GASEOUS STATE

4.1 KINETIC THEORY OF GASES

To explain the behaviour of gases and to derive an expression for the pressure of gas, Claussius, Maxwell and Boltzmann put forward the following postulates:

1. A gas consists of a large number of small particles called molecules.
2. Molecules are always in a state of constant motion in all possible directions.
3. Molecules collide with each other and also with the walls of the container.
4. The pressure of the gas is due to the bombardment of the molecules on the walls of the container.
5. The gas molecules are spherical and the collisions are perfectly elastic.
6. There are no attractive forces between gas molecules.
7. The volume occupied by a single molecule is negligible when compared with the total volume of the gas.
8. The average kinetic energy of the gas molecules is directly proportional to the absolute temperature of the gas.

4.1.1 Derivation of kinetic equation

Consider a cubic vessel having edge length l cm. Let the number of molecules of the gas in the vessel be n each

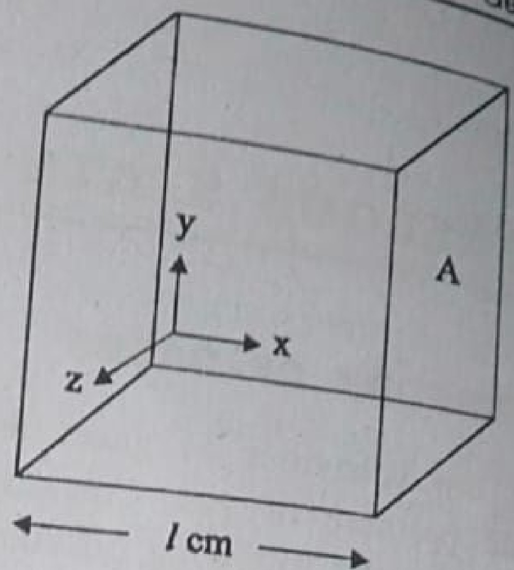


Fig. 4.1 Cubic vessel having edge length l cm

of the mass m. Let the RMS velocity of the molecules be C cm/sec. This is not the average velocity but little bit higher.

Even though the molecules are moving in all possible directions, the velocity of a molecule can be resolved into three components along the three axes x, y and z. Therefore,

$$C^2 = C_x^2 + C_y^2 + C_z^2$$

Let us consider that a molecule moves along the x-axis with a velocity C_x cm/sec. This molecule collides with the wall and rebounds with the same velocity.

$$\left.\begin{array}{l}\text{Momentum before}\\\text{collision}\end{array}\right\} = mC_x$$

$$\left.\begin{array}{l}\text{Momentum after}\\\text{collision}\end{array}\right\} = -mC_x$$

$$\left.\begin{array}{l}\text{Change in}\\\text{momentum}\end{array}\right\} = mC_x - (-mC_x)$$

$$= 2mC_x$$

The molecule travels a distance l cm to hit on the face A. Since the velocity of the molecule is C_x cm/sec, the number of collisions occurring per second is $\frac{C_x}{l}$.

Change in momentum per second (or) Rate of change of momentum $= 2mC_x \times \frac{C_x}{l}$

Rate of change of momentum $= \frac{2mC_x^2}{l}$

According to Newton's second law, the rate of change of momentum is equal to force.

$$\left.\begin{array}{l}\text{Force due to one molecule} \\ \text{along } x-\text{axis}\end{array}\right\} = \frac{2mC_x^2}{l}$$

$$\left.\begin{array}{l}\text{Force due to } n \text{ molecules} \\ \text{along x} -\text{axis}\end{array}\right\} = \frac{2mnC_x^2}{l}$$

$$\left.\begin{array}{l}\text{Force due to } n \text{ molecules} \\ \text{along } y-\text{axis}\end{array}\right\} = \frac{2mnC_y^2}{l}$$

$$\left.\begin{array}{l}\text{Force due to } n \text{ molecules} \\ \text{along } z-\text{axis}\end{array}\right\} = \frac{2mnC_z^2}{l}$$

$$\left.\begin{array}{l}\text{Force due to } n \text{ molecules} \\ \text{along } x, y \text{ and } z-axis\end{array}\right\} = \frac{2mnC_x^2}{l} + \frac{2mnC_y^2}{l} + \frac{2mnC_z^2}{l}$$

$$= \frac{2mn}{l}(C_x^2 + C_y^2 + C_z^2)$$

$$= \frac{2mnC^2}{l}$$

The pressure of a gas is given by:

$$P = \frac{\text{Force}}{\text{Area}}$$

Since a cube has six faces, its total area is $6l^2$.

$$\therefore\ P = \frac{2mnC^2}{l} \times \frac{1}{6l^2}$$

$$= \frac{2mnC^2}{6l^3}$$

$$= \frac{1}{3}\frac{mnC^2}{V}$$

OR $$PV = \frac{1}{3}mnC^2$$

$l^3 = V$

This is called kinetic equation for gases.

4.1.2 Deduction of gas laws from kinetic gas equation

1. Boyle's law

"At constant temperature, the volume of a given mass of gas is inversely proportional to the pressure"

$$V \propto \frac{1}{P}$$ (At constant temperature)

(or) PV = constant (At constant temperature)

According to kinetic gas equation,

$$PV = \frac{1}{3}mnC^2$$

$$= \frac{2}{3} \times \frac{1}{2}mnC^2$$

We know that, $\frac{1}{2}mnC^2 = KE$ at constant T

$$\therefore\ PV = \frac{2}{3}\text{KE}$$

PV = constant (at constant T)

This is Boyle's law.

2. Charles law

"At constant pressure the volume of a given mass of gas is directly proportional to the absolute temperature".

$$V \propto T \qquad \text{when p is constant}$$

According to kinetic gas equation,

$$PV = \frac{1}{3} mnC^2$$

$$= \frac{2}{3} \times \frac{1}{2} mnC^2$$

The average kinetic energy of the gas is directly proportional to absolute temperature.

$$\frac{1}{2} mnC^2 \propto T$$

$$= kT$$

$$\therefore PV = \frac{2}{3} kT$$

$$V = \frac{2}{3} \frac{kT}{P}$$

At constant pressure,

$$V \propto T$$

This is charle's law.

3. Graham's law of diffusion

"At constant pressure, the rate of diffusion of a gas is inversely proportional to the square root of the density of the gas"

$$r \propto \sqrt{\frac{1}{\rho}} \quad \text{.... at constant } P$$

According to kinetic equation,

$$PV = \frac{1}{3} mnC^2$$

$$C^2 = \frac{3PV}{mn} \qquad [\because mn = M]$$

$$= \frac{3PV}{M}$$

$$C = \sqrt{\frac{3PV}{M}}$$

$$= \sqrt{\frac{3P}{\rho}} \qquad \frac{M}{V} = \rho$$

At constant pressure,

$$C \propto \sqrt{\frac{1}{\rho}}$$

The rate of diffusion of a gas is directly proportional to the velocity of the molecules.

$$\therefore r \propto \sqrt{\frac{1}{\rho}}$$

This is Graham's law.

4. Dalton's law of partial pressure

"At constant temperature, the total pressure of a mixture of non-reacting gases is equal to the sum of the partial pressures of the gases".

$$P = P_1 + P_2 + P_3 + \ldots\ldots$$

Partial pressure is defined as the pressure exerted by the gas when it alone occupies the entire volume of the mixture.

Partial pressure = Mole fraction × Total pressure.

$$PV = \frac{1}{3} mnc^2$$

$$= \frac{2}{3} \times \frac{1}{2} mnc^2$$

$$= \frac{2}{3} KE \qquad \therefore mnc^2 = KE$$

$$\therefore KE = \frac{3}{2} PV$$

Since all the gases of the mixture are present in the same vessel, the volume may be taken as V.

$$\underset{\text{(Total)}}{\text{KE}} = \frac{3}{2} P_1 V + \frac{3}{2} P_2 V + \frac{3}{2} P_3 V \ldots$$

P_1, P_2, P_3 – Partial pressures

$$\underset{\text{(Total)}}{\text{KE}} = \frac{3}{2} \text{PV}$$

$$\therefore \frac{3}{2} PV = \frac{3}{2} P_1 V + \frac{3}{2} P_2 V + \frac{3}{2} P_3 V$$

$$= \frac{3}{2} V (P_1 + P_2 + P_3)$$

$$\therefore P = P_1 + P_2 + P_3$$

This is Dalton's law.

5. Avogadro's law

"Equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules".

$$n_1 = n_2$$

Let us consider two gases having the same volume (V) and same pressure (P). Let the number of molecules in the gases be n_1 and n_2 respectively. Let their masses be m_1 and m_2 respectively and let their RMS velocities be C_1 and C_2

$$PV = \frac{1}{3} m_1 n_1 C_1^2 \quad \text{(First gas)}$$

$$PV = \frac{1}{3} m_2 n_2 C_2^2 \quad \text{(Second gas)}$$

$$\therefore \frac{1}{3} m_1 n_1 C_1^2 = \frac{1}{3} m_2 n_2 C_2^2 \quad (1)$$

Since both the gases are at the same temperature, the KE of the molecules must be equal.

$$\frac{1}{3} m_1 C_1^2 = \frac{1}{3} m_2 C_2^2 \quad (2)$$

$$\frac{\frac{1}{3} m_1 n_1 C_1^2}{1/3\, m_1 C_1^2} = \frac{\frac{1}{3} m_2 n_2 C_2^2}{1/3\, m_2 C_2^2}$$

$$n_1 = n_2$$

This is Avogadro's law.

6. Kinetic energy equation

An equation for kinetic energy of gases can be deduced from kinetic equation.

$$PV = \frac{1}{3} mnC^2$$

$$= \frac{2}{3} \times \frac{1}{2} mnC^2$$

But $\frac{1}{2} mnC^2 = KE$

$$\therefore PV = \frac{2}{3} KE$$

For one mole of an ideal gas,

$$PV = RT$$

$$\therefore \frac{2}{3} KE = RT$$

$$\text{(or)}\ KE = \frac{3}{2} RT$$

For n moles,

$$KE = \frac{3}{2} nRT$$

4.1.3 Kinds of velocities

1. RMS velocity

"RMS velocity may be defined as the square root of the mean of the squares of the velocities of the molecules of a gas".

Calculation of RMS velocity

According kinetic gas equation,

$$PV = \frac{1}{3} mnC^2$$

$$C^2 = \frac{3PV}{mn}$$

For one mole of a gas,

$$n = N$$

$$\therefore C^2 = \frac{3PV}{mN} \qquad m \times N = M$$

$$= \frac{3PV}{M}$$

$$C = \sqrt{\frac{3PV}{M}} \qquad ...(1)$$

But $\frac{M}{V} = \rho$ (or) d. Hence,

$$C = \sqrt{\frac{3P}{\rho}}$$

Since $$PV = RT \quad ...(2)$$

$$C = \sqrt{\frac{3RT}{M}} \quad ...(3)$$

Depending upon the data available, one of the above equations can be used to calculate RMS velocity.

2. Average velocity (or) Mean velocity

"Average velocity is defined as the arithmetic mean (or) the average of the velocities of all the molecules present in the system".

$$\overline{C} = \sqrt{\frac{8RT}{\pi M}}$$

Average velocity is slightly less than RMS velocity.

$$\overline{C} = \text{RMS velocity} \times 0.9213$$

3. Most probable velocity

"Most probable velocity is defined as the velocity possessed by the greatest number of molecules present in the system".

$$C_{MP} = \sqrt{\frac{2RT}{M}}$$

$$C_{MP} = \text{RMS V} \times 0.816$$

RMSV: $\overline{C} : C_{Mp} = 1 : 0.9213 : 0.816$

4.1.4 Problems

1. *Calculate the RMS velocity and average velocity of CH_4 molecule at 27°C?*

Solution

Given

$$R = 8.314\ JK^{-1}\ mol^{-1}$$

$$T = 27°C = 300\ K$$

$$M = 16 \times 10^{-3}\ kg\ mol^{-1}$$

$$C = \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{3 \times 8.314 \times 300}{16 \times 10^{-3}}}$$

$$= 683.6\ ms^{-1}$$

$$\overline{C} = \sqrt{\frac{8RT}{\pi M}}$$

$$= \sqrt{\frac{8 \times 8.314 \times 300 \times 7}{22 \times 16 \times 10^{-3}}}$$

$$= \mathbf{630\ ms^{-1}}$$

2. *Calculate the kinetic energy of 2 moles of CO_2 at 27°C in Joules and Cals assuming the gas to be ideal.*

Solution

Given:

$$n = 2\ \text{moles}$$

$$R = 8.314\ JK^{-1}\ mol^{-1}$$

$$T = 27°C = 300\ K$$

(i) **KE in joules**

$$KE = \frac{3}{2} nRT$$

$$= \frac{3}{2} \times 2 \times 8.314 \times 300$$

$$= \mathbf{7482.60}\ \text{Joules}$$

(ii) **KE in cals**

$$KE = \frac{3}{2} nRT$$

$$= \frac{3}{2} \times 2 \times 1.987 \times 300$$

$$= \mathbf{1788.3}\ \text{cals}$$

4.1.5 Maxwell's law of distribution of molecular velocities

Maxwell's law of distribution of molecular velocities may be stated as:

"At constant temperature, the fraction of the total number of molecules moving in a particular range of velocities remains constant".

This law is illustrated in the graph.

The total area under the curve gives the total number of molecules having all velocities. The area enclosed between V_1 and V_2 corresponds to the number of molecules possessing these velocities. Maximum number of molecules are having the velocity near the point MPV. This is known as most probable velocity. It is the velocity possessed by greatest number of molecules.

It can be seen from the graph that the curve slopes down sharply on both the sides. This indicates that only negligible portion of the molecules have very low and very high velocities.

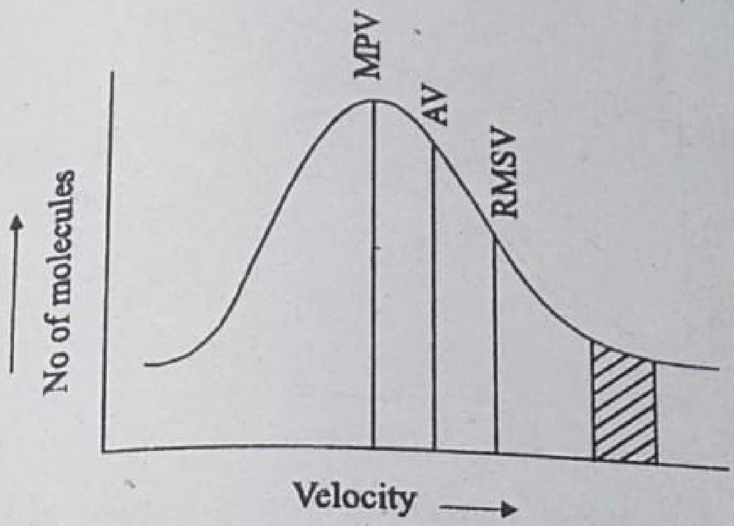


Fig. 4.2 Maxwell's law of distribution of molecular velocities

Maxwell utilized the probability theory to show the actual distribution of molecular velocities in a gas depends on temperature and molecular weight of the gas. Maxwell-Boltzmann distribution law may be represented mathematically as:

$$\frac{1}{n}\frac{dn}{dC} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-MC^2/2RT} \cdot C^2$$

The left-hand side of the equation represents the probability of finding molecules having a particular velocity, C.

It is well known that temperature has a profound influence on the distribution of molecular velocities.

The marked effect of temperature in increasing the probability of molecules having high velocities (or) high kinetic energies is due to the presence of the exponential factor, $e^{-MC^2/2RT}$ in the Maxwell-Boltzmann distribution equation.

When temperature is raised, the kinetic energy also increases. Hence at high temperature there will be a wider distribution of molecular velocities. In other words, at high temperature the number of molecules possessing high velocity

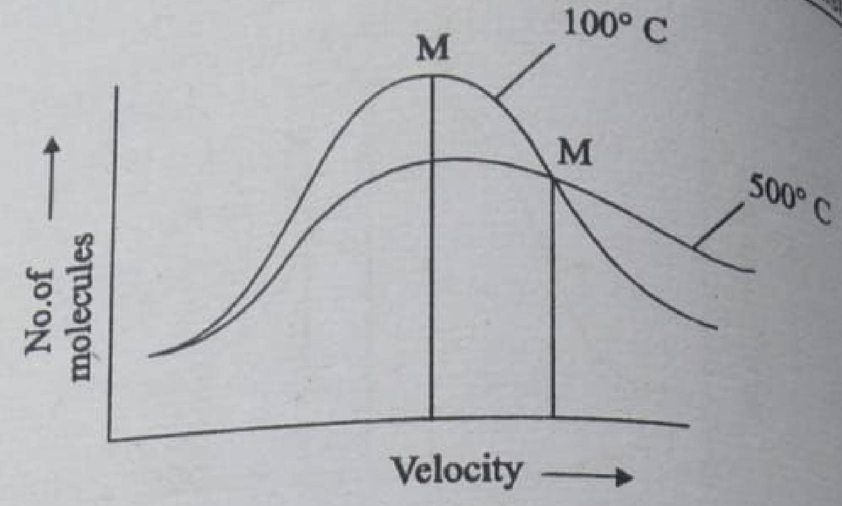


Fig. 4.3 Effect of temperature on molecular velocities

is increased. At higher temperature the maximum point (*M*) is shifted to right and the curve is broadened. Hence all the three velocities increase.

4.1.6 Law of Equipartition of energy

The law of Equipartition of energy was deduced by Maxwell and Boltzmann. According to this principle,

"The total energy possessed by molecules of a gas in thermal equilibrium is distributed equally between every degrees of freedom".

The number of degrees of freedom of an object is the number of independent parameters which are necessary to specify in order to describe completely its state (or) position. A degree of freedom is a possible mode of motion of a molecule.

In the case of a monoatomic gas, the only type of motion possible is motion in a straight line called translatory motion. This motion can be represented by three components mutually at right angles. The system, therefore, has three degrees of freedom. The kinetic energy of a molecule is $1/2\, mV^2$ and this can be resolved into three components.

$$\frac{1}{2}mV^2 = \frac{1}{2}mV_x^2 + \frac{1}{2}mV_y^2 + \frac{1}{2}mV_z^2$$

According to Law of Equipartition of energy,

$$\frac{1}{2}mV_x^2 = \frac{1}{2}mV_y^2 = \frac{1}{2}mV_z^2 = \frac{1}{2}\frac{RT}{n}$$

because the total $KE, \frac{1}{2}mnV^2 = \frac{3}{2}RT.$

Every degree of freedom of this motion (translatory motion) is therefore associated with an amount of energy = 1/2 RT per mole. The total energy is 3/2 RT and the corresponding molar heat capacity is 3/2 R cals. Gases of all kinds have translatory motion and therefore they all have energy 3/2 RT corresponding to this motion.

Consider a molecule composed of N atoms. It has $3N$ degrees of freedom. Three coordinates are necessary to locate the position of the centre of the mass of the molecule which is the point where the whole mass can be assumed to be concentrated. So there remains $3N - 3$ degrees of freedom. These are attributed to other modes of internal motions viz rotation and vibration.

Gas molecules made up of more than one atom may possess vibrational energy which is both potential and kinetic. For a diatomic molecule this motion can only exist in one direction. Hence two degrees of freedom would be assigned to it, one for potential and one for kinetic energy. For a linear polyatomic molecule, the vibrational degrees of freedom are $(3N-5)$. For a non-linear polyatomic molecule, there are $(3N-6)$ vibrational degrees of freedom.

Consider rotational motion. A diatomic (or) a linear polyatomic molecule behaves as a rigid rotor. It can rotate about only two axes. Hence two additional degrees of freedom are required to describe such molecules. In the case of a polyatomic, non-linear molecule, there are three degrees of freedom.

For a diatomic gas, we have three degrees of freedom for translation, two for rotation and two for vibration.

Calculation of energy and heat capacity from equipartition principle

$$E_{Total} = E_{trans} + E_{rot} + E_{vib}$$

For monoatomic gases

$$f_{trans} = 3\ ;\ f_{rot} = 0\ ;\ f_{vib} = 0$$

$$E_{Total} = \left(3 \times \frac{1}{2} RT\right) + 0 + 0$$

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

$$C_v = \frac{3}{2} R$$

For diatomic gases

$$f_{trans} = 3\ ;\ f_{rot} = 2\ ;\ f_{vib} = 1$$

$$E_{Total} = \left(3 \times \frac{1}{2} RT\right) + \left(2 \times \frac{1}{2} RT\right) + RT$$

$$= \frac{7}{2} RT$$

$$C_v = \frac{7}{2} R$$

For linear triatomic gas

$$f_{trans} = 3\ ;\ f_{rot} = 2\ ;\ f_{vib} = 4$$

$$E_{Total} = \left(3 \times \frac{1}{2} RT\right) + \left(2 \times \frac{1}{2} RT\right) + 4RT$$

$$= \frac{13}{2} RT$$

$$C_v = \frac{13}{2} R$$

For a Non-linear triatomic gas

$$f_{trans} = 3\ ;\ f_{rot} = 3\ ;\ f_{vib} = 3$$

$$E_{Total} = \left(3 \times \frac{1}{2} RT\right) + \left(3 \times \frac{1}{2} RT\right) + 3RT$$

$$= 6RT$$

$$C_v = 6R$$

4.1.7 Virial equation

Vander Waals equation and several two constant equations have been proposed to explain the behaviour of real gases. Some important equations are given below:

1. Dieterici equation

$$P = \frac{RT e^{-a/RT}}{(V-b)}$$

This equation gives better results than Van der Waals equation at high pressures.

2. Berthellot's equation

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

This equation gives good agreement between the observed and calculated values particularly at low pressure.

3. Claussius equation

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

This equation is fairly satisfactory but does not hold for all gases.

All these equations were attempts to adjust a two constant equation to accurately represent the behaviour of real gases. Only a limited success could be obtained.

When several of the two constant equations like Van der Waals equation failed to give accurate enough results, it was attempted to convert the general equation, $PV=RT$ to an accurate form algebraically employing more than two constants when necessary. The correction factors were introduced as higher powers of the variables. Such modified, more accurate equations have been called virial equations. The word virial stands for power.

4. Kammnrling - Onnes equation

$$PV=A+BP+CP^2+DP^3+\ldots$$

In this equation A, B, C etc., are respectively called first, second, third virial coefficients. Their values depend on temperature. A equals RT. The second and subsequent terms gain importance as the value of P increases. This equation gives accurate results upto 1000 atmospheres.

5. Beatie and Bridgemann equation

$$PV=RT+\frac{\beta}{V}+\frac{\gamma}{V^2}+\frac{\delta}{V^3}$$

This equation gives very accurate results upto 100 atmosphere down to a temperature of $-150°C$.

4.1.8 Boyle's temperature

The temperature at which a real gas obeys Boyle's law is known as Boyle's temperature. It is denoted by T_B.

In general, the more easily liquefiable gases have high Boyle temperatures whereas the gases difficult to liquefy have low Boyle temperatures. Boyle temperature can be obtained from Van der Waals equation as follows:

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

This can also be written as

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

(or)

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

Differentiating with respect to pressure at constant temperature.

$$\left[\frac{\partial (PV)}{\partial P}\right]_T=\left[\frac{RT}{V-b}-\frac{RTV}{(V-b)^2}+\frac{a}{V^2}\right]\left(\frac{\partial V}{\partial P}\right)_T$$

At Boyle temperature, T_B

$$\left[\frac{\partial (PV)}{\partial P}\right]_T=0$$

$$\therefore\left[\frac{RT}{(V-b)}-\frac{RTV}{(V-b)^2}+\frac{a}{V^2}\right]\left(\frac{\partial V}{\partial P}\right)_T=0$$

But $\left(\frac{\partial V}{\partial P}\right)_T$ cannot be zero.

$$\therefore \frac{RT}{V-b} - \frac{RTV}{(V-b)^2} + \frac{a}{V^2} = 0$$

Hence,

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

when $P \to 0$, the volume will be infinitely large i.e., $(V-b) \approx v$.

$$\therefore RT_B = \frac{a}{b}$$

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

4.1.9 Coefficient of thermal expansion and compressibility

Fluids (Gases and liquids) expand on heating though the expansion of gases is much more than that of liquids. Similarly they can be compressed.

1. Definition for co-efficient of thermal expansion

At constant pressure, the volume of a gas, increases with rise in temperature. The variation of volume with temperature at constant pressure is known as coefficient of thermal expansion (or) coefficient of isobaric expansion (or) expansivity. It is denoted by α. Mathematically α is given by:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

For an ideal gas,

$$PV = nRT$$

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

Differentiating this with respect to temperature at constant pressure, we get

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\therefore \alpha = \frac{1}{V}\frac{nR}{P}$$

$$= \frac{1}{V}\left(\frac{V}{T}\right) = \frac{1}{T}$$

2. **Definition for co-efficient of compressibility**

At constant temperature, the volume of a gas decreases with rise in pressure. The variation of volume with pressure at constant temperature is known as coefficient of isothermal compressibility (or) simply compressibility. It is denoted by β.

Mathematically β is given by:

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

The negative sign indicates the decrease in volume.

For an ideal gas,

$$PV = nRT$$

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

Differentiating this with respect to P at constant T, we get

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{nRT}{P^2}$$

$$= -\frac{V}{P}$$

$$\therefore \beta = -\frac{1}{V}\left(-\frac{V}{P}\right)$$

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

Relation between α and β

We know that

$$V = f(T, P)$$

The total differential can be written as

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

By definition

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Hence

$$\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$$

Similarly,

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Hence

$$\left(\frac{\partial V}{\partial P}\right)_T = -\beta V$$

Substituting these in the equation for dV we get

$$dV = \alpha\, VdT - \beta\, VdP$$

For a condition at constant volume, $dV = 0$.

$$\therefore \alpha\, VdT - \beta\, VdP = 0$$

(or) $\alpha\, VdT = \beta\, VdP$

$$\frac{\alpha}{\beta} = \left(\frac{\partial P}{\partial T}\right)_V$$

4.2 LIQUID STATE

Liquid state may be regarded as an intermediate between solid and gaseous states. In the liquid state, the intermolecular forces of attraction are strong enough to hold the molecules together. But the thermal motions are also strong to impart translational motion to the molecules in the liquids. Even in liquid state, the average kinetic energy of the molecules is directly proportional to the absolute temperature.

4.2.1 General properties of liquids

1. **Volume**

Liquids have definite volume. This is due to the fact that the molecules of a liquid are closely packed. Further liquids are incompressible.

2. **Shape**

Liquids have no definite shape. They assume the shape of the container in which they are kept.

3. **Density**

Liquids have greater density than their vapours and many general gases. The molecules in a liquid are held closer to one another than in a gas. Hence, the density of a substance in the liquid state is greater than the gaseous state.

Example

The density of water at 373 K and 1 atm pressure is 0.958×10^3 kg m^{-3}. But at the same temperature and pressure, the density of water vapour as calculated from ideal gas equation is 0.558 kg m^{-3}.

The density of liquids decrease with increase of temperature. But in H_2O, in the temperature range 0°C – 4°C the density increases with temperature.

4. Diffusion

Diffusion involves the movement of molecules from one position to another. Liquids also diffuse like gases. But the diffusion in liquids is very slow. This is due to the fact that liquid molecules have to encounter a number of collisions with the neighbouring molecules even as they move through a small distance.

5. Evaporation

When a liquid is kept as such, it slowly changes into vapour. The process of conversion of liquid into vapour is called Evaporation. Vapour pressure of a liquid is defined as the pressure exerted by the liquid when the liquid and vapour are in equilibrium at a given temperature. The vapour pressure of a liquid always increases with temperatures.

We can explain the variation of vapour pressure of a liquid with temperatures using Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_v - V_l)}$$

$\frac{dP}{dT}$ – Variation of vapour pressure with temperature.

T – Temperature

ΔH_v – Molar latent heat of vapourisation.

V_v – Molar volume of the vapour.

V_l – Molar volume of the liquid.

When the temperature is far apart from critical temperature,

$$V_v >> V_l$$

$$V_v - V_l \approx V_l$$

If the vapours behave ideally,

$$V_v = \frac{RT}{P}$$

Substituting this in Clapeyron equation, we get

$$\frac{dP}{dT} = \frac{\Delta H_v \cdot P}{TRT}$$

$$\text{(or)}\ \frac{1}{P} \cdot \frac{dP}{dT} = \frac{\Delta H_v}{RT^2}$$

$$\text{Since}\ \frac{1}{P} \cdot \frac{dP}{dT} = \frac{d\ln P}{dT},$$

$$\frac{d\ln P}{dT} = \frac{\Delta H_v}{RT^2}$$

According ΔH_v to remain constant in a given range of temperature the above equation may be integrated between limits:

$$\int_{P_1}^{P_2} d\ln P = \int_{T_1}^{T_2} \frac{\Delta H_v}{R} \cdot \frac{dT}{T^2}$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$= \frac{\Delta H_v}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

This is called Clapeyron-Claussius equation. Using this equation, ΔH_v can be calculated if the values of vapour pressures at two different temperatures are known. On the other hand, if the vapour pressure at one temperature and ΔH_v values are known, the value of vapour pressure at another temperature can be calculated.

Boiling point is defined as the temperature at which its vapour pressure becomes equal to the external pressure.

6. Surface tension

Molecules are more closely packed in the liquid state than in the vapour state. Hence strong intermolecular forces of attraction are operating between molecules of a liquid. The existence of strong intermolecular forces of attraction in liquids gives rise to another important property known as surface tension.

Let us consider two molecules of a substance in the liquid state. Molecule *A* is attracted equally from all direction and the resultant force on the molecule is zero. But the molecule *B* which is on the surface is not attracted equally in all directions. It is attracted only by molecules present

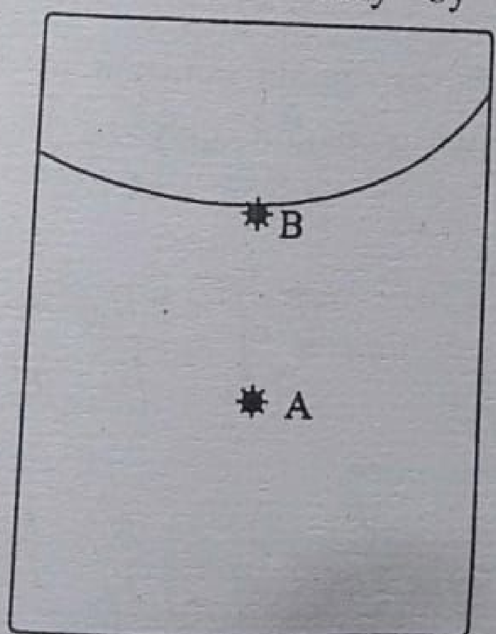


Fig. 4.4 Effect of surface tension on molecules A and B

downwards and sideways. Hence the surface behaves like a stretched membrane. The force that opposes the expansion of surface is known as surface tension.

"Surface tension may be defined as the tangential force acting upon a line of 1 metre length in the surface". It is expressed in Nm^{-1}.

$$(1N = 10^5 \text{ dynes})$$

Floating of metallic needles on H_2O, rise of H_2O level in the capillary tube, presence of liquid drops in spherical shape etc., are only due to surface tension.

Effect of temperature on surface tension

The surface tension of a liquid decreases with increase of temperature. At critical temperature, the surface tension is zero. This is due to the fact that the difference between liquid state and vapour state disappears at the critical temperature.

Ramsay-shield equation gives an empirical relation between surface tension and temperature.

$$\gamma \left(\frac{M}{\rho} \right)^{2/3} = K\,(T_c - T - 6)$$

γ – Surface tension

T_c – Critical temperature

T – Temperature of the experiment

K – Constant

M – Molecular weight

ρ – Density

For normal liquids like benzene, $K = 2.12$. For liquids containing associated molecules, the value of K is found to be less than 2.12.

Measurement of surface tension

Capillary tube method

When one end of the capillary tube is immersed in a liquid, the liquid level rises in the capillary tube. The liquid must be capable of wetting the glass. The liquid rises into the capillary tube and continues to rise till the downward force due to weight by liquid column equals the upward force exerted by surface tension. The radius of the capillary tube should be uniform.

Weight of liquid in the capillary tube $= \pi r^2 hdg$

Total force due to surface tension $= 2\pi r \gamma \cos\theta$

$$2\pi r \gamma \cos\theta = \pi r^2 hdg$$

$$\gamma = \frac{\pi r^2 hdg}{2\pi r \cos\theta}$$

$$= \frac{hdgr}{2\cos\theta}$$

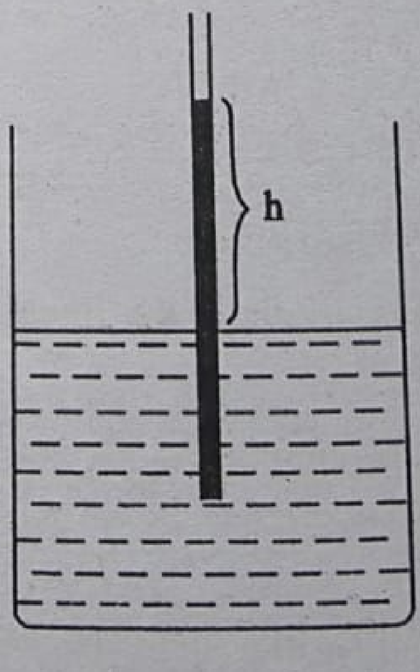


Fig 4.5 Measurement of surface tension by capillary tube method.

If the wetting is perfect,

$$\cos\theta = 1$$

So,
$$\gamma = \frac{hdgr}{2}$$

The height of liquid in the capillary tube can be measured using cathetometer and the radius of the capillary tube can be measured using travelling microscope.

7. **Viscosity**

Flow is a characteristic property of liquids. Some liquids like glycerine, castor oil, honey, coal tar etc., flow very slowly while H_2O, alcohol, ether etc., flow readily. These differences in flow rates result from a property known as viscosity.

Definition: Viscosity

Viscosity may be defined as the resistance of the liquid to flow.

The resistance offered by one part of the liquid moving with a particular velocity to another part of the liquid flowing with a different velocity is called viscosity.

Definition: co-efficient of viscosity

Coefficient of viscosity of a liquid is defined as the tangential force per unit area required to maintain a unit difference of velocity between two parallel layers of the liquid held apart at a unit distance.

Unit:

$$\eta = \frac{\text{Force} \times \text{distance}}{\text{Area} \times \text{velocity}}$$

$$= \frac{\text{dyne} - \text{cm}}{\text{cm}^2 \times \text{cm} \cdot \text{sec}^{-1}}$$

$$= \text{dyne cm}^{-2}\ \text{sec}$$

This unit is called Poise in honour of French scientist Poiseuille.

In SI unit,

$$1 \text{ Poise} = 0.1 \text{ Nsm}^{-2}$$

The reciprocal of coefficient of viscosity is termed as Fluidity (or) mobility represented by ϕ.

$$\phi = \frac{1}{\eta}$$

Factors affecting viscosity

1. Pressure

On increasing the pressure, the viscosity of a liquid increases.

2. Molecular size of the liquid

A larger molecule of the compounds belonging to the same class offers more resistance to flow than a smaller one.

3. Effect of temperature

Viscosity is markedly dependent on temperature. When the temperature of the liquid increases, its viscosity decreases because viscosity is due to intermolecular forces which decreases with rise in temperature. The decrease in viscosity is of the order of about 2% per °C rise in temperature.

The variation of viscosity with temperature is be explained by the empirical relation:

$$\eta = Ae^{-E/RT}$$

Taking logarithms

$$\log \eta = \log A - \frac{E}{2.303\, RT}$$

$A, E -$ Constants.

When $\log \eta$ values are plotted against $1/T$ values a straight line is obtained. The value of the slope is $E/2.303R$. The value of E calculated from the slope corresponds to the activation energy for flow process.

4.2.2 Parachor

The relation between surface tension and density of liquids is represented by Macleod equation as follows:

$$\frac{\gamma^{1/4}}{\rho - \rho'} = C$$

Here C is a constant for non-associated liquids and is independent of temperature over a wide range. Multiplying both the sides of the Macleod equation by molecular weight, we get

$$\frac{M\gamma^{1/4}}{\rho - \rho'} = MC = P$$

M – Molecular weight

P – Parachor

γ – Surface tension

ρ – Density of the liquid

ρ' – Density of the vapour

P is a constant and is called parachor.

Definition

Parachor may be defined as the molar volume of the liquid at a temperature at which its surface tension is unity.

This was introduced by Sudden. Parachor is independent of temperature. At ordinary temperature, $\rho - \rho' = \rho$. Hence,

$$\frac{M\gamma^{1/4}}{\quad} = P$$

If the density of the liquid is determined at a temperature in which surface tension is unity,

$$\gamma^{1/4} = 1$$

$$\frac{M}{\rho} = P = V_m$$

Thus Parachor represents molar volume. Comparison of parachors is equivalent comparison of molar volumes.

Parachor is predominantly an additive property and slightly a constitutive property. Therefore the parachor value of a compound can be split into atoms, groups, bonds and structural parachors. The parachor of C − C bond is chosen as the standard. On this basis, the parachor values of C = C and C ≡ C are 23.2 ml and 46.6 ml respectively. Oxygen atom has a definite value of parachor. This value of oxygen depends on the group (alcohol, ester, carbonyl, phenol etc) in which the oxygen is present. A ring aiso contributes definite parachor value. It depends upon the size and nature of the ring.

Some of the important atomic and structural parachors are given below:

Element	Parachor	Structure (or) bond	Parachor
C	4.8 ml	C = C	23.2 ml
H	17.1 ml	C ≡ C	46.6 ml
O	20.0 ml	Coordinate bond	− 1.6 ml
N	12.5 ml	Six-membered ring	6.1 ml
Cl	54.7 ml	Naphthalene ring	12.2 ml

Applications of parachor

With the help of atomic and structural parachors, the parachor value of a compound can be calculated. This value is used in solving structural problems.

1. Structure of benzene

Many structures were given for benzene. But only kekule structure explains most of the properties of benzene. Parachor measurements confirm that only kekule structure is correct for benzene.

$$HC \equiv C - CH_2 - CH_2 - C \equiv CH$$

$$CH_3 - C \equiv C - C \equiv C - CH_3; \qquad P = 224.6 \text{ ml}$$

6 C	6×4.8	
6 H	6×17.1	$P = 207.1$ ml
3 C = C	3×23.2	
Six membered ring	6.1	

$$P_{experimental} = \frac{M \gamma^{1/4}}{\rho} = 206.2 \text{ ml}$$

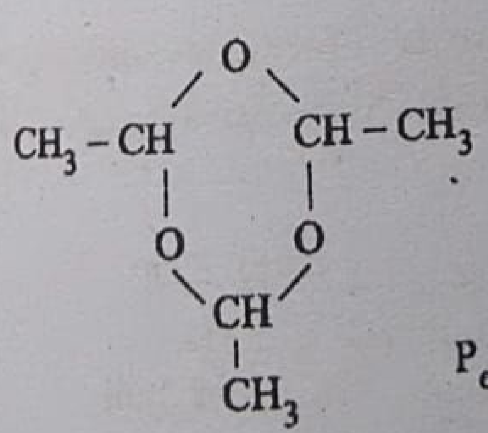
Parachor value calculated on the basis of kekule structure agrees with the experimental value.

2. Structure of paraldehyde

The structure of paraldehyde and paraformaldehyde pose a problem. Paraldehyde does not respond to the reactions of free $-CHO$ group. Parachor measurement shows that only cyclic structure is correct for paraldehyde.

$$(CH_3 - CHO)_3 \qquad P = 121.3 \times 3 = 363.9 \text{ ml}$$

$$CH_3 - \underset{\displaystyle OH}{\underset{|}{C}} - CH_2 - \underset{\displaystyle OH}{\underset{|}{C}} - CH_2 - CHO \qquad P = 317.2 \text{ ml}$$

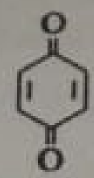


$P = 300.1$ ml

$$P_{expt} = \frac{M\gamma}{\rho} = 298.7 \text{ ml}$$

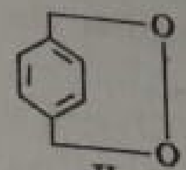
3. Benzoquinone

Two different structures are proposed for benzoquinone.



I

$P_{col} = 236.1$ ml



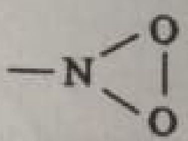
II

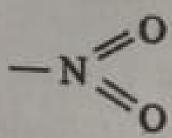
$P_{col} = 219$ ml

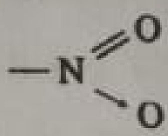
The experimental value is 236.8 ml. Therefore parachor result is in harmony with the diketone structure.

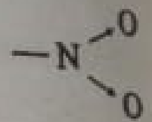
4. Nitro group

The structural problem for $-NO_2$ group was solved by Parachor studies. Nitro group ($-NO_2$) may be represented by any one of the following structures.









	I	II	III	IV
Parachor calculated	**69.2**	**98.9**	**74.1**	**49.3**

The observed parachor of $-NO_2$ was found to be 73 ml. This clearly shows that nitro group should be represented by structure (III).

5. Isocyanide group

Two structures are possible for isocyanide group. The calculated values of parachor for the two structures are given below:

$-N = C$

I

$P_{cal} = 40.5$ ml

$-N \overset{\rightarrow}{\equiv} C$

II

$P_{cal} = 62.3$ ml

The observed value of parachor is 66 ml. This is in favour of structure II. This is also supported by the dipole moment measurement.

6. **Carbon monoxide**

Two structures are proposed for CO:

$$\underset{\substack{\text{I} \\ P_{cal} = 48 \text{ ml}}}{C=O} \qquad \underset{\substack{\text{II} \\ P_{cal} = 69.8 \text{ ml}}}{C \overset{\rightarrow}{=} O}$$

The observed value of parachor is 61.6 ml. This favours II formula. The same conclusion is reached by the dipole moment measurement.

4.2.3 Liquid crystals

Certain solid substances like p-azoxyanisole, p-azoxyphenetole, cholesteryl benzoate etc are found to possess some peculiar properties. These substances when heated melt at definite temperatures to give turbid liquids which on further heating change to clear liquids at equally sharp temperatures. On cooling, the reverse changes take place.

Definition

Liquid crystals (LC) are neither true liquids nor ture solids, but combine the properties of both solids and liquids. The important phase difference between solids and liquids is the orderly arrangement in solids and disordered arrangement in liquids.

Example

p-azoxyanisole when heated, changes into a turbid liquid at 116°C. At 135°C, the turbid liquid changes into a clear liquid. When the clear liquid is cooled, the above charges take place in the reverse direction.

$$\text{Solid} \underset{}{\overset{116°C}{\rightleftharpoons}} \text{Turbid liquid} \underset{}{\overset{135°C}{\rightleftharpoons}} \text{Clear liquid}$$

The turbid liquid possesses peculiar optical properties. It gives interference patterns in polarised light and is found to be doubly refracting. These are the characteristic properties of Anisotropic crystals in which the velocity of light is not uniform in all directions.

Lehmann gave the name liquid crystals for the turbid liquid possessing unusual properties. This name is not satisfactory because the molecules in the turbid liquid are not properly arranged as in the crystal lattice. Hence mesomorphic state is the term used at present to describe such a state. The term mesomorphic state is suitable because the turbid liquid is an intermediate between the solid and the clear liquid. The term Anisotropic liquid is also a suitable term.

The temperature at which the solid melts to give the turbid liquid is called the transition point and the higher temperature at which the turbid liquid becomes clear is called the melting point.

More than 1500 compounds are known to exhibit mesomorphic state. They are all organic compounds. These compounds end in any one of the groups such as $-OCH_3$, $-OC_2H_5$, $-COOCH_3$, $-COOC_2H_5$ etc. In compounds containing benzene ring, only para substituted compounds exhibit mesomorphic state.

Classification of Liquid crystals (mesomorphic state)

Systematic study has revealed that the substances which form liquid crystals can be broadly classified into three classes, called

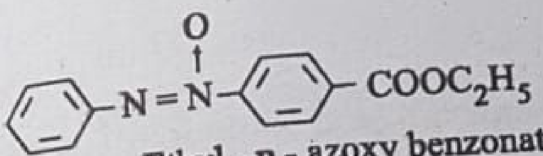
1. Smectic,
2. Nematic and
3. Cholesteric phases.

They are all long chains organic compounds. This classification is based on the arrangement of molecules.

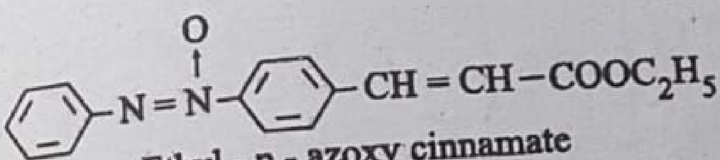
1. **Smectic phase**

In smectic type crystals long-chain molecules are arranged parallel to each other in equally spaced planes. But there is no order within the plane. That is, smectic crystals have two-dimensional order and one-dimensional disorder.

Examples



Ethyl - p - azoxy benzonate

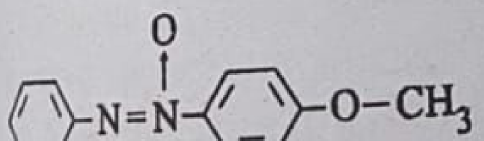


Ethyl - p - azoxy cinnamate

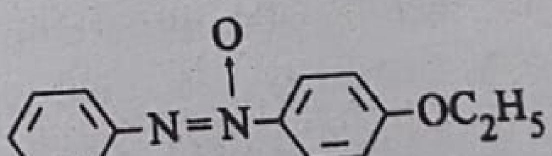
2. **Nematic phase**

In this type of liquid crystals, long-chain molecules are parallel to each other. But there is no planar structure. Hence Nematic type of liquid crystals have one-dimensional order and two-dimensional disorder.

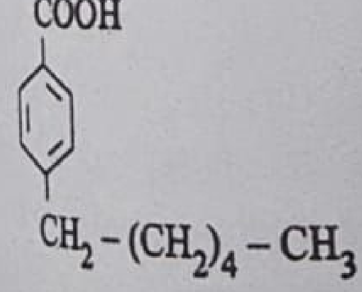
Examples



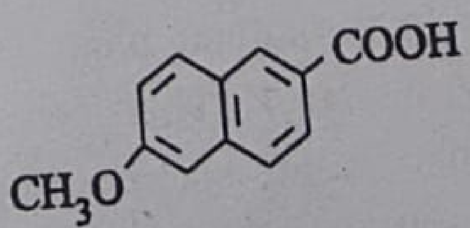
p - Azoxyanisole



p - Azoxyphenetole



p-n-Hexybenzonic acid



6 - Methoxy - 2 - naphthoic acid

3. Cholesteric phase

Even though cholesteric crystals have many special properties of the Nematic crystals, they have some peculiar optical properties. These crystals disperse the white light into bright, individual colours. Twisted molecular layers are present in cholesteric liquid crystals. These are responsible for optical properties.

Examples :

Cholesteryl benzoate and cholesterol derivatives belong to this types.

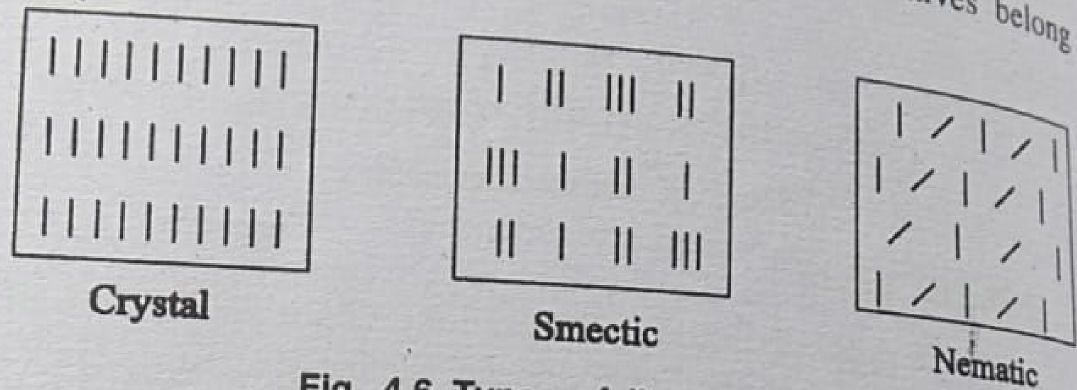


Fig. 4.6 Types of liquid crystals

Theory of liquid crystals (or) Molecular arrangements

The most widely accepted theory of Liquid crystals is the Swarm theory suggested by E.Bose in 1909. According to this theory, the turbid liquid is a mass of large number of very small crystals. Each crystal contains molecules, arranged in a definite pattern. The turbidity of the liquid crystals is due to the scattering of light by small crystals. Though the swarms are distributed at random, all the molecules are approximately parallel to each other so that they have freedom of movement either in horizontal plane (smectic state) (or) in vertical plane (nematic state). This type of orientation of the molecules accounts for the special properties of the liquid crystals. When temperature is raised, molecules scatter from swarm shape. As a result, it is not able to scatter light. Hence turbid liquid becomes a clear liquid on raising the temperature.

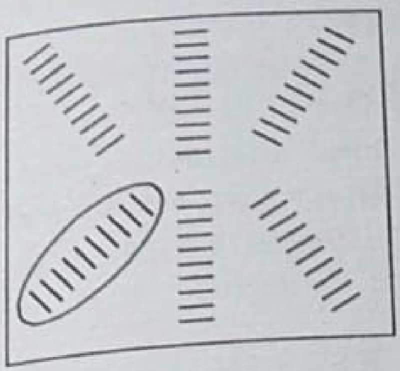


Fig. 4.7 Molecular arrangements in turbidity.

Applications

1. Liquid crystals are used as solvent in the spectroscopic study of the structure of Anisotropic molecules.
2. Liquid crystals consume very low quantity of electrical energy. Hence used in pocket calculators, digital wrist watches etc.
3. The mechanical and electrical properties of liquid crystals are somewhat in between the properties of solid crystals and isotropic liquids. Hence they are used in Gas - liquid chromatography.
4. Certain liquid crystals are used in the separation of meta and para isomers of organic compounds.
5. Nematic crystals are useful tools in NMR studies. NMR studies give information regarding bond angle, bond length, spin-spin coupling etc.
6. Cholesteric type of crystals are used to identify tumours in the body by the method of Thermography.

4.3 SOLID STATE

4.3.1 Nature of the solid state

Out of three states of matter (solids, liquids and gases) solids are characterised by incompressibility, rigidity and mechanical strength. Solids possess both definite shape and definite volume. The molecules, ions (or) atoms are closely packed in solids.

Types of solids

Solids are further classified into two types:

1. Crystalline solids
2. Amorphous solids

A crystalline solid is one in which the constituent structural units (molecules, ions (or) atoms) are arranged in a definite geometrical pattern.

4.3.2 Crystallography

Crystallography is the branch of science which deals with the development and growth of crystals, their properties, geometry and structure.

Laws of crystallography

It is based on three fundamental laws:

1. Stens's law of constancy of interfacial angles.
2. Hauy's law of rationality of indices.
3. Law of symmetry.

1. The laws of constancy of interfacial angles

According to this law, the angle between the corresponding faces (or) planes, forming the external surface of a crystal, remains constant for a given substance, no matter how the face is formed.

A substance may crystallise under different conditions to produce crystals with faces of variable size and shape. The angle of intersection of any two corresponding faces, however, would always be found to be the same. The instrument employed for the measurement of interfacial angle is called Goniometer.

2. Hauy's law of rationality of indices

For any crystal, a set of three coordinate axes can be chosen in such a way that all the faces of the crystal will either intercept the three axes at definite distances from the origin (or) be parallel to some of the axes in which case the intercepts are at infinity.

The law of rationality of indices (or) intercepts proposed by Hauy states that it is possible to choose along the three coordinate axes unit distances (a, b and c) not necessarily of the same length such that the ratio of the three intercepts of any plane in the crystal is given by $ma : nb : pc$ where m, n and p are either integral whole numbers including infinity (or) fractions of whole numbers.

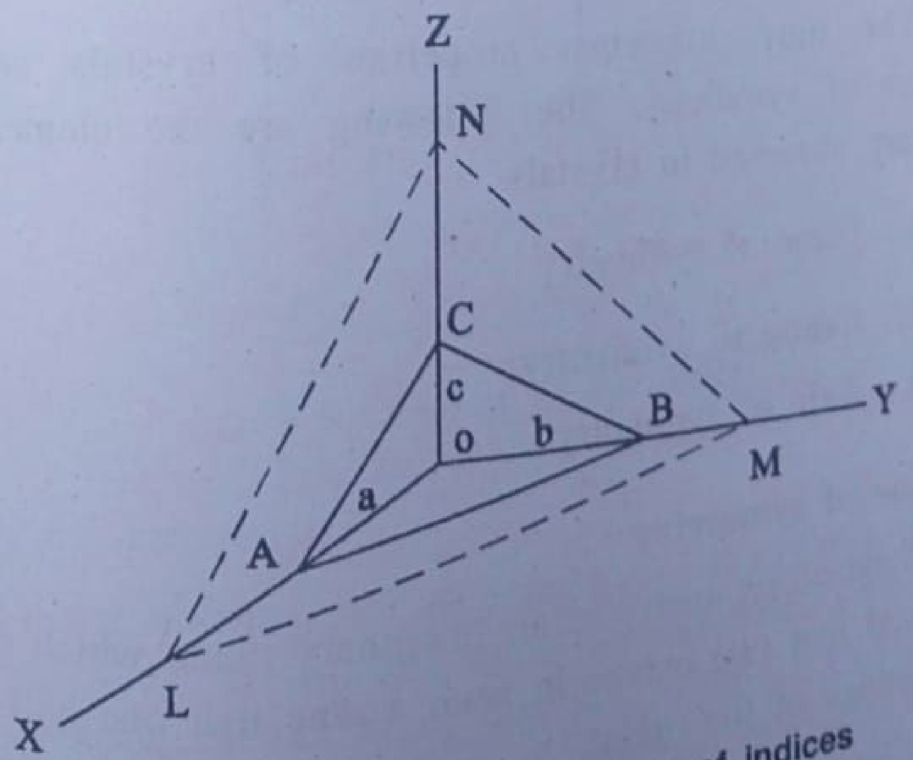


Fig.4.8 Hauy's law of rationality of indices

The coefficients of a, b and c are called Weiss coefficients of a plane. Weiss coefficients are not always simple integral whole numbers. They may have fractional values as well as infinity. Weiss coefficients are replaced by Miller indices.

3. Laws of symmetry

It states that all crystals of the same substance possess the same elements of symmetry. Various elements of symmetry as:

1. Plane of symmetry
2. Centre of symmetry
3. Axis of symmetry

The total number of planes, centres and lines of symmetry of a crystal are called its elements of symmetry. The simple cube has the greatest symmetry. It has nine planes of symmetry, one centre of symmetry and thirteen axes of symmetry, i.e., 23 symmetry elements in all.

4.3.3 Elements of symmetry (or) Symmetry elements

The most important properties of crystals are the elements of symmetry. The following are the elements of symmetry observed in crystals.

1. Plane of symmetry
2. Centre of symmetry
3. Axis of symmetry

1. Plane of symmetry

Plane of symmetry is an imaginary plane which divides the crystal into two halves in such a way that one half is the mirror image of the other.

A simple cube has nine planes of symmetry.

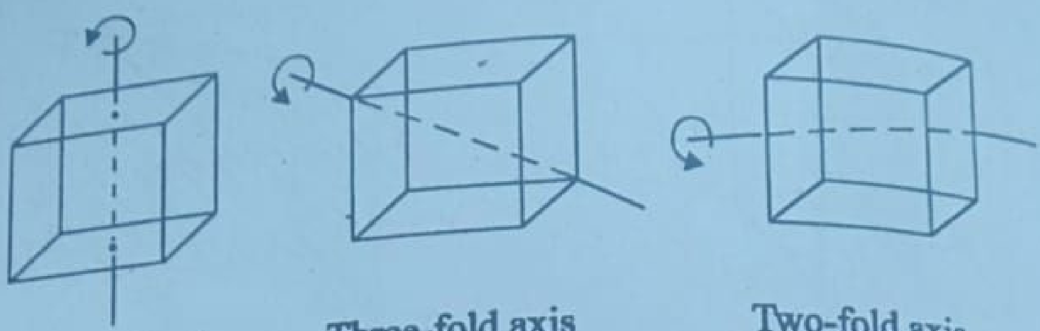


Fig. 4.11 Axis of symmetry

4.3.4 Space lattice and Unit cell

1. Space lattice

Space lattice is an array of points showing of how atoms, ions (or) molecules are arranged in different sites in a three-dimensional space.

2. Unit cell

Unit cell is the smallest repeating unit in the space lattice which when repeated again and again results in the crystal.

4.3.5 Miller indices

Miller indices are integers used for representing planes and surfaces.

Miller indices are the reciprocals of the multiples of unit distances when the three intercepts of a plane are expressed as multiples of unit distances.

Usually Miller indices are obtained by taking the reciprocals of the Weiss coefficients. When it is found necessary, the ratio is multiplied by the least count multiple to get the integral values.

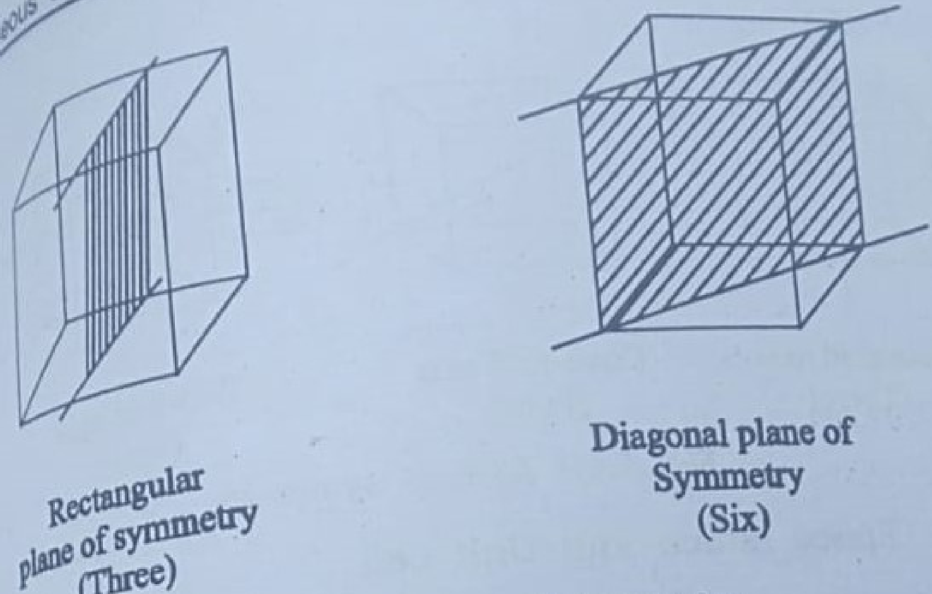


Fig. 4.9 Plane of symmetry

2. Centre of symmetry

Centre of symmetry is an imaginary point within the crystal through which any straight line drawn will intersect the surface at equal distances on either side.

A simple cube has only one centre of symmetry.

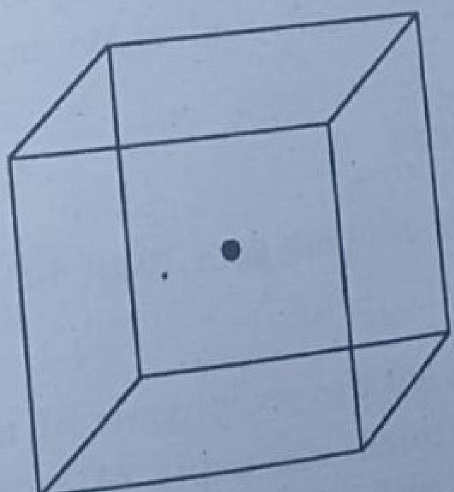
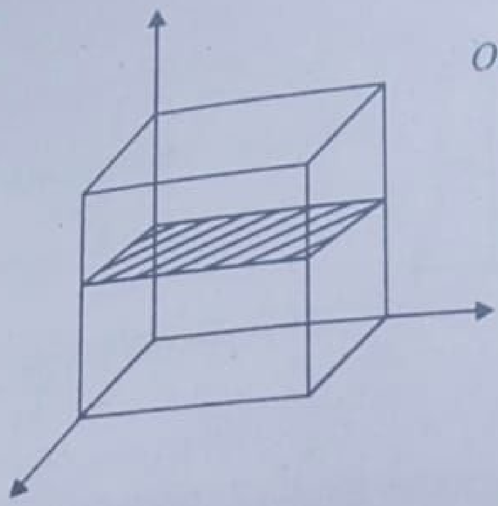


Fig. 4.10 Centre of symmetry

3. Axis of symmetry

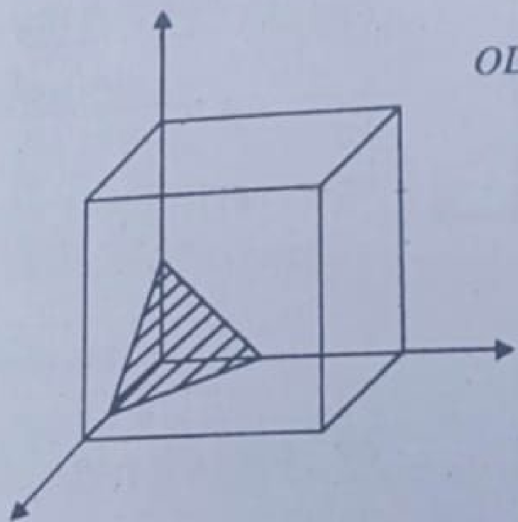
Axis of symmetry is an imaginary line passing through the crystal about which the crystal can be rotated in such a way that during the course of one full rotation it presents the same appearance more than ones.



$$OL : OM : ON = \infty a : \frac{1}{2} b : \infty c$$

$$\frac{1}{\infty} = \frac{1}{1/2} = \frac{1}{\infty}$$

020 plane



$$OL : OM : ON = \frac{1}{2} a : \frac{1}{2} b : \frac{1}{2} c$$

$$\frac{1}{y^2} = \frac{1}{y^2} = \frac{1}{y^2}$$

222 plane

Fig. 4.12 Miller indices

Problem: ***Calculate the Miller indices of a crystal plane which cut through crystal axes at (i) 2a, 3b, c (ii) 6a, 3b, 2c.***

(i) $OL : OM : ON = 2a : 3b : 1c$

$$\frac{1}{2} : \frac{1}{3} : \frac{1}{1}$$

Multiplying the fractions by six $= \frac{1}{2} \times 6 : \frac{1}{3} \times 6 : \frac{1}{1} \times 6$

$= 326$ plane.

(ii) $OL : OM : ON = 6a : 3b : 2c$

$$\frac{1}{6} : \frac{1}{3} : \frac{1}{2}$$

Multiplying by six,

$$= \frac{1}{6} \times 6 : \frac{1}{3} \times 6 : \frac{1}{2} \times 6$$

$$= 123 \text{ plane.}$$

4.3.6 Seven crystal systems

On the basis of elements of symmetry, the crystals have been divided into seven systems. The maximum possible crystal forms are 230 and all are known. These can be grouped into 32 classes which in turn regrouped into 7 systems.

No	System		Axes	Angles
1.	Cubic	$a=b=c$	$\alpha=\beta=\gamma=90°$	KCl, NaCl, CsCl, CaF_2, diamond, FeS_2, ZnS, Pb, Ag etc.
2.	Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90°$	SnO_2, TiO_2, Sn, $PbWO_4$, Urea etc.
3.	Rhombic (or) orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90°$	KNO_3, K_2SO_4, S_R, $BaSO_4$, $PbCO_3$ etc.
4.	Monoclinic	$a\neq b\neq c$	$\alpha=\gamma=90°$ $\beta\neq 90°$	S_M, $CaSO_4 \cdot 2H_2O$, $Na_2SO_4 \cdot 10H_2O$ C_6H_5-COOH etc.
5.	Rhombohedral (or) Trigonal	$a=b=C$	$\alpha=\beta=\gamma\neq 90°$	$NaNO_3$, Calcite, Quartz, As, Sb, Bi etc.
6.	Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90°$	$CuSO_4 \cdot 5H_2O$, H_3BO_3 $K_2Cr_2O_7$ etc.
7.	Hexagonal	$a=b\neq c$	$\alpha=\beta=90°$ $\gamma=120°$	Mg, Graphite, Zn, ZnO, SiO_2, PbI_2

4.3.7 Bravais lattices

Bravais showed from geometrical considerations that there can be only 14 different ways in which similar points can be arranged in three-dimensional space. These are called

Bravais lattices. Thus the total number of space lattices belonging to all seven crystal systems put together is only 14.

Types of Bravais lattices

The crystals belonging to the cubic system have three kinds of Bravais lattices depending upon the shape of the unit cells. These are

1. **Simple cubic lattice**

   There are points only at the corners of each unit.

2. **Body centered cubic lattice**

   There are points at the corners as well as at the centre of the cube.

3. **Face centred cubic lattice**

   There are points at the corners as well as at the centre of each face.

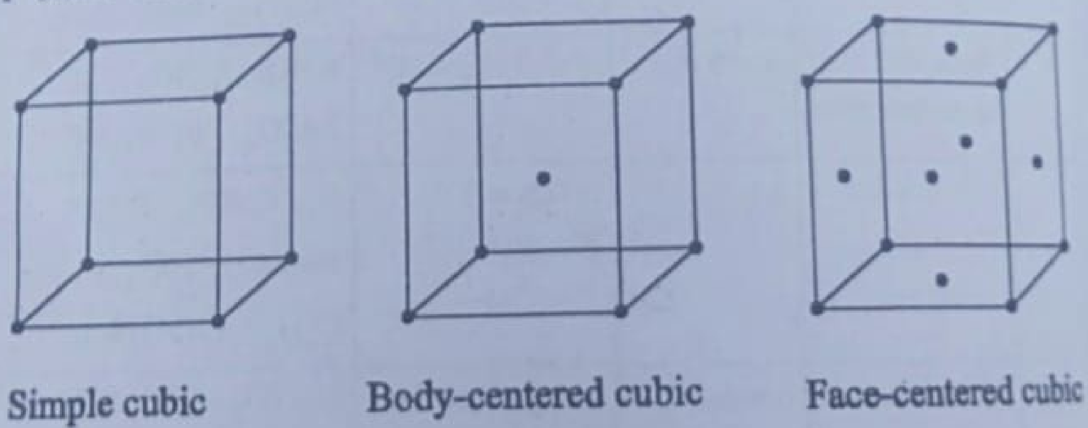


Fig. 4.13 Three kinds of Bravais lattices

Crystals belonging to Orthorhombic system have 4 Bravais lattices. Tetragonal and monoclinic systems have 2 Bravais lattices each. Triclinic, hexagonal and rhombohedral systems have one Bravais lattice each.