Chapter 2

States of Matter (Gases, Liquids and Solids)

GASEOUS STATE

MEASURABLE PROPERTIES OF GASES

1. **Volume :** Gases have tendency to occupy all available space.

   So, volume of gas is equal to volume of container.

2. **Temperature :** It is degree of hotness and coldness.

   Conversion of °C to K

   K = °C + 273.15

3. **Pressure :** It is force exerted by gas per unit area

$$P = \frac{F}{A} = N/m^2$$

> ***Note :*** *1 atm = 760 mm of Hg = 760 torr = 1.01×10^5 Pa*
>
> *1 bar = 10^5 Pa*

BOYLE'S LAW

$$P \propto \frac{1}{V} \text{ at constant n and T.}$$

CHARLES' LAW

$V \propto T$ at constant n and P.

$$V_t = V_0\left(1 + \frac{t}{273}\right)$$

AVOGADRO'S LAW

$V \propto n$ (P and T constant); 1 mole of every gas at STP occupies volume = 22.4 lit.

Ideal Gas Equation

On combining the Boyle's law, Charles' law and Avogadro's law we get an equation known as ideal gas equation which correlates P, V, T, of a gas.

$\boxed{PV = nRT}$ ideal gas equation where R is a constant known as universal gas constant or molar gas constant.

Numerical value of R

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

$= 8.314$ J K^{-1} mol^{-1}

$= 1.987 \approx 2$ cal K^{-1} mol^{-1}

Other form of ideal gas equation.

$$\Rightarrow \boxed{PV = \frac{W}{M}RT}$$

$$\Rightarrow \boxed{P = \frac{dRT}{M}}$$; (where M is the molecular weight)

DALTON'S LAW OF PARTIAL PRESSURE

The total pressure exerted by a mixture of two or more chemically **non-reacting gases** in a definite volume is equal to the sum of individual pressures or partial pressures where p_1, p_2 etc. are partial pressures of individual gases which each gas would exert if it occupies the same volume at a constant temperature

$P_{Total} = p_1 + p_2 + p_3 \ldots$, where p_1, p_2 etc. are partial pressures of individual gases

$$P_{Total} = (n_1 + n_2 + \ldots\ldots) \frac{RT}{V}$$

Partial pressure of a gas = Mole fraction of that gas × Total pressure

$$= \frac{\text{no. of moles of gas}}{\text{Total no. of moles of all gases}} \times \text{Total pressure}$$

By Dalton's law of partial pressure.

> ***Note :*** *P (moist) = P (dry gas) + P (H_2O vapours)*
>
> *P (dry gas) = P (moist) – aq. tension.*

GRAHAM'S LAW OF DIFFUSION

(a) Diffusion is the ability of gas to spread and occupy the whole volume.

(b) Under identical conditions of temperature and pressure, the rate of effusion/diffusion of a gas is inversely proportional to square root of its density.

(c) Rate of diffusion/effusion for two gases are related as

$$\frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \frac{n_1/t_1}{n_2/t_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

Effect of Pressure on Rate of Diffusion :

$$\boxed{\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}}$$ where, V = volume , t = time, M = molar mass, d = density, n = number of moles, P = pressure

KINETIC THEORY OF GASES

The postulates

(1) The gaseous molecules are considered to be point masses.

(2) The volume of a molecule is negligible as compared to total volume of the gas.

(3) There is no force of interaction among the gas molecules.

(4) The collisions are perfectly elastic i.e. there is no loss or gain of energy during the molecular collisions.

(5) The average kinetic energy of molecules is directly proportional to the absolute temperature of the gas.

(6) The effect of gravity on molecular motion is negligible.

Based on Kinetic-Molecular Theory

$$PV = \frac{1}{3} mN\overline{u^2}$$

m = Mass of one molecule

N = Number of molecules in the container

$\overline{u^2}$ = Mean square velocity

KE of n moles = $\frac{3}{2}nRT$, for n = 1 $\boxed{\overline{KE} = \frac{3}{2}RT}$

Average KE per molecule = $\frac{3}{2}\frac{RT}{N_0} = \frac{3}{2}kT$, k = Boltzmann's constant

DISTRIBUTION OF MOLECULAR SPEEDS

(i) Root mean square velocity (u_{rms}) = $\sqrt{\frac{3RT}{M}}$

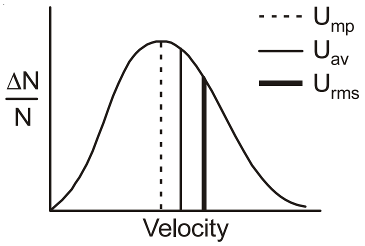
(ii) Average velocity(u_{av}) = $\sqrt{\frac{8RT}{\pi M}}$

(iii) Most probable velocity (u_{mp}) = $\sqrt{\frac{2RT}{M}}$

Note : *$u_{rms} : u_{av} : u_{mp} : : 1.732 : 1.596 : 1.414 : : 1.224 : 1.128 : 1$*

Hence, $u_{rms} > u_{av} > u_{mp}$

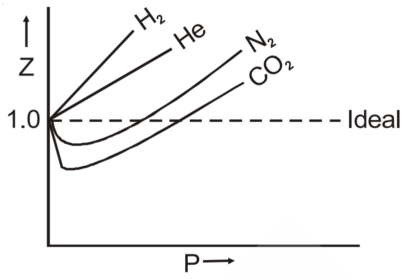
Maxwell Boltzmann's curve



DEVIATION FROM IDEALITY AND van der Waal's EQUATION

A plot of PV- P at constant temperature for a number of gases shows deviations from ideal behaviour. Therefore PV = nRT cannot be applied to these gases. Thus another equation must be sought in order to correlate P,V, T for these gases; which is van der waal's equation.

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



Causes of Deviation

There are two objectionable postulates in kinetic theory of gases.

(1) The volume of a molecule is negligible as compared to total volume of the gas. Actually, gas molecules do posses some volume which account for the deviation. Hence total volume of gas is not equal to volume of the vessel.

(2) There is no intermolecular force of attraction between gaseous molecules.

(There exists force of attraction between gaseous molecules otherwise liquefaction of gases would be impossible).

By correcting these two postulates, we get an equation which can be applied to the gases which deviate from ideal behaviour. The deviation of a gas from ideal behaviour can also be expressed in terms of compressibility factor (Z).

$Z=\frac{PV}{RT}$ [for 1 mole]

for ideal gas $Z = 1$

for real gas $Z > 1$ or $Z < 1$

LIQUID STATE

A liquid is composed of molecules that are constantly moving about at random, each undergoing billions of collisions per second. However strong attractive forces of the dipole-dipole, H-bonds, prevent them from moving as freely and as far apart as in a gas.

(a) **Vapour pressure :** It is the pressure exerted by vapours on surface of liquid at equilibrium. Vapour pressure does not depend on surface area and volume but it depend on temperature and nature of liquid. Vapour pressure increases with rise in temperature.

(b) **Viscosity :** Liquids flows as if they were divided into layers flowing over one another. Resistance offered to this flow is due to friction between two liquid layers and is called viscosity. Reciprocal of viscosity is called fluidity. Viscosity of a liquid decreases with rise of temperature.

(c) **Coefficient of viscosity :** The force in newtons per square metre required to maintain a difference of velocity of one metre per second between two parallel layers of the liquid at a distance of one metre from each other. It is expressed in kg m^{-1} s^{-1}. Liquids having stronger attractive forces are more viscous.

(d) **Surface tension :** The force that acts at right angles to an imaginary line of unit length at the surface of the liquid at rest. It is expressed in J m^{-2} or N m^{-1}. Surface tension generally decreases with the rise of temperature. Liquids exhibit capillary action and make spherical drops. This can be explained on the basis of surface tension.

IMPORTANT POINTS

(1) Critical temperature (T_c) :

It is the temperature above which a real gas cannot be liquefied whatever applied pressure may be

$$\boxed{T_c = \frac{8a}{27Rb}}$$

(2) Critical pressure (P_c) :

It is the minimum pressure required to liquefy the gas at critical temperature

$$\boxed{P_C = \frac{a}{27b^2}}$$

(3) Critical volume (V_c) :

The volume occupied by 1 mole of the gas at critical temperature and critical pressure is known as critical volume.

$$\boxed{V_C = 3b}$$

$$\boxed{V_c = 3 \times 4V_m = 12V_m} \text{ (Since } b = 4V_m)$$

V_m = Volume of one mole of gaseous molecule.

(4) Critical coefficient of a gas :

It is ratio of $\frac{RT_c}{P_cV_c}$ which is equal to 2.66 and remains constant for all the gases.

(5) Boyle's temperature (T_B) :

The temperature at which a real gas obeys ideal gas equation at very low pressure is known as Boyle's temperature.

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

Boyle's temperature of a gas is always higher than its critical temperature (T_c)

(6) Inversion temperature (T_i)

If a compressed gas is allowed to pass through a fine hole, it may show cooling or heating or no change in temperature depending upon the temperature of the gas. For each gas, there exists a characteristic temperature known as inversion temperature (T_i)

If $T > T_i$ heating is produced

If $T < T_i$ cooling is produced

If $T = T_i$ neither heating nor cooling

$$\boxed{T_i = \frac{2a}{Rb} = 2T_B}$$

(7) Excluded volume (b) :

The van der Waal constant 'b' is known as excluded volume. It is 4 times greater than the actual volume of the gas molecule.

$b = 4N_AV$ (where V is the volume of one molecule)

SOLID STATE

ELEMENTS OF SYMMETRY

The total no. of planes, axes and centre of symmetries possessed by a crystal is termed as its elements of symmetry. A simple cubical crystal possesses a total of 23 elements of symmetry.

In a Cube

Planes of symmetry = 3 + 6 = 9

Axis of symmetry = 3 + 4 + 6 = 13

Centre of symmetry = 1

Total number of symmetry elements = 23

TYPES OF CUBIC UNIT CELL

Type of unit cell	Number of atoms			Total number of atoms per unit cubic cell	Radius of ion/atom a = edge length
	At corners	Within body	On faces		
1. Simple cube	$\frac{1}{8}\times 8 = 1$	0	0	1	$r = \frac{a}{2}$
2. Body centred cube (BCC)	$\frac{1}{8}\times 8 = 1$	1	0	2	$r = \frac{\sqrt{3}\,a}{4}$
3. Face centred cube (FCC)	$\frac{1}{8}\times 8 = 1$	0	$\frac{1}{2}\times 6 = 3$	4	$r = \frac{\sqrt{2}\,a}{4}$

Radius ratio $\left(\frac{r^+}{r^-}\right)$

r^+/r^-	Geometry	Co-ordination number	Example
$0.155 \le \frac{r^+}{r^-} < 0.225$	Triangular planar	3	B_2O_3
$0.225 \le \frac{r^+}{r^-} < 0.414$	Tetrahedral	4	ZnS
$0.414 \le \frac{r^+}{r^-} < 0.732$	Octahedral	6	NaCl
$0.732 \le \frac{r^+}{r^-} < 1$	Cubic	8	CsCl

STRUCTURE OF SIMPLE IONIC COMPOUNDS

AB type : Consisting positively and negatively charged ions in the ratio 1 : 1

These compounds can have any one of the following structures

(a) Rock salt (NaCl) type structure

Characteristics

(i) It has fcc or ccp arrangement in which Cl^- ions occupy the corners and face centres of a cube while Na^+ occupy body centres and edge centres (Octahedral voids).

(ii) This structure has 6 : 6 coordination number.

(iii) A unit cell of NaCl consist of 4Na$^+$ ion and 4Cl$^-$ ions.

i.e., Number of Cl$^-$ ions $\left(\frac{1}{8}\times 8\right)+\left(\frac{1}{2}\times 6\right)=4$

Number of Na$^+$ ions $\left(\frac{1}{4}\times 12\right)+1=4$

Examples : Alkali metal halides (except Cs), Halides of Ag (except AgI).

(b) Caesium chloride (CsCl) type structure

Characteristics

(i) It has bcc arrangement

(ii) This structure has 8 : 8 coordination number

(iii) The unit cell of CsCl consists of one Cs$^+$ ion at body centre and eight Cl$^-$ ion at each corner *i.e.* one CsCl formula unit per unit cell.

Examples : CsBr, CsI, CsCN, TlCl, TlBr, TlI, TlCN

(c) Zinc blende (ZnS) type structure

Characteristics

(i) It has ccp arrangement in which S^{2-} ions are present at the corners as well as at the centre of each face of the cube.

(ii) Zn^{+2} ion are present at alternate tetrahedral void [50% of tetrahedral void.]

(iii) This structure has 4 : 4 coordination number.

Examples : CuCl, CuBr, CuI, AgI, and BeS

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