas spontaneously passes through a porous partition while in the case of effusion, the gas is passed out through a small orifice or hole by applying some external pressure.

Graham's law of diffusion states "under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their molecular masses or their densities."

Mathematically , $r \propto \sqrt{\frac{1}{M}}$ or $\sqrt{\frac{1}{d}}$ or, $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$

Where r_1 and r_2 are the rates of diffusion of gases 1 and 2.

M_1 and M_2 are their molecular masses.

d_1 and d_2 are their densities.

◆

Effect of volume on rate of diffusion :

$$\text{Rate of diffusion} = \frac{\text{Volume of gas diffused}}{\text{Time taken for diffusion}}$$

or $$r = \frac{V}{t}$$

Let V_1 be the volume of gas 1 and V_2 be the volume of gas 2, then

$$r_1 = \frac{V_1}{t_1} \qquad r_2 = \frac{V_2}{t_2}$$

$$\therefore \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \frac{V_1 t_2}{V_2 t_1}$$

(i) **Comparison of times taken for the same volume of two gases :**

Let the times of diffusion for the same volume of two gases be t_1 and t_2 respectively. Then

$$\frac{r_1}{r_2} = \frac{V/t_1}{V/t_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \quad \text{or} \quad \frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

(ii) **Comparision of the volumes of the gases that diffuse in same time :**

Let V_1 and V_2 be the volume of two gases that diffuse in same time t. Then,

$$\frac{r_1}{r_2} = \frac{V_1/t}{V_2/t} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \quad \text{or} \quad \frac{r_1}{r_2} = \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

(iii) **Effect of pressure on rate of diffusion :**

Rate of diffusion is proportional to the pressure of the gas in the container.

$$r \propto P \qquad ; \quad \text{again, } r \propto \frac{1}{\sqrt{M}}$$

$$\text{or} \quad r \propto \frac{P}{\sqrt{M}} \qquad \text{or} \quad \frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

◆

Application of graham's law of diffusion in enrichment of isotopes :

Enrichment of Light component :

If a mixture of heavier gas B and a lighter gas A is placed in contact with a porous barrier, the gas passing through will be enriched in lighter component by a factor $\sqrt{\frac{M_B}{M_A}}$, called enrichment factor because lighter molecules effuse more rapidly than heavier ones. The remaining gas will be enriched in the heavier component.

Each passage gives an enrichment factor equal to $\sqrt{\frac{M_B}{M_A}}$ and so thousands of such barrier in succession are necessary to provide sufficient enrichment of heavier component.

Thus, enrichment factor for first barrier or operation $f_1 = \sqrt{\frac{M_B}{M_A}}$

$\therefore$ overall separation or enrichment factor $f = \dfrac{n'_A / n'_B}{n_A / n_B}$

Where n_A, n_B, and n'_A , n'_B are the concentration of two isotopically different components before and after processing. If required enrichment of gas A is attained in x-operation then,

$$(f_1)^x = \frac{n'_A / n'_B}{n_A / n_B} = f$$

or $$x \log f_1 = \log \left[\frac{n'_A / n'_B}{n_A / n_B}\right]$$

or $$x \log \left[\frac{M_B}{M_A}\right]^{1/2} = \log \left[\frac{n'_A / n'_B}{n_A / n_B}\right]$$

or $$\frac{x}{2} \log \left[\frac{M_B}{M_A}\right] = \log \left[\frac{n'_A / n'_B}{n_A / n_B}\right]$$

or $$x = \frac{2 \log \left(\frac{n'_A / n'_B}{n_A / n_B}\right)}{\log \left(\frac{M_B}{M_A}\right)}$$

❑ LIMITATIONS OF THIS LAW

(i) The laws of diffusion and effusion are applicable only when the pressure difference is very small.

(ii) Correctly speaking the rate of diffusion and effusion are not constant throughout the time interval, but these rates may be assumed constant for a small time interval.

Ex. The pressure in a bulb dropped from 2000 to 1500 mm of mercury in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of mercury was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 minutes.

Sol. The molar ratio of oxygen and the other gas in the evacuated bulb = 1 : 1 and the total pressure of the gas mixture is 4000 mm, hence the partial pressure of each gas is 2000 mm.

The drop in the pressure of oxygen after 74 minutes

$$= \frac{(2000 - 1500) \times 74}{47} = 787.2 \text{ mm of Hg}$$

$\therefore$ After 74 minutes, the pressure of oxygen = 2000 – 787.2 = 1212.8 mm of Hg

Let the rate of diffusion of other gas be r_n, then

$$\frac{r_n}{r_{O_2}} = \sqrt{\frac{32}{79}}$$

$\therefore$ Drop in pressure for the other gas $= 787.2 \text{ Ч } \sqrt{\frac{32}{79}} = 501.01$ mm of Hg

$\therefore$ Pressure of the other gas after 74 minutes = 2000 – 501.01 mm = 1498.99 mm of Hg

Molar ratio $= \dfrac{\text{Moles of unknown gas}}{\text{Moles of } O_2} = \dfrac{1498.99}{1212.8} = 1.236 : 1$

Ex. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Determine the molecular formula of the compound.

Sol. Rate of diffusion, $r \propto p$

$$r \propto \sqrt{1/M} \text{ or } r \propto \frac{p}{\sqrt{M}}$$

or $$\frac{r_2}{r_1} = \frac{p_2}{p_1}\left(\frac{M_1}{M_2}\right)^{1/2}$$

Again, $$r \propto \frac{1}{t}$$

or $$\frac{t_1}{t_2} = \left(\frac{p_2}{p_1}\right)\left(\frac{M_1}{M_2}\right)^{1/2}$$

or $$M_2 = \left(\frac{p_2 t_2}{p_1 t_1}\right)^2 M_1$$

$$M_2 = \left(\frac{1.6}{0.8} \times \frac{57}{38}\right)^2 \times 28 = 252 \text{ g mol}^{-1}$$

Let the molecular formula of the unknown compound be XeF_n.

$$M_{xe} + nM_F = 252$$

or $$131 + 19\,n = 252$$

$$n = \frac{252 - 131}{19} = 6.36 \approx 6$$

Hence, the molecular formula of the gas is XeF_6.

Ex. At 1200°C, mixture of Cl_2 and Cl atoms (both in gaseous state) effuses 1.16 times as fast as krypton effuses under identical conditions. Calculate the fraction of chlorine molecules dissociated into atoms. M (Kr) = 83.8 g mol^{-1}.

Sol. $$Cl_2 \rightleftharpoons 2Cl$$

$$\frac{r(Cl_2 \text{ and } Cl \text{ mix})}{r(Kr)} = 1.16 \quad \sqrt{\frac{M(Kr)}{M_{av}(Cl_2 + Cl)}} \qquad = \sqrt{\frac{83.8}{M_{av}}}$$

$$\therefore \quad M_{av} = \frac{83.8}{(1.16)^2} = 62.28 \text{ g mol}^{-1}$$

	$Cl_2 \rightleftharpoons$	$2Cl$
Initial mole	1	0
After dissociation	(1 − x)	2x

(x = degree of dissociation)

Total moles after dissociation = 1 − x + 2x = (1 + x)

$$\therefore \quad \frac{(1-x)M(Cl_2) + 2x\,M(Cl)}{(1+x)} = 62.28$$

$$\frac{(1-x) \times 71 + 2x \times 35.5}{1+x} = 62.28$$

$$\frac{(1-x+x)71}{1+x} = 62.28$$

$$\frac{1}{1+x} = \frac{62.28}{71} = 0.88$$

$$1 + x = 1.14$$

$$x = 0.14$$

$\therefore$ % dissociation = 14%

Alternately, following formula can also be used to determine degree of dissociation when there is equilibrium mixture.

$$x = \frac{m(\text{normal}) - m(\text{average})}{m(\text{average})} = \frac{71 - 62.28}{62.28} = 0.14$$

❑ **Connecting Containers** :

(1) When we are connecting two or more containers then the movement of any component of gas occurs in other container till the final pressure of that component in all the container become equal (that means partial pressure becomes equal).

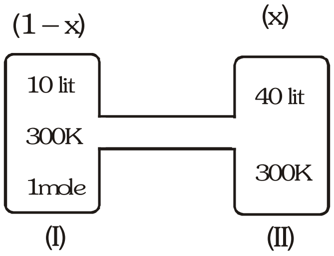
(2) To calculate composition of gaseous mixture in any container, we will use law of diffusion.

Ex. A 10 liter container consist of 1 mole of gas at 300 K. It is connected to another container having volume 40 liter and is initially at 300 K. The nozzle connecting two containers is opened for a long time and once the movement of gas stopped, the larger container was heated to a temperature of 600 K. Calculate

(a) Moles and pressure of gas in both the containers before heating.

(b) Moles and pressure in two containers after heating. (assume that initially the larger container is completely evacuated.)

Sol. (a) Before heating :



$$PV = nRT$$

$$\frac{(1-x)R \times 300}{10} = \frac{x \times R \times 300}{40}$$

$$X = 0.8 \text{ moles}$$

$$\text{Pressure} = \frac{x \times R \times T}{V} = \frac{0.8 \times R \times 300}{40} = 0.492 \text{ atm}$$

(b) After heating :

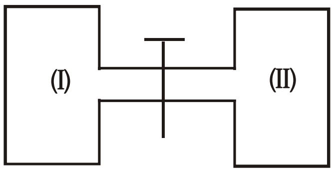
$$\frac{(1-x_1)R \times 300}{10} = \frac{x_1 \times R \times 600}{40}$$

$$X_1 = 0.67 \text{ moles, Given } T_1 = 600 \text{ K}$$

$$\text{Pressure} = \frac{x_1 \times R \times T_1}{V} = \frac{0.67 \times .0821 \times 600}{40} = 0.821 \text{ atm}$$

Pro85. A mixture containing 1.12 litre D_2 and 2.24 litre of H_2 at NTP is taken inside a bulb connected to another bulb through 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 now found to contain 0.10 g of D_2. Determine the % by weight of the gases in second bulb.

Sol. At STP



$$\text{Before diffusion} \quad \left.\begin{aligned} D_2 &= 1.12 \text{ lit. at STP} = 0.2\text{ g} = 0.05 \text{ mole} \\ H_2 &= 2.24 \text{ lit. at STP} = 0.2\text{ g} = 0.1 \text{ mole} \end{aligned}\right\} \text{in I bulb}$$

When these moles are placed in the bulb, the partial pressure of gas will be different because V and T are constant. Also $P \propto n$

$$\text{Thus,} \quad \frac{P_{D_2}}{P_{H_2}} = \frac{0.05}{0.10} = \frac{1}{2}$$

After diffusion D_2 left in I bulb = 0.1 g

or D_2 diffuses from I into II (bulb) = 0.2 − 0.1 = 0.1 g

Now for diffusion of D_2 and H_2

$$\frac{r_{D_2}}{r_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{D_2}}} \times \frac{P_{D_2}}{P_{H_2}}$$

$$\because \quad \frac{w_{D_2}}{t_{D_2}} \times \frac{t_{H_2}}{w_{H_2}} = \sqrt{\frac{M_{D_2}}{M_{H_2}}} \times \frac{P_{D_2}}{P_{H_2}}$$

$$\therefore \quad \frac{0.1}{t} \times \frac{t}{w_{H_2}} = \sqrt{\left(\frac{4}{2}\right)} \times \frac{1}{2}$$

$$\therefore \quad w_{H_2} = 0.14 \text{ g}$$

$\therefore$ Wt. of gases in II bulb = wt. of D_2 + wt. of H_2

= 0.10 g + 0.14 g = 0.24 g

$\because$ % D_2 by wt. $= \frac{0.10}{0.24}$ Ч 100 = 41.66 %

% H_2 in bulb II = 58.33%

Ex. Calculate the relative rates of diffusion for $^{235}UF_6$ and $^{238}UF_6$ in gaseous form. Also if naturally occurring uranium ore having U^{235} and U^{238} in the ratio 0.72 and 99.28%, and if it is desired to enrich the U^{235} to 10% of the sample, making use of relative rates of diffusion of UF_6 having U^{235} and U^{238} isotopes, how many diffusion stages are required ?

Sol. M.wt of $^{235}U\,F_6$ = 235 + 19 Ч 6 = 349

M.wt of $^{238}U\,F_6$ = 238 + 19 Ч 6 = 352

From Graham's law at same P and T

$$\frac{r_1}{r_2} = \sqrt{\left(\frac{M_2}{M_1}\right)}$$

$$\frac{r_{U^{235}F_6}}{r_{U^{238}F_6}} = \sqrt{\left(\frac{352}{349}\right)} = 1.0043$$

$$\text{Also} \quad x = \frac{2\log\left(\frac{n'_A / n'_B}{n_A / n_B}\right)}{\log\left(\frac{M_B}{M_A}\right)}$$

Here, $n_A = U^{235}$ in $U^{235}F_6 = 0.72$ and $M_B = M_{U^{238}F_6}$

$n_B = U^{238}$ in $U^{238}F_6 = 99.28$ and $M_A = M_{U^{235}F_6}$

$n'_A = U^{235}$ in $U^{235}F_6 = 10$

$n'_B = U^{238}$ in $U^{238}F_6 = 90$

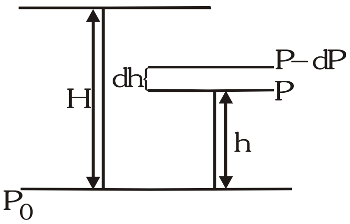
$$\therefore \quad x = \frac{2\log\left(\frac{(10/90)}{(0.72/99.28)}\right)}{\log\left(\frac{352}{349}\right)} = 638 \text{ steps}$$

❑ BAROMETRIC PRESSURE DISTRIBUTION

In case of air (ideal gas) density depends on pressure. So we can not calculate pressure difference between two points directly as 'hdg'.

Assume in case of air, composition of air and temperature is constant throughout.

Suppose pressure at height 'h' from the ground level is 'P' and as height increase by 'dh' the pressure decreases by 'dP'. So the pressure difference between two points is :



$(P - dP) - P = dh \text{ Ч } d \text{ Ч } g$

$$-dP = dh \text{ Ч } \frac{PM}{RT} \text{ Ч } g \qquad [PM = dRT]$$

$$\int_{P_0}^{P} \frac{-dP}{P} = \frac{Mg}{RT}\int_{0}^{H} dh$$

$$[\ell_n P]_{P_0}^{P} = \frac{-Mg}{RT}[h]_0^H$$

$$\ell n\frac{P}{P_0} = \frac{-MgH}{RT}$$

$$P = P_0 e^{-\left(\frac{MgH}{RT}\right)}$$

M = molar mass of air (kg/mole)

$g = 9.8 \text{ m/sec}^2$

H = height in meter

R = 8.314 J/mole/K

Ex. Calculate the expression for density of air at any height 'H' metre from the ground level. If at the ground level atmospheric pressure is P_0 atm and average molar mass of air is 'M' and temperature is 'T' kelvin. Given that average molar mass and temperature are constant.

Sol.

$$P = P_0 e^{-\left(\frac{MgH}{RT}\right)}$$

$$\frac{dRT}{M} = P_0 e^{-\left(\frac{MgH}{RT}\right)}$$

$$d = \left(\frac{P_0 M}{RT}\right) e^{-\left(\frac{MgH}{RT}\right)}$$

$\because$ Density at ground level $= d_0 = \frac{P_0 M}{RT}$

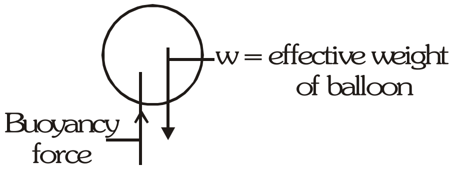
$\therefore \quad d = d_0 \, e^{-\left(\frac{MgH}{RT}\right)}$

❑ PAYLOAD OF BALLOON

Payload of a balloon is defined as maximum weight which a bolloon can carry with it upward direction.

V = Volume of Balloon , d_{out} = density of autside air,

d_{in} = density of gas inside, m = mass of balloon.



Payload $= d_{out} \text{ Ч } V \text{ Ч } g - [d_{in} V \text{ Ч } g + mg]$

= [Buoyancy force] – [effective wt. of Balloon]

Ex. Calculate payload of a balloon having volume 100 litre. It is filled with helium gas at 0.2486 atm pressure and 300 K. Density of air is 1.3 gm./litre and mass of material of bolloon is 20 gm.

Sol. $PM = dRT$

$$d_{in} = \frac{PM_{He}}{RT} = \frac{0.2486 \times 4}{0.0821 \times 300} = \frac{1}{25}$$

$$\text{Payload} = 1.3 \times 100 \times 10 - \left[\frac{1}{25} \times 100 \times 10 + 20 \times 10\right]$$

$$= \frac{13}{10} \times 100 \times 10 - [4 \times 10 + 200] = 1300 - 240 = 1060$$

(A) CALCULATION OF PAYLOAD OF BALLOON AT CONSTANT HEIGHT

(1) At constant volume of balloon

$$\text{Payload} = d_{out} V.\, g - [w]$$

$$d_{out} = d_0\, e^{\left(-\frac{Mgh}{RT}\right)}$$

$$\text{Payload} = d_0\, e^{-\frac{Mgh}{RT}}\, V.g - w$$

Density of outside air decreases with increase in height so buoyancy force decreases and payload of balloon decreases with increase in height.

(2) At variable volume of balloon

$$PV = nRT$$

$$PV = \text{constant}$$

$$P_0V_0 = P_h \times V_h$$

$$P_0V_0 = P_0\, e^{\left(-\frac{Mgh}{RT}\right)} \times V_h$$

$$V_h = V_0\, e^{\left(\frac{Mgh}{RT}\right)}$$

$$\text{Now payload} = d_{out} \times V \times g - w$$

$$= d_0\, e^{-\frac{Mgh}{RT}}\, V_0 e^{\left(\frac{Mgh}{RT}\right)} x g - w \quad = d_0\, V_0\, g - w$$

$$= \text{constant}$$

In this case buoyancy force at any height is same so payload will remain constant throughout.

(B) Maximum height at which balloon will burst

Maximum volume = V_{max}

$$V_{max} = V_0 e^{\left(\frac{Mgh_{max}}{RT}\right)}$$

$$\frac{V_{max}}{V_0} = e^{\left(\frac{Mgh_{max}}{RT}\right)}$$

$$\ell n\left(\frac{V_{max}}{V_0}\right) = \left(\frac{Mgh_{max}}{RT}\right)$$

$$\boxed{h_{max} = \frac{RT}{Mg}\ell n\left(\frac{V_{max}}{V_0}\right)}$$

Prob 8 Calculate the payload of balloon of diameter 20 meter weight 100 kg. If it is filled with He at 1.0 atm and 27°C. Density of air is 1.2 kgm^{-3}. [$R = 0.082\ dm^3\ atm\ K^{-1}\ mol^{-1}$]

Sol. Weight of balloon = 100 kg = 10×10^4 g

Volume of balloon $= \frac{4}{3}\pi r^3 = \frac{4}{3}\times\frac{22}{7}\times\left(\frac{20}{2}\times 100\right)^3$

$= 4190 \times 10^6\ cm^3 = 4190 \times 10^3$ litre

Weight of gas (He) in balloon $= \frac{PV}{RT} = \frac{1\times 4190\times 10^3\times 4}{0.082\times 300} = 68.13 \times 10^4$ g

Total weight of gas and balloon $= 68.13 \times 10^4 + 10 \times 10^4 = 78.13 \times 10^4$ g

Weight of air displaced $= \frac{1.2\times 4190\times 10^6}{10^3} = 502.8 \times 10^4$ g

$\therefore$ Payload = wt. of air displaced – (wt. of balloon + wt. of gas)

$\therefore$ Payload $= 502.8 \times 10^4 - 78.13 \times 10^4 = 424.67 \times 10^4$ g $= 4.2467 \times 10^6$ g

Ex.1 A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 20 atmpsphere at 27°C. If the cylinder can hold 2.82 litre of water at NTP, calculate the number of balloons that can be filled up.

Sol. Radius of the balloon $= \frac{21}{2}$ cm = 10.5 cm

Volume of the balloon $= \frac{4}{3}\pi r^3 = \frac{4}{3}\times\frac{22}{7}\times (10.5)^3$cc = 4851 cc

Pressure $= 1 \times 76 \times 13.6 \times 981 = 1.014 \times 10^6$ dynes/cm^2

$\therefore$ No. of mole of H_2, the balloon can contain at NTP $= \frac{PV}{RT} = \frac{1.014\times 10^6\times 4851}{8.314\times 10^7\times 273} = 0.2167$

No. of mole in the cylinder $= \frac{20\times 76\times 13.6\times 981\times 2820}{8.314\times 10^7\times 300} = 2.2929$

When the balloons are being filled, the pressure in the cylinder will decreases, when the pressure of the cylinder will drop to 1 atm, gas cannot be withdrawn.

Now, no. of moles of H_2 remaining in the cylinder unused $= \frac{1.014\times 10^6\times 2820}{8.314\times 10^7\times 300} = 0.1146$

$\therefore$ No. of balloons that can be filled $= \frac{\text{No. of moles of } H_2 \text{ in the cylinder that can be used}}{\text{No. of moles of } H_2 \text{ in one balloon can contain}}$

$= \frac{2.2929 - 0.1146}{0.2167} = 10$

Ex.4.14

(a) How much H_2 (in moles) is needed to inflate a balloon of radius 3.0 m to a pressure of 1.0 atm in an ambient temperature of 25°C at sea level ?

(b) What mass can the balloon lift at sea level, where the density of air is 1.22 kg m^{-3} ?

(c) What would be the payload if He were used instead of H_2 ?

Sol. (a) $PV = n_{H_2}RT$

where $P = 1$ atm $= 1.0132 \times 10^5\ N\ m^{-2}$,

$V = \frac{4}{3}\times \pi \times (3)^3\ m^3$,

$R = 8.314\ J\ mol^{-1}\ K^{-1}$, $T = 298$ K

$$n_{H_2} = \frac{PV}{RT} = \frac{1.0132\times10^5\times\frac{4}{3}\times\frac{22}{7}\times(3)^3}{8.314\times298} = 4.62 \times 10^3 \text{ mol}$$

(b) Density of air = 1.22 kg m^{-3}

hence, mass of air = volume of balloon × density

$$= \frac{4}{3}\pi r^3 \times d = \frac{4}{3}\times\frac{22}{7} \times (3)^3 \times 1.22 \text{ kg} = 138.03 \text{ kg}$$

mass of H_2 = $n_{H_2} \times M_w$ of H_2 = $4.62 \times 10^3 \times 2 = 9.24$ kg

hence, the mass that the balloon can lift

= mass of air – mass of H_2 = 138.03 – 9.24 = 128.79 kg

(c) Payload if He were used instead of H_2 = 138.03 – 18.48 = 119.55 kg

[Mass of He = $n_{He} \times M_w$ of He = $4.62 \times 10^3 \times 4$ = 18.48 kg]

CALCULATION OF VAPOUR DENSITY OF MIXTURE IN REACTION :

It is given that initially only reactant A is present with vapour density (D). It has degree of dissociation α and finally vapour density 'd'

$$A_n \longrightarrow nB$$

	A_n	nB
Moles before dissociation	1	0
Moles after dissociation	$1-\alpha$	$n\alpha$

∴ total no. of moles after dissociation = $1 + (n-1)\alpha$

Since, mol. wt. $\propto \frac{1}{\text{no. of particles present}}$

$$\therefore \quad \frac{1}{\text{Normal mol. wt}} \propto \text{no. of particles before dissociation}$$

$$\therefore \quad \frac{1}{\text{Experimental mol. wt}} \propto \text{no. of particles after dissociation}$$

$$\therefore \quad \frac{\text{Normal mol. wt.}}{\text{Experimental mol. wt}} \propto \frac{\text{no. of particles after dissociation}}{\text{no. of particles before dissociation}}$$

$$\therefore \quad \frac{M_{\text{Normal}}}{M_{\text{exp}}} = \frac{1+(n-1)\alpha}{1}$$

The entire conclusion can represented in a general way as –

$$\frac{P_{\text{Normal}}}{P_{\text{experimental}}} = \frac{D_{\text{Normal}}}{D_{\text{experimental}}} = \frac{M_{\text{Normal}}}{M_{\text{experimental}}} = 1 + (n-1)\alpha$$

KINETIC THEORY OF GASES

The theoretical model for all the experimental gas laws can be analys with the help of kinetic theory of gases which is based on following assumptions :

(a) All the gases consists of very small molecules or atoms whose volume is negligible compared to volume of container (in case volume of container is very small, then this assumption will be violated)

(b) There is no interaction between gaseous particles (the interaction may appreciably affected under certain conditions of temperature and pressure).

(c) The gaseous molecules are under a continuous state of motion which is unaffected by gravity (the random straight line motion is known as brownian motion)

(d) Due to the continuous motion, collision between gaseous molecules with the wall of cantainer occurs. The collision with the wall of container are responsible for pressure exerted by the gas on the wall of container.

(e) The molecule moves with different speed, however the speed of each molecule keep on changing as the collision occur.

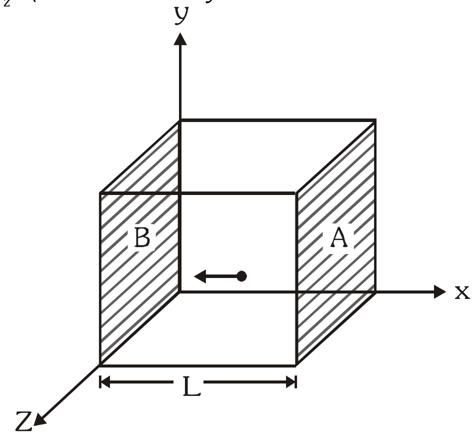
(f) All the collision occuring are considered to be perfectely elastic which implies that there is no loss of energy.

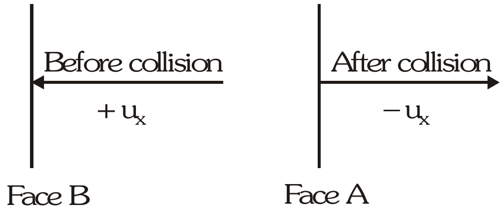
(g) The average kinetic energy of gas will depends on absolute temperature only.

◆ Derivation of Equation for kinetic molecular theory

Let us consider a cube of side L, that has N_0 molecules each of mass m moving with velocity u in all direction and thus colliding with one each other and against sides of the container. Velocity u can be resolved into three components u_x, u_y and u_z along there axes such that

$$u^2 = u_x^2 + u_y^2 + u_z^2 \text{ (assume velocity in ms}^{-1}\text{ and distance in meter)}$$





For a simplest case we consider motion of a molecule along x-axis only in which it moves towards face B with velocity u_x. After collision against face B it moves towards face A with velocity ($-u_x$) collissions being elastic (which results in change in direction but not velocity)

$\therefore$ Momentum before collision on face B = mu_x

Momentum after collision on face B = $-mu_x$

Change in momentum due to one collision on face B

$$= mu_x - (-mu_x) = 2mu_x$$

To strike face B again distance travelled = 2L

Time taken to strike face B again = $\dfrac{2L}{u_x}$ seconds

$\therefore$ Number of collisions per second on face B along x-axis = $\dfrac{u_x}{2L}$

$\therefore$ Change in momentum due to $\dfrac{u_x}{2L}$ collisions per second on face B along x-axis = $2mu_x \cdot \dfrac{u_x}{2L} = \dfrac{mu_x^2}{L}$

Change in momentum per second due to collisions of one molecule on opposite faces A and B along x-axis = $\dfrac{2mu_x^2}{L}$

Similarly for y-axis change in momentum per second = $\frac{2mu_y^2}{L}$ and for z-axis = $\frac{2mu_z^2}{L}$

Total change in momentum per second due to collisions of a single molecule on six faces along three axes

$$= \frac{2mu_x^2}{L} + \frac{2mu_y^2}{L} + \frac{2mu_z^2}{L}$$

$$= \frac{2m}{L}(u_x^2 + u_y^2 + u_z^2) = \frac{2mu^2}{L}$$

But rate of change in momentum per second = Force

$$\therefore \quad \text{Force} = \frac{2mu^2}{L}$$

$$\therefore \quad \text{Pressure} = \frac{\text{Force}}{\text{Area of six faces}} = \frac{\frac{2mu^2}{L}}{6L^2} = \frac{mu^2}{3L^3} = \frac{mu^2}{3V} \qquad [L^3 = \text{volume V}]$$

$\therefore$ Pressure due to collisions of N_0 molecules on six faces of a cube = $\frac{1}{3}$ mN_0u^2

$$PV = \frac{1}{3} mN_0u^2 = \frac{1}{3} Mu^2$$

mN_0 = M (molar mass)

N_0 = Avogadro's number

u = root mean square velocity (U_{rms})

- **Translational kinetic energy of n moles**

$$\frac{1}{2} Mu^2 = \frac{3}{2} PV = \frac{3}{2} nRT$$

- **Average translational kinetic energy per molecule**

$$= \frac{3}{2}\frac{RT}{N_0} = \frac{3}{2} KT$$

Where $K\left(=\frac{R}{N_0}\right)$ is called Boltzmann's constant.

Its numerical value is 1.38 Ч 10^{-16} erg K^{-1} molecule^{-1}

Thus average K.E. is proportional to absolute temperature.

If T = 0 K (i.e., – 273.15°C), then average KE = 0

Thus, absolute zero (0 K) is the temperature at which molecular motion ceases.

DIFFERENT TYPES OF MOLECULAR VELOCITIES

- $PV = \frac{1}{3} MU_{rms}^2$

(i) Root mean square velocity (U_{rms}) : It is defined as the square root of the mean of the squares of the velocities possessed by all the molecules present in the given sample of gas

$$U_{rms} = \sqrt{\frac{U_1^2 + U_2^2 + \ldots U_n^2}{N}}$$

$$\therefore \quad U_{rms} \text{ (root mean square velocity)} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

Where d is the density.

- If N_1 molecules have velocity u_1 and N_2 molecules have velocity u_2, then

$$U_{rms} = \sqrt{\frac{N_1u_1^2 + N_2u_2^2}{N_1 + N_2}}$$

(ii) Average velocity (U_{av}) : It is given by the arithmetic mean of square of the different velocities possessed by the molecules of the gases at a particular temperature.

$$U_{av} = \frac{U_1^2 + U_2^2 + \ldots U_n^2}{n}$$

- ◆ U_{av} (average velocity) $= \sqrt{\frac{8RT}{\pi M}}$

(iii) Most probable velocity (U_{mp}) : It is defined as the velocity possessed by the maximum number of molecules of a gas at a given temperature.

- ◆ U_{mp} (most probable velocity) $= \sqrt{\frac{2RT}{M}}$
- ◆ If P and T both are given, use equation in terms of temperature i.e. use

$$U_{rms} = \sqrt{\frac{3RT}{M}} \text{ and not } \sqrt{\frac{3PV}{M}}$$

- ◆ To have velocity in ms^{-1} (MKS) take $R = 8.314\ J\ mol^{-1}K^{-1}$, M in kg.
- ◆ If density is in $kg\ m^{-3}$ and P in $N\ m^{-2}$, velocity will be in ms^{-1}.

Relation between rms velocity, average velocity and most probable velocity.

- ◆ $U_{rms} : U_{av} : U_{mp} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{2RT}{M}} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = 1.2248 : 1.1284 : 1$

$$U_{rms} = 1.2248\ U_{mp}$$
$$U_{av} = 1.1284\ U_{mp}$$
$$U_{mp} = 1.0854\ U_{av}$$

❑ Distribution of molecular speeds :

(a) The speed of a molecule of a gas changes continuously as a result of collisions with other molecules and with the walls of the container. Thus, the net result is that we cannot speak of the speed of individual molecule; hence must consider the statistical averages of the speeds of the whole collection of gas molecules.

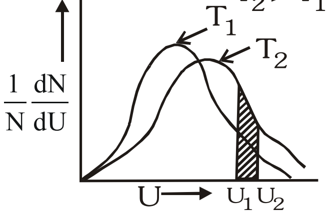
(b) The manner in which the molecules of a gas are distributed over the possible speed ranges, from zero to very high values, was first investigated by Maxwell using the theory of probability. His results are expressed as the law of distribution of molecular speeds, one form of which is

$$dN = 4\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mu^2}{2\pi KT}} u^2 du$$

(c) The above expression gives the no. of molecules dN having speeds between U and U + du in terms of total no. of molecules, N present in the gas m is mass of single gas molecule and T is the absolute temperature of gas.

(d) The Maxwell distribution of speeds is customarily plotted with the fraction $\frac{1}{N}\left(\frac{dNu}{dU}\right)$ as the ordinate and U as the abscissa.

$$\frac{1}{N}\left(\frac{dN}{dU}\right) = \frac{1}{du}\left(\frac{dN}{dU}\right)$$



So, the term, $\frac{1}{N}\frac{dN}{dU}$ represents the fraction of molecules in the speed range of u to u + du per unit interval of speed. Roughly speaking, this gives the probability of finding a molecule with a speed between u and (u + du). The distribution of two temperatures is shown in the fig.

(e) The curve at any temperature is parabolic near the origin, since the factor u^2 is dominant in this region, the exponential function being approximately equal to unity. At high values of u, however, the exponential factor dominates the behaviour of the function, causing it to decrease rapidly in value. As a consequence of the contrasting behaviour of two factors, the product function passes through a maximum at a speed known as the most probable speed (U_{mps}). Thus, the most probable speed is the speed possessed by the maximum fraction of the molecules.

(f) It can be seen from the given figure, that the fraction of molecules having either very low speeds or very high speeds are small in numbers. The total area under the curve gives the total no. of molecules in the collection i.e. the no. of molecules comprising of all speeds. The area under the curve between any two speeds, for example, U_1 and U_2, gives the total no. of molecules having speed between these two values.

(g) The given figure illustrates the distribution of speeds at two temperatures T_1 and T_2. Since the total no. of molecules is the same at both temperatures, increases the K.E. of the molecules, it follows that fraction of molecules having lower speed range decreases whereas fraction of molecules having higher speed range increases on increasing the temperature.

(h) Also the curve at the higher temperature T_2 has its U_{mps} shifted to a higher value compared with that for T_1, whereas corresponding fraction of molecules has decreased. But at the same time, the curve near U_{mps} has become broader at the higher temperature indicating the more molecules possess speeds near to most probable speed.

(i) The value of U_{mps} can be calculated easily, based on the concept of maximum or minimum value of a function.

$$dN = 4\pi N\left(\frac{m}{2\pi RT}\right)^{3/2} e^{-mU^2/2KT}\, u^2\, du$$

or
$$\frac{1}{N}\frac{dN}{du} = 4\pi\left(\frac{m}{2\pi RT}\right)^{3/2} e^{-mU^2/2KT}\; u^2$$

Differentiating both sides with respect to U

$$\frac{d}{du}\left(\frac{1}{N}\frac{dN}{du}\right) = 4\pi\left(\frac{m}{2\pi RT}\right)^{3/2}\left[2u\, e^{-mu^2/2KT} + u^2\left(-\frac{2mu}{2KT}\right)e^{-mu^2/2KT}\right]$$

For maximum

$$\frac{d}{du}\left(\frac{1}{N}\frac{dN}{du}\right) = 0$$

$$\therefore \quad 4\pi\left(\frac{m}{2\pi RT}\right)^{3/2}\left[2u\, e^{-mu^2/2KT} + u^2\left(-\frac{2mu}{2KT}\right)e^{-mu^2/2KT}\right] = 0$$

or
$$2u\, e^{-mU^2/2KT}\left[1 - \frac{mu^2}{2KT}\right] = 0$$

Now at the condition of mps, $U \neq 0$ and $e^{-mU^2/2KT} = 0$ when $U = \infty$, but at the condition of U_{mps}, $U \neq \infty$.

$$\therefore \quad e^{-mU^2/2KT} = 0$$

$$\therefore \quad 1 - \frac{mU^2}{2KT} = 0 \Rightarrow \frac{mU^2}{2KT} = 1$$

or
$$U = \sqrt{\frac{2KT}{m}}$$

$$\therefore \quad U_{mps} = \sqrt{\frac{2KT}{m}} = \sqrt{\frac{2RT}{M}}$$

◆ **Maxwell Distribution curve for energy :**

$$E = \frac{1}{2}MU^2$$

$$U = \sqrt{\frac{2E}{M}}$$

$$dE = \frac{1}{2}M \times 2\ UdU$$

$$dE = MU\ dU$$

$$UdU = \frac{dE}{M}$$

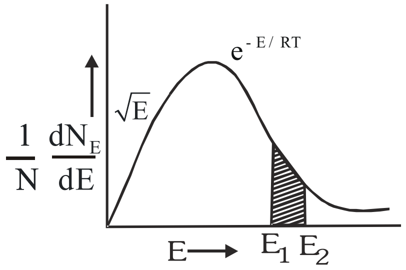
By Maxwell equation :

$$dN = 4\pi\ N\left(\frac{M}{2\pi RT}\right)^{3/2}.e^{\frac{-Mu^2}{2RT}}\ U.\ UdU$$

$$dN_E = 4\pi N\left(\frac{M}{2\pi RT}\right)^{3/2}.e^{-\left(\frac{E}{RT}\right)}\sqrt{\frac{2E}{M}}\ \frac{dE}{M}$$

$$dN_E = 2\pi N\left(\frac{1}{\pi RT}\right)^{3/2}.e^{\frac{-E}{RT}}\sqrt{E}\ dE$$

$$\frac{1}{N}\left(\frac{dN_E}{dE}\right) = 2\pi\left(\frac{1}{\pi RT}\right)^{3/2}\sqrt{E}\ e^{-E/RT}$$



The shaded area of this graph indicates the fraction of particle having energy between E_1 and E_2.

From maxwell equation we are able to calculate the total no. of particles which are having energy greater than threshold energy (Activation energy) [for a chemical reaction to occur, reactant need some minimum amount of energy which is called as threshold energy or activation energy].

$$dN_E = 2\pi N\left(\frac{1}{\pi RT}\right)^{3/2}\int_{E_a}^{\infty}\sqrt{E}\ e^{-\sqrt{\frac{E}{RT}}}\ dE$$

From the above equation we calculate the total no. of particles which will participate in chemical reaction.

Ex. (a) Calculate the pressure exerted by 10^{23} gas molecules, each of mass 10^{-25} kg, in a container of volume 1×10^{-3} m^3 and having root mean square velocity of 10^3 ms^{-1}.

(b) Also calculate total kinetic energy and

(c) temperature of the gas.

Sol. (a) By kinetic theory

$$P = \frac{1}{3}\frac{mNu^2}{V} = \frac{1\times10^{-25}\times10^{23}\times(10^3)^2}{3\times10^{-3}} = 3.33 \times 10^6\ N\ m^{-2}$$

(b) Total KE $= \left(\frac{1}{2}mu^2\right) \times N$

$$= \frac{1}{2} \times 10^{-25} \times (10^3)^2 \times 10^{23} = \frac{1}{2} \times 10^4 = 0.5 \times 10^4\ J$$

(c) Also total KE $= \frac{3}{2}nRT$, where n (mole) $= \frac{10^{23}}{N_A} = \frac{10^{23}}{6.023\times10^{23}}$

$$0.5 \times 10^4 = \frac{3}{2} \times \frac{10^{23}}{6.023 \times 10^{23}} \times 8.314 \times T$$

$$\therefore \qquad T = \frac{0.5 \times 10^4 \times 2 \times 6.023}{3 \times 8.314} = 2415 \text{ K}$$

Ex. A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of 7.57×10^3 Nm^{-2}. Calculate the root mean square velocity of the gas molecules.

Sol. No. of gas molecules = 2×10^{21}

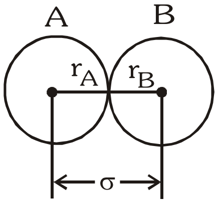
6.023×10^{23} molecules of nitrogen weight = 28 g

2×10^{21} molecules of N_2 weights = $\frac{28 \times 2 \times 10^{21}}{6.023 \times 10^{23}}$ g = 0.093 g

$$\therefore \qquad \text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{0.093}{1} \text{ g/L} = \frac{0.093 \times 10^{-3}}{10^{-3}} = 0.093 \text{ kg/m}^3$$

$$U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}} = U_{rms} = \sqrt{\frac{3 \times 7.57 \times 10^3}{0.093}} = 494.16 \text{ m/s}$$

❑ COLLISION THEORY



Collision diameter : It is the closest distance between the centres of two molecules taking part in collision.

collision diameter (σ) = $r_A + r_B$

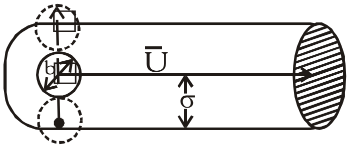
Collision Frequency :

It is the number of molecular collisions taking place per second per unit volume of the gas.

Determination of number of bimolecular collisions :

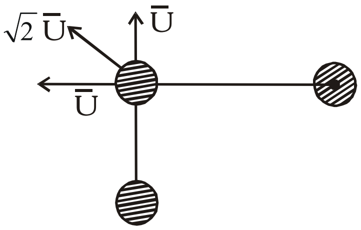
(a) While considering the molecules among themselves the molecules to be rigid, non-interacting and spherical with diameter σ. It is also assumed that all the molecules move with the same speed. The arithmetic mean of speed is $\overline{U}$.

(b) Two identical molecules of diameter σ will just touch each other when the distance separating their centres is σ. Thus, a moving molecule will collide with other molecules whose centres come within a distance of σ from its centre. The quantity $\pi\sigma^2$ is called the collision cross-section for the rigid spherical molecule. It is obvious that this collision cross-section is an area of an imaginary sphere of radius σ around the molecule within which the centre of another molecule cannot penetrate.



(c) If the molecule is moving with an average speed $\overline{U}$, then in a unit time area swept out by a single molecule is $\pi\sigma^2$ $\overline{U}$. If N* is the no. of molecules within the volume $\pi\sigma^2$ $\overline{U}$, the no. of collisions by a single molecule in a unit time will be $\pi\sigma^2$ $\overline{U}$ N*.

(d) So, far, we have assumed that only one molecule is moving and all other are stationary. In practice however, this is not true. In order to account for the movements of all molecules, we must consider the average velocity along the line of centres of two colliding molecules instead of average velocity of a single molecule. If it is assumed that, on an average, molecules collide while approaching each other perpendicularly, then the average velocity along their centre is $\sqrt{2}\ \overline{U}$ as shown below.



∴ The no. of collisions made by a single molecule with other molecules per unit time (collision number) are given by

$$z_1 = \sqrt{2}\,\pi\sigma^2\ \overline{U}\,N^*$$

(e) The total number of bimolecular collision per unit time is given as z_{11} (collision frequency)

$$z_{11} = \frac{1}{2}(z_1N^*) = \frac{1}{2}\,\text{Ч}\ N^*\ \text{Ч}\ \sqrt{2}\ \pi\sigma^2\ \overline{U}\ N^*$$

$$= \frac{1}{\sqrt{2}}\ \pi\sigma^2\ \overline{U}\ N^{*2}$$

(f) If the collisions involve two unlike molecules, the no. of bimolecular collision is given as z_{12}.

$$z_{12} = \frac{1}{\sqrt{2}}\ \pi{\sigma_{12}}^2 < u_0 > N_1N_2$$

Where N_1 and N_2 are the no. of molecules per unit volume of the two types of gases, σ_{12} is the average diameter of two molecules, that is

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \quad \text{or} < u_0 > = [u_1^2 + u_2^2\ 7]^{1/2} \text{ and}$$

$$u_1^2 = \frac{8RT}{\pi M_1}, \qquad u_2^2 = \frac{8RT}{\pi M_2}$$

◆ **Determination of mean free path and its dependence on pressure and temperature :**

(a) The mean free path is the average distance travelled by a molecule between two successive collisions. We can express it as follows :

$$\lambda = \frac{\text{Average distance travelled per unit time}}{\text{No. of collsions made by single molecule per unit time}}$$

$$\lambda = \frac{\overline{U}}{z_1} = \frac{\overline{U}}{\sqrt{2}\pi\sigma^2\overline{U}N^*} = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

(b) According to ideal gas equation,

$$PV = nRT = \frac{N^1}{N_A}RT$$

or $$P = \left(\frac{N^1}{V}\right)\left(\frac{R}{N_A}\right)T = \left(\frac{N^1}{V}\right)KT$$ (where K is known as Boltzmann's constant)

Now $\frac{N^1}{V} = N^*$,

∴ $$P = N^*\ KT \quad \text{or} \quad N^* = \frac{P}{KT} \quad \text{or} \quad N^* \propto \frac{P}{T}$$

(c) $$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

$$\lambda = \frac{1}{N^*} \quad \text{or} \quad \lambda \propto \frac{T}{P}$$

Since, according to gas law $P \propto T$ at constant volume

∴ λ = constant at constant volume.

Thus there will no effect of changing T or P on λ, if the volume of the gas is kept constant.

(d) Now $z_1 = \sqrt{2}\,\pi\sigma^2\,\overline{U}\,N^*$

$\overline{U} \propto \sqrt{T}$ $\therefore$ $\overline{U} = K_1\sqrt{T}$

$N^* \propto \frac{P}{T}$ $\therefore$ $N^* = K_2\frac{P}{T}$

$$\therefore\ z_1 = \sqrt{2}\,\pi\sigma^2 K_1 K_2 \frac{P}{\sqrt{T}}$$

$$\therefore\ z_1 = K'\frac{P}{\sqrt{T}}$$

Now $z_1 \propto P$ when T constant and $z_1 \propto \frac{1}{\sqrt{T}}$ when pressure is held constant.

At constant volume $P \propto T$ or $P = K''\,T$

$$\therefore\quad z_1 = \frac{K'K''T}{\sqrt{T}}$$

or $z_1 \propto \sqrt{T}$ when volume is constant.

Again $z_1 \propto \sqrt{P}$ when volume is constant.

(e) $z_{11} = \frac{1}{\sqrt{2}}\,\pi\sigma^2\,\overline{U}\,N^{*2}$

or $z_{11} \propto \overline{U}\,N^{*2}$

or $z_{11} \propto \sqrt{T}\left(\frac{P}{T}\right)^2$

or $z_{11} \propto \frac{P^2}{T^{3/2}}$

Thus $z_{11} \propto p^2$ when temperature is held constant and $z_{11} \propto T^{-3/2}$ when pressure is held constant

At constant volume

$z_{11} \propto T^{-1/2}$ and $z_{11} \propto P^{1/2}$.

❑ IDEAL AND REAL GAS

An ideal gas is a hypothetical gas whose pressure, volume and temperature behaviour is completely described by the ideal gas equation. Actually no gas is ideal or perfect in nature. All gases are real gases.

Real gases do not obey the ideal gas laws exactly under all conditions of tamperature and pressure.

Real gases deviates from ideal behaviour because of mainly two assumptions of "Kinetic theory of gases".

(i) The volume of gas particle is negligible compared to volume of container (while the real gas particle have some significant volume).

(ii) There is no interaction between gaseous particles (while attraction forces exist between real gas particles).

◆ Deviation from Ideal behaviours :

Compressibility factor :

The extent to which a real gas departs from the ideal behaviour may be expressed in terms of compressibility factor (Z), where Z is

$$Z = \frac{V_m}{V_{m(ideal)}} = \frac{PV_m}{RT} \quad [V_m = \text{molar volume}]$$

When $Z > 1$, $V_m > 22.4$ lit at STP ; When $Z < 1$, $V_m < 22.4$ lit at STP

◆ **Plots of compressibility factor vs pressure :**

(i) For an ideal gas Z = 1 and is independent of temperature and pressure.

(ii) Exceptional behaviour of H_2 and He :

for these gases Z > 1. For such gases repulsive forces predominants.

(iii) Effect of pressure :

At very low P, $PV \approx RT$ i.e. $Z \approx 1$

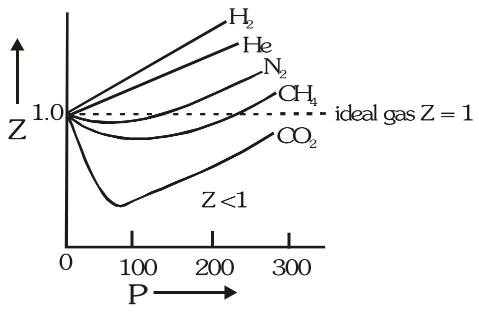
At low P, $PV < RT$ i.e. $Z < 1$

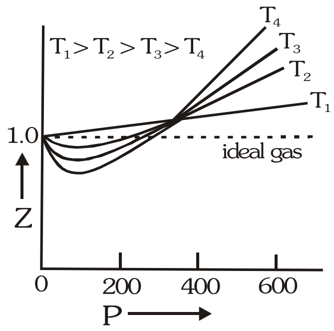
At moderate P, $PV \approx RT$ i.e. $Z \approx 1$

At high P, $PV > RT$ i.e. $Z > 1$

(iv) For the gases which are easily liquefied (e.g. CO_2) Z dips sharply below the ideal line in the low pressure region.

(v) Effect of temperature : An increase in temperature shows a decrease in deviation from ideal behaviours i.e. PV approaches unity or Z approaches unity with increase in temperature.





◆ **Boyle's temperature :**

The temperature at which a real gas behaves like an ideal gas over an appreciable range of pressure is known as Boyle's temperature (T_B). It means that at this temperature, the value of PV remains constant for an appreciable range of pressure, i.e. Boyle's Law is abeyed. Mathematically we may express the Boyle temperature or Boyle point as the temperature where $\frac{\partial(PV)}{\partial P} = 0$ when $P \to 0$.

So to use ideal gas equation for real gas, we will use some correction factor for volume as well as for pressure.

(A) **Volume correction** : Anil ahlawat (Page 154-)

In the ideal gas equation, $P_iV_i = nRT$, V_i represents the ideal volume where the molecules can move freely. In real gases, a part of the total volume is occupied by the gas molecules. Hence the free volume V_i is the total volume V minus the volume occupied by the gas molecules.

i.e. Real volume of gas = Actual volume of container − volume occupied by N molecules in motion.

$V_i = V - b$ for one mole of gas

$V_i = V - nb$ for n mole of gas

Where b is termed the 'excluded volume' or 'co-volume'.

It is constant and characteristic for each gas.

$b = \left(\frac{4}{3}\pi r^3\right) \times 4N$

[where r = radius of gas molecule, N = Avogadro's number]

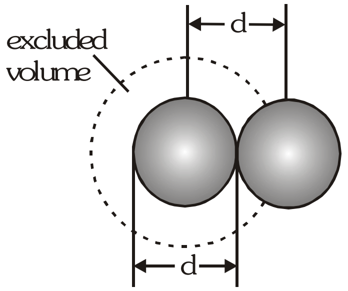
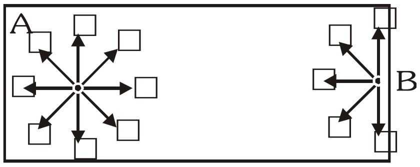


Illustration of excluded volume

(B) Pressure correction :

In order to take account the effect of intermolecular forces of attraction, let us consider a molecule A is the midst of the vessel.



This molecule is surrounded by other molecules in a symmetrical manner and is being attracted uniformly on all sides by the neighbouring molecules with the result that this molecule on the whole experiences no net force of attraction.

Now, consider a molecule B near the side of the vessel, which is about to strike one of its sides, thus contributing towards the total pressure of the gas. There are molecules only on one side of the vessel, i.e. towards its centre, with the result that this molecule experiences a net force of attraction towards the centre of the vessel. This results in decreasing the velocity of the molecule, and hence its momentum. Thus, the molecule does not contribute as much force as it would have, had there been no force of attraction. Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas.

Van der Walls noted that the total force of attraction on any molecule about to hit a wall is proportional to the concentration of neighbouring molecules, n/V. However, the number of molecules about to hit the wall per unit wall area is also proportional to the concentration n/V. Therefore, the force per unit wall area, or pressure, is reduced from that assumed in the ideal gas wall by a factor proportional to n^2/V^2. Letting a be the proportionality constant, we can write

$$P\text{ (actual)} = P\text{(ideal)} - n^2a/V^2$$

or $$P\text{ (ideal)} = P\text{(actual)} + n^2a/V^2$$

'a' is a constant which depends upon the nature of the gas, V is the volume of 1 mole of gas.

Combining the two corrections, for 1 mole of gas

$$\left(P+\frac{a}{V^2}\right)(V - b) = RT$$

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

The constants 'a' and 'b' :

Van der Waals constant for attraction 'a' and volume 'b' are characteristic constants for a given gas.

(i) The 'a' values for a given gas are measure of intermolecular forces of attraction. More are the intermolecular forces of attraction, more will be the value of a.

(ii) For a given gas van der Waals constant of attraction 'a' is always greater than van der Waals constant of volume 'b'.

(iii) The gas having higher value of 'a' can be liquefied easily and therefore H_2 and He are not liquefied easily.

(iv) Unit of 'a' is $\text{lit}^2\ \text{mole}^{-2}$ atm or $\text{cm}^4\ \text{mole}^{-2}$ dyne.

(v) Unit of 'b' is lit mole^{-1} or $\text{cm}^3\ \text{mole}^{-1}$.

(vi) At low pressure, volume correction for 1 mole of gas is negligible,

$\therefore$ b = 0

The gas equation can be written as

$$\left(P+\frac{a}{V^2}\right)V = RT \qquad \text{or} \qquad Z = \frac{PV_m}{RT} = 1 - \frac{a}{V_mRT}$$

where V_m = molar volume

where Z is known as the compressibility factor.

(vii) At higher pressures, the pressure correction for 1 mole of gas is negligible

$$\therefore \frac{a}{V^2} = 0$$

or $(P + 0)(V - b) = RT$ or $P(V_m - b) = RT$

or $PV_m = RT + Pb$ or, $Z = \frac{PV_m}{RT} = 1 + \frac{Pb}{RT}$

❑ The van der Walls constants for some common gases

Gas	a (dm^6 atm mol^{-2})	b ($dm^3 mol^{-1}$)
Ammonia	4.17	0.0371
Argon	1.35	0.0322
Carbon dioxide	3.59	0.0427
Carbon monoxide	1.49	0.0399
Chlorine	6.49	0.0562
Ethane	5.49	0.0638
Ethanol	2.56	0.087
Ethylene	4.47	0.0571
Helium	0.034	0.0237
Hydrogen	0.024	0.0266
Hydrogen chloride	3.67	0.0408
Hydrogen bromide	4.45	0.0433
Methane	2.25	0.0428
Neon	0.21	0.0171
Nitric oxide	1.34	0.0279
Nitrogen	1.39	0.0319
Oxygen	1.36	0.0318
Sulphur dioxide	3.71	0.0564
Water	5.44	0.0305

❑ LIQUEFACTION OF GASES AND CRITICAL POINTS

The phenomenon of converting a gas into liquid is known as liquefaction. The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that exist in the liquid. A gas can be liquefied by :

(a) **Increasing pressure** : An increase in pressure results in an increase in attraction among molecules.

(b) **Decreasing temperature** : A decrease in temperature results in a decrease in kinetic energy of molecules.

❑ ANDREWS ISOTHERMS :

The essential conditions for liquefaction of gases were discovered by Andrews (1869) as a result of his study of P–V–T relationship for CO_2.The types of isotherms are shown in figure.

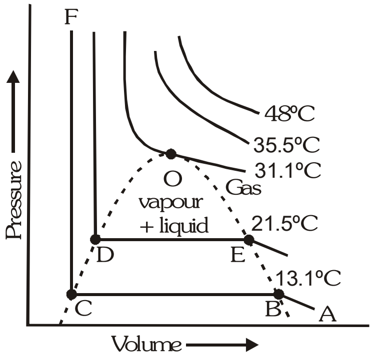


Fig : Isotherms for carbon dioxide showing critical region

❑ Observations from figure :

(a) **At low temperatures** : For the curve ABCF, as the pressure increases, volume of the curve decreases (curve A to B).

At point B, at constant pressure, liquefaction commences and the volume decreases rapidly (because gas is converted to liquid with higher density).

At point C, liquefaction is complete. The line CF represents the variation of V with P of the liquid state. The steepness of the line CF indicates that the liquid cannot be easily compressed. Thus AB, represent gaseous state, BC represent liquid and vapour in equilibrium.

CF represent liquid state.

The pressure corresponding to the line BC is there vapour pressure of the liquid.

(b) **At higher temperatures** : Similar type of curve as in case (a) is obtained but the width of the horizontal portion is reduced. The pressure corresponding to this portion is higher than at lower temperatures.

(c) **At high temperatures** : (like 48°C), the isotherms are like those of ideal gas.

(d) **At temperature (31.1°C)** : The horizontal portion is reduced to a point.

The isotherm at T_C is called **critical isotherm**.

At point O, $\frac{dP}{dV} = 0$.

The point O is called the **point of inflection**.

Critical temperature (T_C) : The maximum temperature at which gas can be liquefied by the application of pressure alone i.e. the temperature above which a liquid cannot exit is called the critical temperature T_C.

Critical pressure (P_C) :The minimum pressure required to liquefy the gas at the temperature T_C is called the critical pressure P_C.

Critical volume (V_C) :The volume occupied by one mole of the gas at critical temperature, T_C and critical pressure, P_C is called the critical volume (V_C) of the gas.

Determination of value of P_C, V_C and T_C :

(a) The vander waal's equation is

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

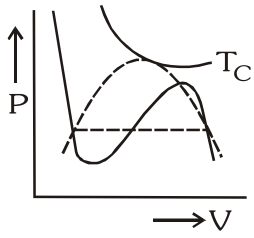
or $$PV_m + \frac{a}{V_m} - Pb - \frac{ab}{V_m^2} = RT$$

or $$V_m + \frac{a}{P} \times \frac{1}{V_m} - b - \left(\frac{ab}{P}\right)\frac{1}{V_m^2} = \frac{RT}{P}$$

or $$V_m^3 + \frac{a}{P}V_m - bV_m^2 - \frac{ab}{P} = \frac{RTV_m^2}{P}$$

or $$V_m^3 - \left(b + \frac{RT}{P}\right)V_m^2 + \frac{a}{P}V_m - \frac{ab}{P} = 0 \qquad \text{.... (1)}$$

(b) This equation has three roots in V_m for given values of a, b, P and T. It is found that either all the three roots are real or one is real and the other two are imaginary.



(c) The main characteristics of the figure are as follow :

(i) At higher temperature than T_C the isotherm exhibits a maximum and a minimum for certain values of pressures, the equation gives three roots of volume e.g., V_1, V_2 and V_3 at pressure P_1.

(ii) On increasing the temperature, the three roots become closer to each other and ultimately at critical temperature, they become identical. Thus, the cubic equation V_m can be written as

$$(V_m - V')(V_m - V'')(V_m - V''') = 0$$

At the critical point $V' = V'' = V''' = V_C$

$\therefore$ the equation becomes,

$$(V_m - V_C)^3 = 0$$

or $$V_m^3 - V_C^3 - 3V_C V_m^2 + 3 V_C^2 V_m = 0$$

from eq. (1)

$$V_m^3 - \left(b + \frac{RT}{P}\right)V_m^2 + \frac{a}{P}V_m - \frac{ab}{P} = 0$$

(d) By comparing the coefficients

$$3V_C = b + \frac{RT_C}{P_C},\quad 3V_C^2 = \frac{a}{P_C},\quad V_C^3 = \frac{ab}{P_C}$$

By solving, $V_C = 3b$, $P_C = \frac{a}{27b^2}$ and $T_C = \frac{8a}{27Rb}$

(e) Therefore the value of critical compressibility factor in terms of vander wall's constants is given by

$$Z = \frac{P_CV_C}{RT_C} = \frac{\frac{a}{27b^2} \times 3b}{R \times \frac{8b}{27Rb}} = \frac{\frac{a}{9b}}{\frac{8Ra}{27Rb}} = \frac{\frac{a}{9b}}{\frac{8a}{27b}}$$

$$Z = \frac{P_CV_C}{RT_C} = \frac{a}{9b}\ \text{Ч}\ \frac{27b}{8a} = \frac{3}{8} = 0.375$$

(f) If we compart the value of $\frac{P_CV_C}{RT_C} = 0.375$, with the experimental values, it has been found that the agreement is very poor.

(iv) Boyle temperatures in terms of van der Waals constant :

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

Critical constants of gases

Gas	P_C (atm)	$V_{m,c}$ (cm^3mol^{-1})	T_C (K)
He	2.26	57.9	5.2
Ne	26.9	41.7	44.4
Ar	48.1	75.2	150.7
Xe	58.0	119.0	289.7
H_2	12.8	65.5	33.3
O_2	50.1	78.2	154.8
N_2	33.5	90.1	126.2
CO_2	72.8	94.0	304.2
H_2O	218.0	55.6	647.3
NH_3	111.5	72.5	405.0
CH_4	45.6	98.7	190.6
C_2H_6	48.2	148.0	305.4

EQUATION OF CORRESPONDING STATE :

All the equation defined for real gases involved gas dependent constant, hence if for two real gases n,P, V are same then the fourth parameter need not to be same and can be calculated only when the gas dependent constant is known. However instead of pressure, temperature, moles and volume, new reduced parameter are defined such that-

$$P_r = \left(\frac{P}{P_C}\right) \quad \Rightarrow \text{Reduced Pressure}$$

$$T_r = \left(\frac{T}{T_C}\right) \quad \Rightarrow \text{Reduced temperature}$$

$$V_r = \left(\frac{V}{V_C}\right) \quad \Rightarrow \text{Reduced volume}$$

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

$$\left[P_rP_c+\frac{a}{(V_rV_c)^2}\right](V_rV_c - b) = R \text{ Ч } T_rT_c$$

$$\left(P_r+\frac{3}{V_r^2}\right)(3V_r - 1) = 8\ T_r$$

From this equation the law of corresponding state can be stated two real gas having same no. of moles are at same reduced temperature and same reduced volume then they have same reduced pressure.

Ex. For 1 mole gas reduced temperature is 3 and reduced volume is 10. If critical pressure is 42 atm then calculate the pressure exerted by 1 mole of real gas.

Sol.

$$\left(P_r+\frac{3}{V_r^2}\right)(3V_r - 1) = 8\ T_r$$

$$\Rightarrow \left(P_r+\frac{3}{(10)^2}\right)(3\text{Ч }10 - 1) = 8 \text{ Ч } 3 \qquad \Rightarrow \quad P_r = \frac{24}{29}-\frac{3}{100}$$

$$P = P_rP_c = \left(\frac{24}{29}-\frac{3}{100}\right)42 = 33.49 \text{ atm}$$

Law of equiparition of energy :

This law states that is energy of the molecule (due to translational, rotational, vibrational motion) is represented as a sum of independent significant terms (which are proportional to v^2 (velocity), ω^2 (angular velocity) and x^2 (displacement) then each of the significant term contribute to $\frac{RT}{2}$ in average K.E. per mole of the system).

DEGREE OF FREEDOM :

Number of independent co-ordinates or axis required to represent position or motion of the molecules is called as degree of freedom (for a system comprising of N atoms, total 3N degree of freedom are available, out of which some of translational, some are rotational and the other are vibrational).

Translation Degree of Freedom :

Motion of any molecule can be represented along three independent coordinates or axis so translational degree of freedom is always three (these are significant at all temperatures for the gas).

$$\text{T.E.} = \frac{1}{2}mV_x^2 + \frac{1}{2}mV_y^2 + \frac{1}{2}mV_Z^2$$

$$\text{T.E. (per mole)} = \frac{RT}{2} + \frac{RT}{2} + \frac{RT}{2} = \frac{3RT}{2}$$

Each degree of freedom contributes to $\frac{RT}{2}$ in average K.E. per mole.

◆ **Rotational Degree of Freedom** :

(i) For monoatomic molecule rotational energy is $\frac{1}{2}I\omega^2$ will be insignificant (if rotation is about its own axis.)

(ii) For polyatomic gases :

(a) Non-linear complete rotation can be represented along three perpendicular axis (this is significant at moderate temperature).

(b) Linear : only two independent axis are required to represent total energy due to rotation.

For non Linear (NL) :

$$\text{R.E.} = \frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2 + \frac{1}{2}I\omega_z^2 \qquad \text{(Here I = moment of Inertia)}$$

$$\text{R.E. per mole} = \frac{RT}{2} + \frac{RT}{2} + \frac{RT}{2} = \frac{3RT}{2}$$

For Linear :

$$\text{R.E.} = \left(\frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2\right) \text{ or } \left(\frac{1}{2}I\omega_y^2 + \frac{1}{2}I\omega_z^2\right) \text{ or } \left(\frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_z^2\right)$$

$$\text{R.E. per mole} = \frac{RT}{2} + \frac{RT}{2} = RT$$

These are influencial only at moderate temperature.

◆ **Vibrational degree of freedom** :

(a) For linear molecule = 3N – 5.

(b) For non-linear molecule = 3N – 6.

where N is no. of atoms present in a molecule.

Each vibrational degree of freedom comprises of two energy terms.

$$\text{V.E.} = \frac{1}{2}mv^2 + \frac{1}{2}Kx^2$$

vibrational degree of freedom contributes RT to average K.E. per mole.

These are significant only at a very high temperature.

❑ **HEAT CAPACITY**

It is the amount of heat required to raise the temperature of 1 mole or 1 gram of a substance through 1°C or 1 K.

If it is measured per mole of substance then it is called as molar heat capacity.

If it is measured in per gram of substance then it is called as specific heat.

$$C = \frac{q}{n \times \Delta T} \qquad \text{(C = molar heat capacity, q = Heat given)}$$

(i) Heat capacity at constant pressure

$$C_P = \frac{q_p}{n \times \Delta T} = \frac{\Delta H}{n\Delta T}$$

$q_p = \Delta H$ = Enthalpy change.

(ii) Heat capacity at constant volume

$$C_V = \frac{q_p}{n\Delta T} = \frac{\Delta U}{n \times \Delta T}$$

$q_V = \Delta U$ = change in internal energy

molar heat capacity is a function of temperature.

$C = f(T)$

$C = (a + bT + CT^2 + ...)$ (where a, b, c are constant)

$$q = n\int_{T_1}^{T_2} C\,dT$$

$$q_V = C_V\,(T_2 - T_1) = \text{K.E./ mole}$$

K.E./ mole = $C_V\,(\Delta T)$

$$C_V = \frac{\text{K.E/mole}}{\Delta T}$$

at T temperature :

$$C_V = \frac{\text{K.E/mole}}{T}$$

For ideal gas $C_P - C_V = R$ (here R = ideal gas constant)

	C_V	C_P	$C_P/C_V = \gamma$ (Poission's Ratio)
Monoatmic gas	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{3} = 1.66$
Diatomic gas	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{9}{7} = 1.28$

For 'N' atomic molecules the degree of dissociation is 3N.

(i) If the gas is monoatomic :

(a) It will have three degree of freedom for K.E. since each degree of freedom provides $\frac{1}{2}KT$ amount of energy therefore total K.E. is $\frac{3}{2}KT$ (It will not have any rotational or vibrational degree of freedom).

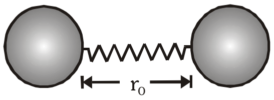
(ii) If gas is diatomic : Total degree of freedom is six.

(a) Out of which 3 is translational degree of freedom, therefore total energy $\frac{3}{2}KT$.

(b) Out of which 2 will be rotational degree of freedom -

$$\text{R.E.} = \frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2 = \frac{1}{2}KT + \frac{1}{2}KT = KT$$

(c) Remaining is vibrational degree of freedom is one.



Energy concerned with the vibration motion corresponds to energy because of relative motion + change in position from equilibrium position.

$$\text{V.E.} = \frac{1}{2}m\left(\frac{dr}{dt}\right)^2 + \frac{1}{2}K\,(r_o - r)$$

$$= \frac{1}{2}m\left(\frac{dr}{dt}\right)^2 + \frac{1}{2}Kx^2 \text{ (Here x is displacement from equilibium position)}$$

$$= \frac{1}{2}KT + \frac{1}{2}KT = KT$$

So each vibrational degree of freedom will provide KT amount of energy.

We consider the vibrational degree of freedom at very high temperature.

(iii) If gas is triatomic : Total degree of freedom is nine.

(a) Out of which $\frac{3}{2}KT$ is translational.

(b) If linear then it will have two degree of freedom of rotational.

(c) Vibrational will have four degree of freedom

$$T.E. = \frac{3}{2}KT + KT + 4KT = \frac{13}{2}KT$$

	C_V	C_P	$C_P/C_V = \gamma$ (Poission's Ratio)
Triatomic (linear)	$\frac{13}{2}R$	$\frac{15}{2}R$	$\frac{15}{3} = 1.15$
Non linear	6R	7R	$\frac{7}{6} = 1.16$

If vibration is ignored at lower temperature.

	C_V	C_P	$C_P/C_V = \gamma$
Diatomic	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5} = 1.4$
Triatomic (linear)	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5} = 1.4$
Triatomic (Non linear)	3R	4R	$\frac{4}{3} = 1.33$

Temperature above which gases gives heating effect and below this cooling effect in process of adiabatic expansion.

$T_{exp.} > T_i \longrightarrow$ heating

$T_{exp.} < T_i \longrightarrow$ Cooling

$T_{exp.} = T_i \longrightarrow$ No cooling, No heating

$$T_i = \frac{2a}{Rb} = 2 \text{ Ч } T_b$$

T_i for H_2 gas = 193 K

T_i for He gas = 33 K

Ex. Calculate the pressure exerted by 5 mole of CO_2 in one litre vessel at 47°C using van der waal's equation. Also report the pressure of gas if it behaves ideal in nature.

Given that a = 3.592 atm lt^2 mol^{-2}, b = 0.0427 L/mol. Also, if the volume occupied by CO_2 molecules is negligible, then calculate the pressure exerted by one mole of CO_2 gas at 273 K.

Sol. Vander waal's equation

$$\left[p + \frac{n^2a}{V^2}\right][V - nb] = nRT$$

$n_{CO_2} = 5$, V = 1 litre, T = 320 K, a = 3.592, b = 0.0427

$$\therefore \quad \left[P + 25 \times \frac{3.592}{1}\right][1 - 5 \text{ Ч } 0.0427] = 5 \text{ Ч } 0.0821 \text{ Ч } 320$$

$$\therefore \quad P = 77.218 \text{ atm}$$

For ideal behaviour of gas, PV = nRT

∴ P Ч 1 = 5 Ч 0.0821 Ч 320

∴ $P = 131.36$ atm

For one mole $\left[P+\frac{a}{V^2}\right][V - b] = RT$

$$\therefore \quad P = \frac{RT}{V} - \frac{a}{V^2}$$

$$\therefore \quad P = \frac{0.0821 \times 273}{22.4} - \frac{3.592}{(22.4)^2}$$

∴ $P = 0.9922$ atm

The volume occupied by 1 mole at 273 K is 22.4 litre if b is negligible.

Ex. Two moles of ammonia gas are enclosed in a vessel of 5 litre capacity at 27°C. Calculate the pressure exerted by the gas, assuming that

(i) the gas behaves like an ideal gas (using ideal gas equation).

(ii) the gas behaves like a real gas (using van der Waal's equation)

Given that for ammonia, $a = 4.17$ atm litre^2 mol^{-2} and $b = 0.037$ litre mol^{-1}.

Sol. Given,

$n = 2$ moles

$V = 5$ litres

$T = 27°C = (27 + 273)\ K = 300\ K$

$a = 4.17$ atm litre^2 mol^{-2}

$b = 0.037$ litre mol^{-1}

Also, we know that

$R = 0.0821$ litre atm K^{-1} mol^{-1}

(i) If the gas behaves like an ideal gas, we have

$$PV = nRT$$

$$\therefore \quad P = \frac{nRT}{V} = \frac{2 \times 0.0821 \times 300}{5} = 9.85 \text{ atm}$$

(ii) If the gas behaves like a real gas, we apply van der Waal's equation i.e.

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

$$\text{or} \quad P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} = \frac{2 \times 0.0821 \times 300}{5 - 2 \times 0.037} - \frac{4.17 \times (2)^2}{(5)^2} = 9.33 \text{ atm.}$$

Ex. 1 mole of CCl_4 vapours at 77°C occupies a volume of 35.0 L. If vander 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.

Sol. (a) Under low pressure region, V is high

∴ $(V - b) \approx V$

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

$$PV + \frac{a}{V} = RT$$

$$\frac{PV}{RT}+\frac{a}{RTV} = 1$$

$$Z = \frac{PV}{RT} = \left(1-\frac{a}{RTV}\right) = 1 - \frac{20.39}{0.0821\times350\times35} = 0.98$$

(b) Under high pressure region, P is high,

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

$\therefore$ $P\ (V - b) = RT$

$$PV - Pb = RT$$

$$\frac{PV}{RT}-\frac{Pb}{RT} = 1$$

$\therefore$ $Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$ $\qquad \left(\because \frac{PV}{RT}=1, \text{ or } \frac{P}{RT}=\frac{1}{V}\right)$

$$Z = 1 + \frac{b}{V} = 1 + \frac{0.1383}{35} = 1 + 0.004 = 1.004$$

Ex. One way of writing the equation of state for real gases is $PV = RT\left[1+\frac{B}{V}+\ldots\right]$ where B is a constant. Derive an approximate expression for B in terms of van der Waal's constants a and b.

Sol. According to van der Waal's equation

$$\left[P+\frac{a}{V^2}\right][V - b] = RT$$

or $P = \frac{RT}{(V-b)}-\frac{a}{V^2}$

Multiply by V, then

$$PV = \frac{RTV}{(V-b)}-\frac{a}{V}$$

or $PV = RT\left[\frac{V}{V-b}-\frac{a}{VRT}\right]$

or $PV = RT\left[\left(1-\frac{b}{V}\right)^{-1}-\frac{a}{VRT}\right]$

$\because$ $\left[1-\frac{b}{V}\right]^{-1} = 1 + \frac{b}{V}+\left(\frac{b}{V}\right)^2 + \ldots.$

$\therefore$ $PV = RT\left[1+\frac{b}{V}+\ldots-\frac{a}{VRT}\right]$

$$PV = RT\left[1+\left(b-\frac{a}{RT}\right).\frac{1}{V}+\ldots\right]$$

$\therefore$ $B = b - \frac{a}{RT}$

Ex. The critical temperature and pressure of CO_2 gas are 304.2 K and 72.9 atm respectively. What is the radius of CO_2 molecule assuming it to behave as vander Waal's gas ?

Sol. $T_C = 304.2$ K $\quad P_C = 72.9$ atm

$$T_C = \frac{8a}{27Rb} \qquad P_C = \frac{a}{27b^2}$$

$$\therefore \quad \frac{T_C}{P_C} = \frac{\frac{8a}{27Rb}}{\frac{a}{27b^2}} = \frac{8a}{27Rb} \text{ Ч } \frac{27b^2}{a} = \frac{8b}{R}$$

or $\quad b = \dfrac{RT_C}{8P_C} = \dfrac{1}{8} \times \dfrac{0.082 \times 304.2}{72.9} = 0.04277$ lit mol^{-1}

$\quad b = 4\ N_A \text{ Ч } \dfrac{4}{3}\pi r^3 = 42.77\ cm^3$

$\therefore \quad 4 \text{ Ч } N_A \text{ Ч } \dfrac{4}{3}\pi r^3 = 42.77$

or $\quad r^3 = \dfrac{3 \times 42.77 \times 10^{-23}}{16 \times 6.023 \times 3.14}$

or $\quad r^3 = 0.424 \text{ Ч } 10^{-23} = 4.24 \text{ Ч } 10^{-24}$

or $\quad r = (4.24)^{1/3} \text{ Ч } 10^{-8}$ cm $= 1.62 \text{ Ч } 10^{-8}$ cm

$\therefore \quad$ radius of CO_2 molecule = 1.62 E

LIQUID STATE

❑ THE LIQUID STATE

Liquid state is intermediate between gaseous and solid states. The liquids posses fluidity like gases but incompressibility like solids.

The behaviour of liquids explained above gives some characteristic properties to the liquids such as definite shape, incompressibilty, diffusion, fluidity (or viscosity), evaporation (or vapour pressure), surface tension, etc.

Properties of liquids can be explained on the basis of kinetic molecular theory which has the following postulates :

(i) A liquid is made up molecules; atoms in rare cases, e.g., Hg (mercury)
(ii) The molecules of the liquid are quite close together.
(iii) The intermolecular forces of attraction in a liquid are quite large.
(iv) The molecules of liquids are in a state of constant rapid motion.
(v) The average kintetic energy of the molecules of a liquid is directly proportional to their absolute temperature.

A liquid state is regarded as a condensed gas or a molten solid. Liquid state, however, has much more in common with solid state than with gaseous state. The following general characteristics are exhibited by liquids.

(i) Shape :

Liquids have no shape of their own but assume the shape of the container in which they are kept. No doubt, liquids are mobile but they do not expand like gases as to fill up all the space offered to them but remain confined to the lower part of the container.

(ii) Volume :

Liquids have definite volume as the molecules of a liquid are closely packed and the cohesive forces are strong. The molecules are quite free to occupy any space.

(iii) Density :

As the molecules in liquids are closely packed, the densities of liquids are much higher than in gaseous state. For example, density of water at 100° C and 1 atmospheric pressure is 0.958 g mL^{-1} while that of water vapour under similar conditions as calculated from ideal gas law $\left(d = \frac{MP}{RT}\right)$ is 0.000588 g mL^{-1}.

(iv) Compressibility :

The molecules in a liquid are held in such close contact by their mutual attractive forces (cohesive forces) that the volume of any liquid decreases very little increased pressure. Thus, liquids are relatively incompressible compared to gases.

(v) Diffusion :

When two miscible liquids are put together, there is slow mixing as the molecules of one liquid move into the other liquid. As the space available for movement of molecules in liquids is much less and their velocities are small. Liquids diffuse slowly in comparison to gases.

(vi) Evaporation :

The process of changes of liquid into vapour state on standing is termed **evaporation**. Evaporation may be explained in terms of motion of molecules. At any given temperature all the motion of molecules do not possess the same kinetic energy (average kinetic energy is, however same). Some molecules move slowly, some at intermediate rates and some move very fast. A rapidly moving molecule near the surface of the liquid may possess sufficient kinetic energy to overcome the attraction of its neighbours and escape. Evaporation is accomparried by cooling as average kinetic energy of remaining molecules decreases.

(a) **Nature of the liquid** : The evaporation depends on the strength of intermolecular forces (cohesive forces). The liquids having low intermolecular forces evaporate faster in comparison to the liquids having high intermolecular forces. For example, ether evaporates more quickly than alcohol, and alcohol evaporates more quickly than water, as the intermolecular forces in these liquids are in the order :

Ether < Alcohol < Water

$$\underset{\text{Increasing extent of hydrogen bonding}}{\xrightarrow{\text{Alcohol < glycol < glycerol}}}$$

(b) **Surface area :** Evaporation is a surface phenomenon. Larger the surface area, greater is the oportunity of the molecules to escape. Thus, rate of evaporation increases with increase of surface area.

Rate of evaporation α Surface area

(c) **Temperature :** Rate of evaporation increases with the increase of temperature as the kinetic energy of the molecules increases with the rise of temperature.

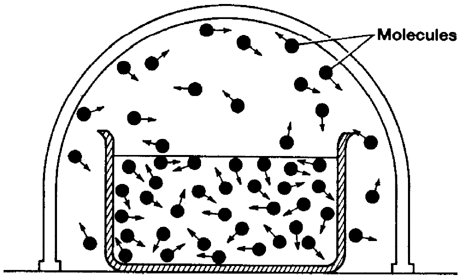
Rate of evaporation α Temperature

(d) **Flow of air current over the surface :** Flow of air helps the molecules to go away from the surface of liquid and, therefore, increases the evaporation.

(vii) Heat of vaporisation :

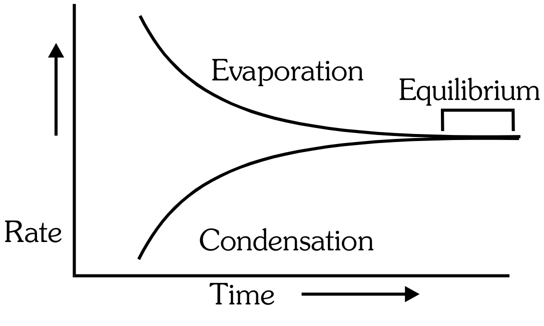
The quantity of heat required to evaporate a unit mass of a given at constant temperature is known as heat of vaporisation or heat evaporation. The heat of vaporisation depends on the strength of the intermolecular forces with in the liquid. The value of heat of vaporisation generally decreases with increase in temperature. It becomes zero at the critical temperature. When the vapour is condensed into a liquid, heat is evolved. This is called **heat of condensation**. It is numerically equal to the heat of vaporisation at the same temperature.

(viii) Vapour pressure :



When the space above the liquids is closed, the molecules cannot escape into open but strike the walls of the container, rebound and may strike the surface of the liquid, where they are trapped. The return of the molecules from the vapour state of the liquid state is known as **condensation**. As evaporation proceeds, the number of molecules in the vapour state increases and, in turn, the rate of condensation increases.

The rate of condensation soon becomes equal to the rate of the evaporation, i.e., the vapour in the closed container is in equilibrium with the liquid.



At equilibrium the concentration of molecules in the vapour phase remains unchanged. The pressure exerted by the vapour in equilibrium with liquid, at a given temperature, is called the **vapour pressure**. Mathematically, it is given by the gas equation.

$$P = \frac{n}{V}RT = CRT$$

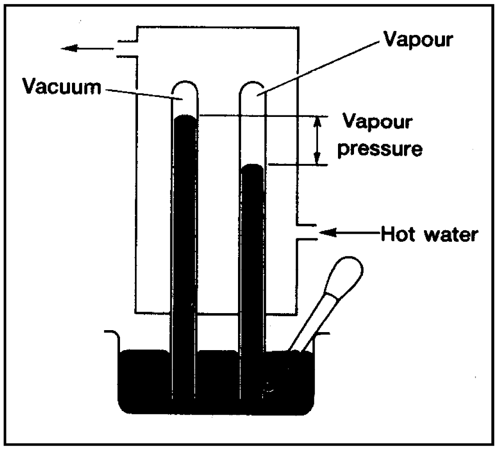
Where C is the concentration of vapour, in mol/litre.

Since the rate of evaporation increases and rate of condensation decreases with increasing temperature, vapour pressure of liquids always increases as temperature increases. At any given temperature, the vapour pressures of different liquids are different because their cohesive forces are different. Easily vaporised liquids are called **volatile liquids** and they have relatively high vapour pressure. Vapour pressure values (in mm of Hg) for water, alcohol and ether at different temperatures are given in the following table :

Substance	Temperatures				
	0° C	20° C	40° C	80° C	100° C
Water	4.6	17.5	55.0	355.5	760.3
Ethyl alcohol	12.2	43.9	812.6	1693.3	
Diethyl ether	185.3	442.2	921.1	2993.6	4859.4

It is observed that non-polar or less polar liquids such as diethyl ether alcohol possess fairly high vapour pressure on account of weak intermolecular forces (cohesive forces) whereas polar molecules such as water which have stronger intermolecular forces posses relatively lower vapour pressure.

The simplest method for measuring vapour pressure is the **barometric method**. It consists of two barometer tubes as show in Figure. A small quantity of the liquid is intruduced into one of the tubes. It changes into vapour and rises into vaccum above the mercury. Some more of the liquids is introduced and the process is continued till a small amount of the liquids is visible on the surface of mercury. The difference in the levels of mercury in the surface of mercury in the two tubes is noted and this measurs the vapour pressure of the liquid at atmospheric temperature. The measurement can also be made at any desired temperature by surrounding the buts with a jacket maintained at that temperature.



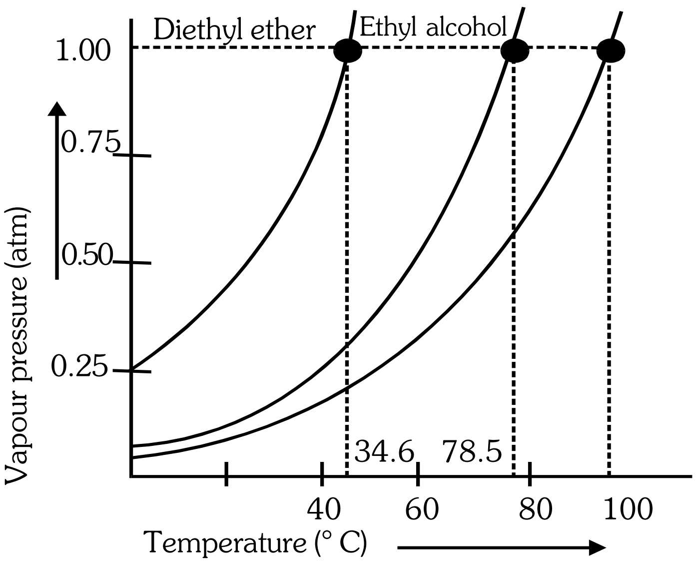
The vapour pressure of a given liquid at two differnt temperatures can be compared with the help of **Clausius-Clapeyron equation.**

$$\text{og}\times\frac{P_2}{P_1}=\frac{\Delta H}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Where ΔH is the latent heat of vaporisation and R is the molar gas constant.

(ix) Boiling point :

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called the **boiling point** of the liquid. When a liquid is heated under a given applied pressure, bubbles of vapour begin to form below the surface of the liquid. They rise to the surface and burst releasing the vapour into the air. This process is called **boiling**. The normal boiling point is the temperature at which the vapour pressure of a liquid is equal to exactly one standard atmospheric pressure (760 mm of Hg). Figure shows that normal boiling points of di-ethyl ether, ethyl alcohol and water are 34.6° C, 78.5° C and 100° C respectively.



The temperature of the boiling remains constant until all the liquid has been vaporised. Heat must be added to the boiling liquid to maintina the temperature because in the boiling process, the high energy molecules are lost by the liquid. The higher the rate at which heat is added to the boiling liquid, the faster in boils.

The boiling point of a liquid changes with the change in external pressure. A liquid may boil at temperatures higher than normal under external pressures greater than one atmoshpere; conversely, the boiling point of a liquid may be lowered than normal below one atmosphere. Thus, at high altitudes where the atmospheric pressure is less than 760 mm, water boils at temperatures below its normal boiling water is lower than it would be nearer the sea level. The Temperature of boiling water in a pressure cooker is higher than the normal, thus making it possible to cook foods faster than in open vessels.

If a liquid decomposes when heated, it can be made to boil at lower temperatures by reducing the pressure. This is the principle of vacuum distillation. Unwanted water is removed from many food products by boiling it away under reduced pressure.

Boiling and evaporation are similar processes (conversion of liquid into vapour) but differ in following respects :

(a) Evaporation takes place spontaneously at all temperatures but boiling occurs at a particular temperature at which the vapour prssure is equal to the atmospheric pressure.

(b) Evaporation is surface phenomenon. It occurs only at the surface of the liquid whereas boiling involves formation of bubbles below the surface of the liquid.

(c) In vaporisation, the vapour molecules diffuse from the liquid into the atmosphere but in boiling, molecules escape with sufficient pressure into the space over the surface of liquid.

(x) Freezing point :

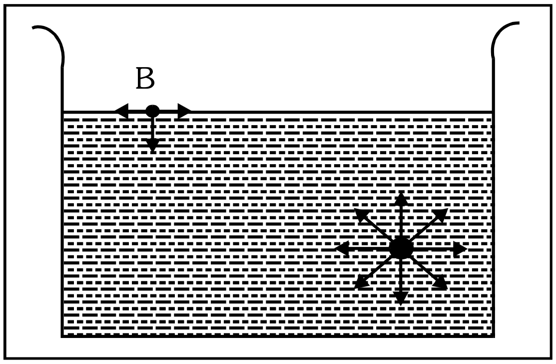
When a liquid is cooled, the kinetic energy of the molecules goes on decreasing. A stage comes when the intermolecular forces become stronger and the translational motion is reduced to minimum. At this stage, the formation of solid begins and the liquid is seen to freeze out. The point (temperature) at which the vapour pressure of solid and liquid forms of a substance become equal is termed as **freezing point.**

Normal freezing point of a liquid is the temperature at which is liquid and solid forms are in equilibrium with each other under a pressure of one atmosphere. The freezing point of a liquid is the same as the melting point of its solid-liquid system remains constant until all the liquid is forzen. The amount of heat that must be removed to freeze a unit mass of the liquid at the freezing point is called the **heat of fusion.**

The freezing point of a liquid is affected by the change of external pressure. With increased external pressure, the freezing point of some liquids rises while of others falls.

(xi) Surface tension :

It is the property of liquids caused by the intermolecular attractive forces. A molecule within the bulk of the liquid is attracted equally in all the directions by the neighbouring molecules. The resultant force on any one molecule in the centre of the liquid is, therefore, zero. However, the molecules on the surface of the liquid are attracted only inward and sidewasys. This unbalanced molecular attraction pulls some of the molecules into the bulk of the liquid, i.e., are pulled inward and the surface area is minimized.



Surface tension is a measure of this inward force on the surface of the liquid. It acts downwards perpendicular to the plane of the surface. The unit of surface tension is dyne cm^{-1}. Surface tension is, thus, defined **as the force in dyne acting on the surface at right angles to any line of unit length.** As the intermolecular forces of attraction decreases with the rise of temperature, the surface tension of a liquid, thus, decreases with increase in temperature. Similarly, addition of chemicals to a liquid reduces its surface tension. For example, addition of chemicals like soaps, detergents, alcohol, camphor, etc., lowers the surface tension of water.

Many common phenomena can be explained with the help of surface tension. Some are described here :

(a) **Small droplets are spherical in shape :** The surface tension acting on the surface of the liquid tries to minimise the surface area of a given mass of a liquid. It is known that for a given volume, a sphere has the minimum surface area. On account of this, drops of liquids acquire a spherical shape.

(b) **Insects can walk on the surface of water :** Many insects can walk on the surface of water without drowing. This is due to the existence of surface tension. The surface tension makes the water surface to behave like an elastic membrane and prevents the insects from drowning.

(c) **Cleaing action of soap and detergents :** Soap and detergent solutions due to thier lower surface tensions penetrate into the fibre and surround the greasy substances and wash them away.

(d) **Capilary action :** The tendency of a liquid to rise into narrow pores and tiny openings is called capillary action. The liquids rise in the capillary tubes due to the surface tension. The molecules of glass of the capillary tube is greater than the force of cohesion between water molecules. Due to this, surface of water in a glass capillary tube curves upwards in convex shape and then the force of surface tension of water pulls the water up into the tube. The water rises into a capillary tube to such a height that the weight that the weight of resulting water column is just balanced by the force of surface tension.

The rise of a oil in a lamp wick and flow of water from the roots of a tree to upper parts are also the examples of capillary action. In general, the liquids which wet the material show capillary always show deprssion, e.g., glycerine, honey, mercury, etc.

When a liquid reises in a column, its upper surface becomes concave and when the liquid goes down in a capillary, its upper surface becomes conves.

(e) **Surface Energy :** The work in erg required to be done to icrease or extend surface area by 1 sq. cm is called surface energy. The units of surface energy are, therfore, erg per sq. cm (or joule per sq. metre, i.e. J m^{-2} in S.I. system)

Measurement of surface tension : The surface tension of a liquid is measured by the drop count method using a stalagmometer.

Ley γ_1 and d_1 be the surface tension and density of water and γ_2 and d_2 be surface tension and density of the liquid whose surface tension is to the determined. Using a stalagmometer the number of drops formed by the same volume of water and liquid is determined.

$$\frac{\gamma_1}{\gamma_2} = \frac{n_1 d_2}{n_2 d_1}$$

Using the above relation, the surface tension of the liquid, γ_2, can be calculated.

(xii) Viscosity :

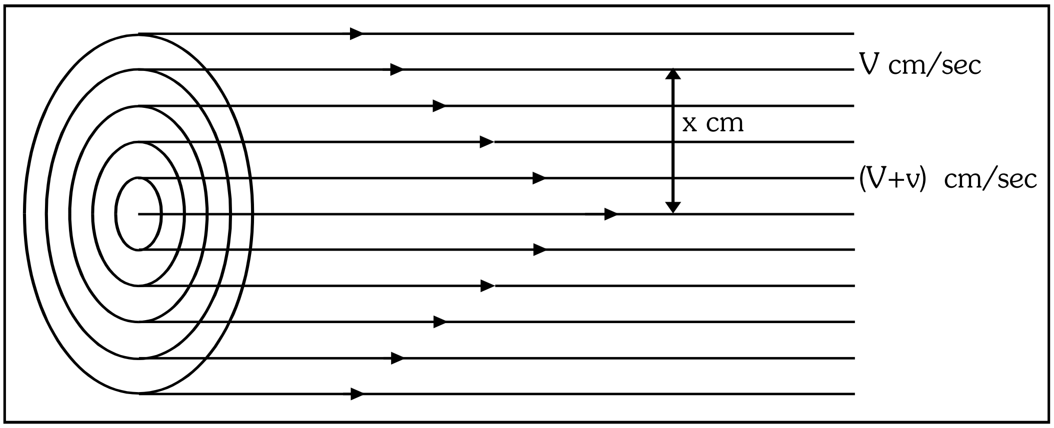
All the liquids have a characteristic property of flow. Some liquids like water, alcohol, ether, etc., flow quickly while glycerine, castor oil, molasses, etc., flow very slowly. **The property of the liquids which determines their resistance to flow, is called viscosity.**

When a liquid flows through a pipe, all parts of it do not move at the same rate. The thin layer in immediate contact with the wall of the pipe is almost stationary. The velocity of flow of each successive layer of liquid increases progressively as we proceed inward towards the centre. At the centre the flow becomes fastest. Each layer of liquid moving with greater velocity over the one having lower velocity will experience a retarding effect due to the internal friction between the friction between the two layers. **This internal friction or resistance is called viscosity.**

Imagine a liquid to be made up of a friction 'f' between two cylindrical layers each having area 'A' sq. cm separated by a distance 'x' cm and having a velocity difference υ cm/sec. is given by

$$f \alpha A \frac{\upsilon}{x}$$

$$f = \eta A \frac{\upsilon}{x}$$



Here η is a constant known as coefficinet of viscosity. If $x = 1$ cm, $A = 1$ cm^2 and $\upsilon = 1$cm/sec then $f = \eta$

Thus, coefficient of viscosity can be defined as **the force per unit area neede to maintain unit difference of velocity between two cinsecutive parallel layers of the liquid which are one centimetre apart.** Coefficient of viscosity is expressed in dyne cm^{-2} sec. It is more commonly expressed to poise, centipoise (10^{-2} poise) and millipoinse (10^{-3} poise), after the name of **Poiseuille** who derived the formula and gave the method for its determination. One poise is eaual to a force of one dyne per unit area which maintains a velocity of one cm per second betweeen two parallel consecutive layers of the liquid one cm apart.

The reciprocal of the coefficient of viscosity is called **Fluidity** (ϕ)

$$\phi = \text{Fluidity} = \frac{1}{\eta}$$

Liquids with low viscosity are termed mobile and others with high viscosity are called viscous.

Viscosity depends on the following factors :

(a) **Intermolecular forces** : The liquids with high intermolecular attractive forces offer greater resistance to the flow of molecules and thus possess high viscosity.

(b) **Molecular mass** : The flow of molecules inversely proportional to its mass. Liquids having high molecular mass possess greater viscosity.

(c) **The structure and shape of molecules** : Viscosity generally increases as the branching in the chain increases. Symmetrical molecules have low viscosity.

(d) **Temperature** : Intermolecular forces decrease with rise in temperature. Thus, viscosity decreases with the increase of temperature.

(e) **Pressure** : The increase of pressure increases the intermolecular forces. Thus, the viscosity of a given liquid increases with increase of pressure.

2. NATURE OF FORCES IN LIQUIDS

(I) Non-polar liquids :

There are only weak forces called van der Waals' forces in non-polar liquids like carbon tetrachloride, diethyl ether and carbon disulphide. This is because there is no net dipole moment in the molecules. These molecules are symmetrical and the dipole moment acting in one part is balanced by that in the other part. Such liquids have the following characteristics.

(a) They have a low viscosity and surface tension.
(b) They have a low heat of vaporisation and low boiling point.
(c) They have a high vapour pressure.

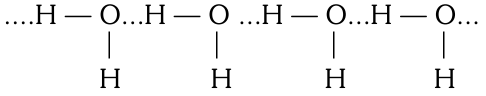
(II) Polar liquids :

They have a net dipole moment because they consist of hetero-atomic molecules where the forces are not balanced. Examples of such liquids are water, ammonia and ethyl alcohol. As a result of strong dipole-dipole interactions, they show the following characteristics :

(a) They have a high viscosity and surface tension.
(b) They have a high value of heat of vaporisation and high boiling point.
(c) They have a low vapour pressure.

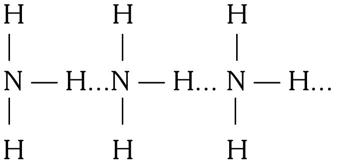
(III) Hydrogen bonding :

In the case of some liquids, there is a strong interaction between the molecules. If a molecule is constituted of hydrogen and an electronegative atom like oxygen, nitrogen or sulphur, such a molecule will show intermolecular interactions. Hydrogen-bonding in water is represented as under ;



$$\ldots.H-\underset{\underset{H}{|}}{O}\ldots H-\underset{\underset{H}{|}}{O}\ldots H-\underset{\underset{H}{|}}{O}\ldots H-\underset{\underset{H}{|}}{O}\ldots$$

Due to electronegativity difference, there is a weak bond between hydrogen or one molecule and oxygen of the other. This is called **hydrogen bond**. Such a bond continues indefinitely through a hundred or thousand molecules, thus, displaying strong interaction. It is also displayed by ammonia as :



$$\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-H\ldots\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-H\ldots\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-H\ldots$$

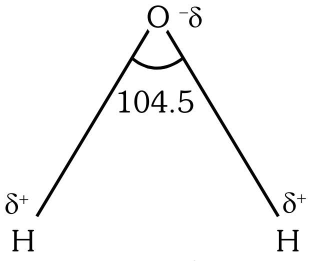
Due to increased inter-molecular attractions, the properties change as detailed above.

3. WATER — AN UNUSUAL LIQUID

Nearly 75% of the earth's surface is covered with water. Animal and plant life would not be possible without water. We need water for drinking, cleaning and washing clothes. It would be difficult to think of life without water. It plays a vital role in all life processes.

(I) **Structure of water** : Water has a V-shape structure. It is believed to formed by sp^3 hybridisation of oxygen. The angle HOH is 104.5°. The normal angle in a molecule formed by sp^3 hybridisation is 109° 28'. Deviation from this angle is explained in terms of a lone pair of electrons on oxygen.

Because of a big difference in the electronegativities of hydrogen and oxygen the latter dreaw some charge and becomes negatively charged (Figure) with hydrogens acquiring a positive charge.



Structure of H_2O

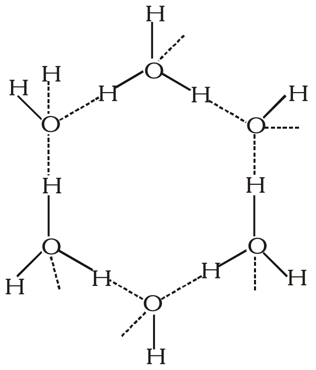
Due to these positive and negative charges, hydrgoens of molecules become bonded to oxygens of other molecules by weak bonds called **hyderogen bonds.** Thus, association of the molecules of water takes place. This association is responsible for some unusual properties of water.

(II) **Unusual Properties of Water :**

1. Water, a hydride of oxygen, is a liquid at room temperature, whereas the hydrides of other elements of the oxygen family like H_2S and H_2Se are gases at room temperature. This is because there is hydrogen bonding in water and no hydrogen bonding in H_2S and H_2Se. But it is definitely a boon for the mankind that water is a liquid at room temperature otherwise life would have been miserable.

2. Water has an abnormally high value of dielectric constant which helps in the processes of ionisation and electrolysis. It is again because of the association of the molecules.

3. Water freezs to ice at 0° C and ice is lighter than water. Generally, with the decrease of temperature, the density increases. But the situation is different in the case of water. This is because of hydrogen bonding in a particular fashion in ice as shown in Figure. There is a lot of empty space within the water moleucles in ice, thus, increasing the volume. This consequently decreases the density and that is reason why ice is lighter and floats on water.



(III) **Maximum density of water at 4° C :**

When ice at 0° C is heated, the above hydrogen-bonded structure of ice collapses. The vacent space inside is filled with water molecules and, therefore, the density increases. But this happens only upto 4° C. Further, heating has the normal effect of expansion of liquid with temperature and there after the density decreases.

4. SOLUTIONS

A solution is defined as a homogeneous mixture of two or more chemically non-reducing substances whose relative amounts can be varied within certain limits. Examples of these are : common salt in water, alcohol in water etc.

A solution may be gaseous, liquid or solid of variable composition within a wide range.

A solution which is a homogeneous mixture of two substance only is called a **binary solution**. The components of a binary solution are referred to as **solute** and **solvent**. A solute is a substance which dissolves in a solution and the dissolving medium. The substance in which solute dissolves is called **solvent.** Thus, for in solutions in which one component is a gas or solid and the other is a liquid, the former is the solute and the latter is the solvent. When both the components have same state as of solution, the component present in smaller amount is called solute and the other present in larger amount is called the sovent.

(I) **Concentrated solution :** A solution containing a very small amount of solute dissolved in large amount of solvent is called **dillute solution.** On the other hand, if a solution is prepared by dissolving an appreciable amount of the solute dissolved in it, it is called a **concentrated solution**.

(II) **Saturated solution :** When a solid substance is gradually shaken to dissolve in a liquid at a given temperature after some time a point is reached when no more solid will dissolve. Such a solution is said to be a **saturated solution** and is defined as a solution which is in equlibrium with undissolved solid (solute) at a given temperature. The amount of solute dissolved in 100 gm of the solvent to form a saturated solution at a given temperature measures the **solubility** of the solute.

(III) **Unsaturated solution :** A solution containing less quantity of solute than that of the saturated solution at a given temperature is called **unsaturated solution.**

(IV) **Aqueous and Non-aqueous solutions :** A solution containing water as solvent is called **aqueous solution** and that which contains solvent other than water is called **non-aqueous solution.**

5. TYPES OF SOLUTIONS

Depending upon the physical states of components of binary solutions, the various types of solutions are given below in table

TYPE OF BINARY SOLUTIONS.

Sr. No.	Solute	Solvent	Examples
1.	Gas	Gas	Any mixture of gases like air, etc.
2.	Liquid	Gas	Water vapour or vapour or any liquid in air.
3.	Solid	Gas	I_2 vapour in air, smoke
4.	Gas	Liquid	O_2 dissolved in water, CO_2 in aerated drinks, etc.
5.	Liquid	Liquid	Alcohol in water.
6.	Solid	Liquid	Sugar in water, etc.
7.	Gas	Solid	Dissolved gases in minerals, adsorption of gases by metals, e.g., adsorption of H_2 by palladium
8.	Liquid	Solid	Liquid mercury in amalgated Zn ; Hydrated salts like $CuSO_4 . 5H_2O$, $FeSO_4 . 7H_2O$, etc.
9.	Solid	Solid	Alloys, e.g. brass is a solid-solid solution of Zn and Cu.

6. FACTORS AFFECTING THE SOLUBILITY OF A SOLID IN A LIQUID

The solubility of a solid in a liquid depends upon two factors :

(a) **Maximum randomness factor :** Since randomness of solid solute in solution is greater than in its solid state, therefore this favours dissolution.

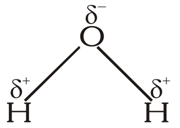
(b) **Manimum energy factor :** Since the energy of the solid particles in a solution is greater than in solid state, therefore, energy factor opposes dissolution, i.e., favours precipitation.

If randomness factor is greater than enrgy factor, dissolution process takes place. These two effects further depend upon the following factors :

1. Nature of the solute and the solvent.
2. Size of the solute particles.
3. Pressure.
4. Temperature.

1. **Nature of the solute and the solvent :** It is, generally, found that a solid dissolves in a liquid which is chemically similar to it. It is quoted in chemistry as "Like dissolves like". Thus, ionis (Polar) compounds are soluble in polar solvents such as water is very little soluble or almost insoluble in non-polar solvents such as carbontetrachloride, benzene, etc. Similarly, non-polar compounds (e.g. organic compounds) are, generally, soluble in non-polar solvents and are very little soluble or almost insoluble in a polar solvent like water. As a rule, inorganic substances are more soluble in water than in organic solvents while reverse is in the case of organic substances. There are, however, some exceptions to such a general statement. Thus, the solubilities of different substances will be different in the same solvent at the same temperature, e.g. at 20° C, the solubility of ammonium nitrate in water is 192g/100 g of water while the solubility of mercuric chloride at the same temperature is 6.5 g/100 g of water.

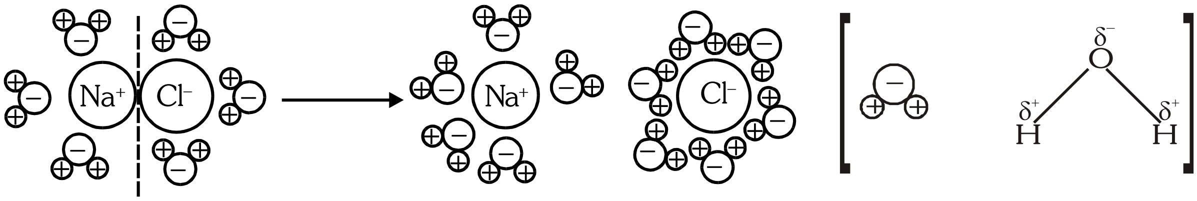
A. **For ionic compounds soluble in polar solvents :** The solubility of ionic compounds in polar solvents like water, etc, can be explained in terms of energy changes. When a crystal of an ionic compound such as sodium chloride is placed in a polar solvent like water, there exist strong electrostatic forces of attraction between the ions of the crystal and the polar molecules of water as shown in Figure. The negative ions are attracted by the positive poles (i.e., hydrogen end) of the water molecules and the positive ions by the negative poles (i.e., the oxygen end) of the solvent molecules.



$$NaCl + H_2O \longrightarrow \underset{(aq)}{Na^+} + \underset{(aq)}{Cl^-}$$

(Na^+ and Cl^- ions in solution)

The attachement of polar solvent molecules to ions is known as solvation (or hydration in case of water) of ions. The solvation process helps in two ways.



Dissolution of NaCl in water

(i) A large amount of energy knwon as the solvation energy (or hydration energy) is released because of the attraction between the polar molecules of solvent and the ions of the ionic substance. This energy helps the ions to be detached from the lattice of the crystal for which energy (Lattice energy) is required. Thus, an ionic substance dissolves if there is lowering of energy (i.e., evolution of energy). It will be so if hydration energy (or solvation energy) is greater than the lattice energy.

(ii) The solvation sheath (or envelop) of solvent molecules around the ions prevents the recombination of the ions. The solvated (or hydrated) ions, thus, move freely in the solution and, therefore, increase entropy of the system.

B. For non-polar compounds soluble in non-polar solvents :

The dissolution of non-polar substances in non-polar solvents like benzene, CCl_4, etc. takes place when solute-solvent interactions overweight the solute-solute and solvent-solvent interactions, e.g., in solubility of I_2, molecules of solid iodine are held together be weak van der Waals' forces and, similarly, CCl_4 molecules are also held together by the same type of forces. It is, thus, easy for both the molecules to penetrate into each other to form the solution of iodine in CCl_4, but on the other hand, iodine is almost insoluble in water. This is because in water, hydrogen bonding exists and so attraction between water-water molecules is much stronger than iodine-water attraction and iodine molecules can not penetrate into the associated structure of water molecules. In the light of this discussion, solubility of polar organic solids like alcohols, amines, carbohydrates, etc., in water can be explained. It is because hydroxy and amino groups of these solute molecules form hydrogen bonds with water molecules.

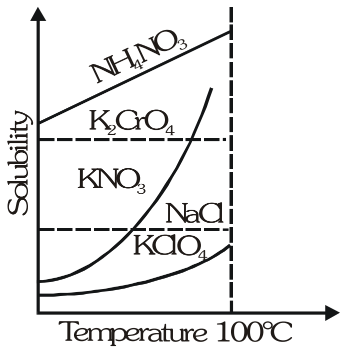
2. Size of the solute particles :

It is a general fact that smaller the size of the particles of a solute, the greater is its solubility. It is because of the greater chances of contact between the ions or molecules of the solute and the molecules of the solvent. For example, the solubility of barium sulphate becomes almost double when the size of its particle is decreased from 1.8 micron to 0.1 micron.

3. Effect of pressure on solubility :

Pressure change has a little effect on the solubility of a solid in a liquid. According to Le-chatelier Braun principle, if a solid dissolves in a liquid with decreases of volume, its solubility increases with increase of pressure (e.g. solubility of NaCl in water) and if the solid dissolves with increase of volume, solubility decreases with increase of pressure (e.g., solubility of ammonium chloride).

4. **Effect of temperature — Solubility curves :**



The temperature has a significant effect on the solubility of a solute a particular solvent. The change of the solubility of a substance in a solvent with the change of temperature depends on the heat of solution. In case of most of the ion solutes, process of dissolution is endothermic, i.e.

$$\text{Solute + Solvent + Heat = Solution}$$

or

$$\text{Solute + Solvent = Solution, } \Delta H = -\,q \text{ kJ.}$$

According to Le-chatelier's principle, as the temperature is increased equilibrium will shift in a direction in which the heat is absorbed, i.e., in the forward direction and so more of the solute passes into solution. On the other hand, if a substance dissolves with the evolution of heat, the solubility decreases with rise in temperature. The graph showing the relation between the solubility and temperature is called solubility curve. Figure show the solubility curves of some substance.

7. CHEMICAL ARITHMATIC OF SOLUTIONS

In this section, we shall describe various methods of an expressing concentration of a solution.

1. **Strength of a solution** : The amount of solute in grams dissolved in one litre (1000 ml) of the solution is called strength of the solution and is expressed in g/litre.

For example, when 4 g of NaOH is dissolved and solution made up to 100 ml, the strength of solution is

$$\frac{4 \times 1000}{100} = 40 \text{ g/litre.}$$

2. **Percent strength :** It is expressed as the number of parts by wieght of solute present per 100 parts by weight of solution. It is also defined as the amount of solute in grams dissolved in 100 g of solution.

For example, 2.0 g of NaCl in 50 g solution means 4% solution

10% of KCl solution means that 10 g of KCl are present in 100 g of solution.

3. **Molarity** : The molarity of a solution expresses the number of gram molecular weight (moles) of the solute dissolved per litre of solution. It is symbolised as M. Solution which contians one gram molecular weight (1mole of the solute per litre of the solution) is called a **molar solution.**

Mathematically,

Molarity = Number of moles/Litre

$$\because \quad \text{Number of gram moles} = \frac{\text{Weight in gram}}{\text{Gram molecular weight}}$$

$$\therefore \quad \text{Molarity} = \frac{\text{Strength of solute in gm / litre}}{\text{Gram molecular weight of solute}}$$

For example, the molecular formula of hydrochloric acid is HCl.

The molecular weight = 1 Ч 1 + 35.5 Ч 1 = 36.5

Gram molecular weight = 36.5 g

36.5 g of HCl dissolved/litre = 1 M HCl

18.25 g of HCl dissolved/litre = M/2 HCl

4. **Molality** : The molality of a solution expresses the number of moles of solute dissolved in 1000 g of the solvent. It is symbolised as m.

Mathematically,

$$\text{Molality = Number of moles of solute/kg of solvent} = \frac{\dfrac{\text{Weight of solute}}{\text{Mol. weight of solute}}}{\text{Weight of solvent}} \times 1000$$

or $\quad = \dfrac{\text{Number of gram moles of solute}}{\text{Weight of solvent}} \times 1000$

For example, 1 mole sodium hydroxide solution is obtained by dissolving one mole, i.e., 40 g of sodium hydroxide in 1000 g of water.

Similary, a solution prepared by dissolving 5.6 or $\frac{1}{10}$ mole of KOH in 1000 g of water will be called decimolal $\frac{m}{10}$ solution of KOH.

5. **Normality :**

$$\text{Normality} = \frac{\text{Strength of solute in g/litre}}{\text{Equivalent weight of solute}} = \frac{\text{Number of gram equivalent weight}}{\text{Volume in litres}}$$

A solution is said to be one normal when the equivalent weight of the substance in grams is dissolved in one litre of the solution.

For example, a solution containing 53 g of Na_2CO_3 (1 gram equivalent) per litre of the solution is said to be noraml solution.

Similary, a solution of hydrochloric acid containing :

(i) 1 g equivalent weight (36.5 g) per litre is 1 N HCl

(ii) 1/10 g equivalent weight (3.65 g) per litre is N/10 HCl.

Sub-normal solution : A solution whose normality is less than one is called a sub-normal solution.

For example, $\frac{N}{2}, \frac{N}{10}, \frac{N}{5}$, etc., all sub-normal solution.

6. **Mole fraction :**

It is the ratio of the number of the solute (one component) to the total number of moles of both the components in the solution.

If the number of moles of solute = n and the number of moles of the solvent = N.

Then, the total number of moles in the solution = n + N

Hence, the mole fraction of solute = $\frac{n}{n+N}$

Similarly, the mole-fraction of the solvent = $\frac{N}{n+N}$

If a solution is prepared by dissolving x g of a solute (of mol. wt. say m) in W g of the solvent (or mol. wt. say M).

Then, mole fraction of solute in the solution = $\dfrac{n}{n+N} = \dfrac{\frac{x}{m}}{\frac{x}{m}+\frac{W}{M}}$

Similarly, mole fraction of the solvent = $\dfrac{N}{n+N} = \dfrac{\frac{W}{M}}{\frac{x}{m}+\frac{W}{M}}$

Ex.1 Calculate the mole fraction of the solute in an aqueous solution containing 3.0 g of urea (mole. wt. = 60) per 250 g of water.

Sol. 3.0 g of solute = $\frac{3}{60}$ moles = 0.05 moles.

250 g of water = $\frac{250}{18}$ moles = 13.88 moles.

$\therefore$ Mole fraction of the solute = $\dfrac{0.05}{0.05+13.88} = \dfrac{0.05}{13.93} = 0.00358$

Ex.2 Calculate the mole fractions of ethanol and water in a sample of rectified spirit which contains 95 per cent of ethanol by weight.

Sol.

$\because$ The rectified spirit contains 95% of ethanol by weight

$\therefore$ The weight of ethanol in the spirit = 95 g

The weight of water in the spirit = 5 g

95 g of ethanol (C_2H_5OH) = $\frac{95}{46}$ moles of ethanol = 2.07 moles (Mol. wt. C_2H_5OH = 46)

5 g of water (H_2O) = $\frac{5}{18}$ moles of water = 0.28 moles (Mol. wt. H_2O = 18)

$\therefore$ Mole fraction of ethanol = $\frac{2.07}{2.07+0.28} = \frac{2.07}{2.35} = 0.88$

$\therefore$ Mole fraction of water = 1 – 0.88 = 0.12.

Ex.3 Following solutions were prepared in water :

NaOH	12 g per 250 ml
H_2SO_4	9.8 g per 250 ml

Calculate the molarity of the solutions.

Sol. For NaOH solution

$$\text{Molarity} = \frac{\text{Strength of NaOH in g/lire}}{\text{Mol. mass of NaOH}} = \frac{12 \times 4}{40} = 1.2\text{ M.}$$

For H_2SO_4 solution

$$\text{Molarity} = \frac{\text{Strength of } H_2SO_4 \text{ in g/lire}}{\text{Mol. mass of } H_2SO_4} = \frac{9.8 \times 4}{98} = 0.4\text{M}$$