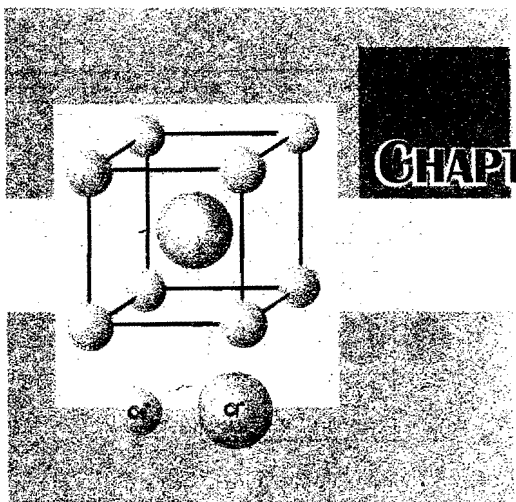




CHAPTER

4

STATES OF MATTER

4.1 INTRODUCTION

Matter is capable of existing in three physical states: solid, liquid and gas. Matter is anything which has mass and occupies space. Any substance can exist in either of three states depending on temperature and pressure. Liquid and solid states are condensed states as they have much higher densities. Both liquids and gases are termed as fluids as they have flowing ability.

The three states of a substance are interconvertible by variation of temperature and pressure. A liquid state is intermediate between the gaseous state (complete molecular randomness) and the solid state (orderly arrangement of molecules).

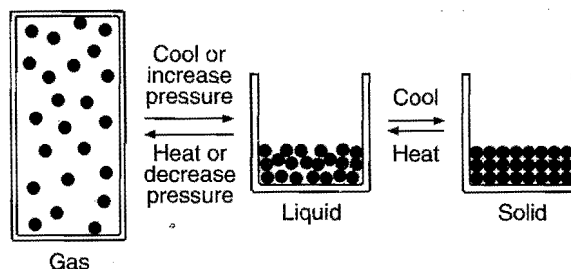


Fig. 4.1 Schematic representation of states of matter

Some common characteristics of three forms of matter are summarised below:

S.No.	Gases	Liquids	Solids
1.	No definite shape; can fill uniformly any volume available; have indefinite volume.	No definite shape, <i>i.e.</i> , assume the shape of the container; have definite volume.	Have definite shape and definite volume.
2.	Extremely disordered particles; much empty space; particles have random motion; intermolecular attraction very small but high kinetic energies (particles are free to move in all directions).	Disordered clusters of particles; quite close to each other; random motion; considerable intermolecular attraction; kinetic energy is less (particles free to move but always remain in contact with each other).	Ordered arrangement of particles; distances between the particles are very small and fixed. Intermolecular forces are high; vibrational motion only.
3.	Low density.	Intermediate density.	High density.
4.	Compressible.	Slightly compressible.	Nearly incompressible.
5.	Fluid, diffuse rapidly.	Fluid; diffuse through other liquids.	Not fluid; diffuse very slowly only through solids.

SECTION 1 : GASEOUS STATE

4.2 THE GASEOUS STATE

Of the three states of matter, the gaseous state is the simplest and shows greatest uniformity in behaviour. Gases have the following general characteristics:

(i) Gases are highly compressible. These can be compressed into smaller volumes, *i.e.*, increasing their densities by applying increased pressure.

(ii) Gases expand without limit. A gas sample can occupy completely and uniformly the volume of any container.

(iii) Gases exert pressure on the walls of the container uniformly in all directions.

(iv) Gases diffuse rapidly through each other to form a homogeneous mixture. Conversely, different gases in a mixture like air do not separate on standing.

(v) The characteristics of gases are described fully in terms of **four parameters** (measurable properties):

- the volume, V , of the gas
- its pressure, P
- its temperature, T
- the amount of the gas (*i.e.*, mass or number of moles).

(a) **The volume** of the container is the volume of the gas sample. Volume is expressed in litre (L), millilitre (mL) or cubic centimetre (cm^3) or cubic metre (m^3).

$$1 \text{ L} = 1000 \text{ mL}; 1 \text{ mL} = 10^{-3} \text{ L}$$

$$1 \text{ L} = 1 \text{ dm}^3; 1 \text{ dm}^3 = 10^3 \text{ cm}^3$$

$$1 \text{ m}^3 = 10^3 \text{ dm}^3 = 10^6 \text{ cm}^3 = 10^6 \text{ mL} = 10^3 \text{ L}$$

(b) **The pressure** of the gas is the force exerted by the gas per unit area of the walls of the container. The pressure of gases is measured by a device known as manometer. Two types of manometers, open-end manometer and closed-end manometer, are commonly used to measure gaseous pressure.

Pressure of one atmosphere (1 atm) is defined as the pressure that can support a column of mercury of 76 cm height at 0°C (density of mercury = $13.5951 \text{ g cm}^{-3}$) and at standard gravity = $980.665 \text{ cm s}^{-2}$. One atmosphere is also referred to as 760 torr.

$$1 \text{ atm} = 76.0 \text{ cm of mercury} = 760 \text{ mm of mercury} \\ = 760 \text{ torr}$$

SI unit of pressure is pascal (Pa) which is defined as the pressure exerted when a force of 1 newton acts on a 1 m^2 area.

$$1 \text{ atm} = 101.325 \times 10^3 \text{ N m}^{-2} = 101.325 \text{ kPa}$$

An older unit of pressure is 'bar' which is equal to 10^5 Pa .

(c) **The temperature** of the gas is measured in centigrade degree ($^\circ\text{C}$) or celsius degree with the help of thermometers.

SI unit of temperature is **Kelvin (K)** or **absolute degree**.

$$\text{K} = ^\circ\text{C} + 273$$

(d) Mass of gas is expressed in gram or kilogram.

$$1 \text{ kg} = 10^3 \text{ g}$$

The mass of the gas is also expressed in number of moles.

$$\text{moles of gas } (n) = \frac{\text{Mass in grams}}{\text{Molar mass}} = \frac{m}{M}$$

(vi) All gases obey certain laws called **gas laws**.

4.3 GAS LAWS

(i) **Boyle's law:** It relates the volume and the pressure of a given mass of a gas at constant temperature.

The relationship between the volume and the pressure of a gas was studied by **Robert Boyle** in 1662. He found that increasing the pressure at constant temperature on a sample of a gas causes the volume of the gas to decrease proportionately, *i.e.*, if the pressure is doubled, the volume becomes half and so on. Boyle's law states that **at constant temperature, the volume of a sample of a gas varies inversely with the pressure.**

$$V \propto \frac{1}{P} \quad (\text{when temperature is kept constant})$$

The proportionality can be changed into an equality by introducing a constant, k , *i.e.*,

$$V = \frac{k}{P} \quad \text{or} \quad PV = k$$

Alternatively, Boyle's law can also be stated as follows:

Temperature remaining constant, the product of pressure and volume of a given mass of a gas is constant.

The value of the constant depends upon the amount of a gas and the temperature.

Mathematically, it can be written as,

$$P_1V_1 = P_2V_2 = P_3V_3 = \dots$$

Boyle's law can be verified by any one of the following three ways graphically (Fig. 4.2):

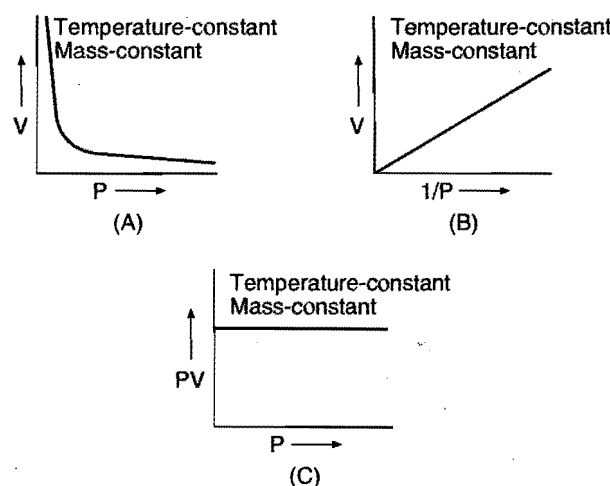


Fig. 4.2

The first curve shows the variation of volume of a given mass of gas with pressure at constant temperature. The shape of the curve is rectangular hyperbola. This curve is also called **isotherm**.

The second curve showing the relationship between volume and reciprocal of pressure is a straight line. It confirms the statement that at constant temperature, volume of a given mass of gas is inversely proportional to the pressure. The third curve shows a straight line parallel to pressure-axis. This confirms that the product of pressure and volume of a given mass of a gas at constant temperature is constant.

Location of straight line and curve changes with temperature in the isotherm.

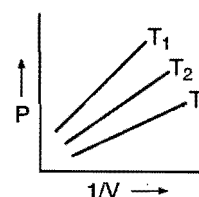


Fig. 4.2(D)

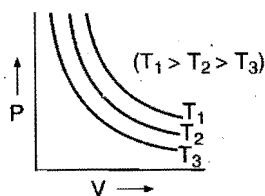


Fig. 4.2(E)

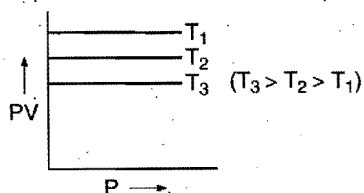


Fig. 4.2(F)

According to Boyle's law, $PV = \text{constant}$ at constant temperature

$$\therefore \log P + \log V = \text{constant}$$

$$\log P = -\log V + \text{constant}$$

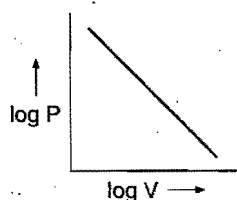


Fig. 4.2(G)

(ii) **Charles' law:** It relates the volume and temperature of a given mass of a gas at constant pressure.

Experiments have shown that when 273 mL sample of a gas at 0°C is heated to 1°C , its volume increases by 1 mL, i.e., it becomes 274 mL. At 10°C , the volume increases to 283 mL if the pressure remains constant in both cases. Similarly, when 273 mL sample of gas at 0°C is cooled to -1°C , its volume decreases to 272 mL while at -10°C , the volume decreases to 263 mL if the pressure remains constant.

Thus, all gases expand or contract by the same fraction of their volumes at 0°C per degree change of temperature, i.e., for each degree change of temperature, the volume of a sample of a gas changes by the fraction $\frac{1}{273}$ of its volume at 0°C .

Let the volume of a given amount of a gas be V_0 at 0°C . The temperature is increased by $t^\circ\text{C}$ and the new volume becomes V_t .

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

$$\text{or } V_t = V_0 \left(\frac{273 + t}{273} \right) \quad \dots (i)$$

A new temperature scale was introduced known as **Kelvin scale** or **absolute scale** named after the British physicist and mathematician **Lord Kelvin**. The lower limit of the scale is

called absolute zero which corresponds to -273°C . At absolute zero or -273°C , all molecular motions would stop and the volume of the gas would become zero. The gas would become a liquid or solid. Thus, **absolute zero is that temperature at which no substance exists in the gaseous state**. The temperature in absolute is always obtained by adding 273 to the temperature expressed in $^\circ\text{C}$.

$$K = (^\circ\text{C} + 273)$$

This new temperature scale may be used for deducing Charles' law.

By substituting T for $273 + t$ and T_0 for 273 in Eq. (i),

$$V_t = \frac{V_0 \times T}{T_0}$$

$$\text{or } \frac{V_t}{T} = \frac{V_0}{T_0}$$

$$\text{or } \frac{V}{T} = \text{constant (if pressure is kept constant)}$$

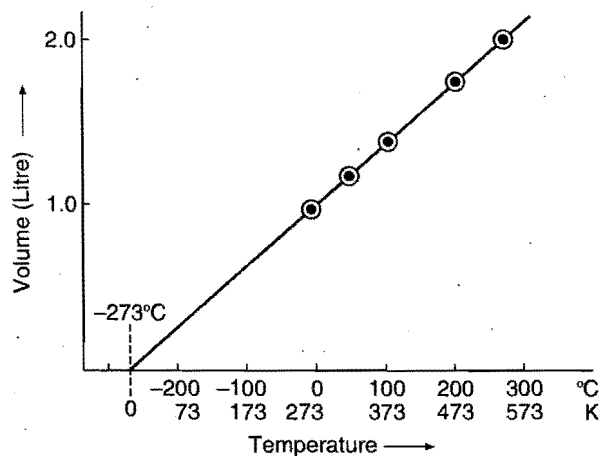


Fig. 4.3

This is Charles' law. It can be stated as follows:

The volume of a given amount of a gas at constant pressure varies directly as its absolute temperature.

$$V \propto T \quad (\text{if pressure is kept constant})$$

Charles' law can be verified experimentally by plotting the values of volumes of a given amount of a gas under respective absolute temperatures at constant pressure. The straight line confirms the above statement.

(iii) **Pressure-temperature law:** It relates the pressure and absolute temperature of a given mass of a gas at constant volume.

Volume remaining constant, the pressure of a given mass of a gas increases or decreases by $\frac{1}{273}$ of its pressure at 0°C per degree change of temperature.

$$P_t = P_0 + \frac{P_0 \times t}{273}$$

$$\text{or } P_t = P_0 \left(1 + \frac{t}{273} \right)$$

$$\text{or } P_t = P_0 \left(\frac{273 + t}{273} \right) = P_0 \frac{T}{T_0}$$

$$\text{or } \frac{P_t}{T} = \frac{P_0}{T_0}$$

$$\text{or } P \propto T \text{ (if volume is kept constant)}$$

At constant volume, the pressure of a given amount of a gas is directly proportional to its absolute temperature.

4.4 IDEAL GAS EQUATION

This equation is obtained by combining Boyle's and Charles' laws.

$$V \propto \frac{1}{P} \quad \dots \text{(i) (at constant temperature and definite mass)}$$

$$V \propto T \quad \dots \text{(ii) (at constant pressure and definite mass)}$$

Combining eqs. (i) and (ii), we get

$$V \propto \frac{T}{P} \quad \text{(for definite mass)}$$

$$\frac{PV}{T} = \text{constant} \quad \dots \text{(iii)}$$

From the above relation, we have

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \dots \text{(iv)}$$

From eq. (iii),

$$\frac{PV}{T} = R$$

$$\text{or } PV = RT \text{ for 1 mole gas}$$

$$PV = nRT \text{ for } n \text{ mole gas} \quad \dots \text{(v)}$$

When mass of the gas is taken in grams, the value of n will be given by:

$$n = \frac{\text{Mass of the gas in gram}}{\text{Mol. mass of the gas in gram}}$$

Let w and M be the mass and molecular mass of a gas; then

$$n = \frac{w}{M}$$

Hence, eq. (v) becomes

$$PV = \frac{w}{M} RT \quad \dots \text{(vi)}$$

$$\text{or } P = \frac{w}{M} \cdot \frac{RT}{V} \left[\frac{w}{V} = \frac{\text{Mass}}{\text{Volume}} = \text{Density } (d) \right]$$

$$\text{or } P = \frac{d}{M} RT \quad \dots \text{(vii)}$$

Eqs. (vi) and (vii) are modified forms of gas equation. The above equations are strictly followed by ideal gases.

Nature of Molar Gas Constant R

Gas equation for one gram mole,

$$PV = RT$$

$$\text{or } R = \frac{P \times V}{T} = \frac{\text{Pressure} \times \text{Volume}}{\text{Temperature}}$$

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{Force}}{(\text{Length})^2}$$

$$\text{Volume} = (\text{Length})^3$$

$$\text{So, } R = \frac{\frac{\text{Force}}{(\text{Length})^2} \times (\text{Length})^3}{\text{Temperature}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Temperature}}$$

$$= \frac{\text{Work}}{\text{Temperature}}$$

Thus, the value of R should always be expressed in units of work per degree kelvin per mole.

Numerical Values of R

$$R = \frac{PV}{T}$$

One gram mole of a gas at one atmospheric pressure and 0°C (273 K) occupies a volume 22.4 litre.

$$P = 1 \text{ atmosphere, } T = 273 \text{ K, } V = 22.4 \text{ litre}$$

$$\text{So, } R = \frac{1 \times 22.4}{273}$$

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

If pressure is taken in dyne/cm² and volume in mL,
 $P = 76 \times 13.67 \times 981 \text{ dyne/cm}^2$, $V = 22400 \text{ mL}$ for 1 mole,
 $T = 273 \text{ K}$

$$\text{So, } R = \frac{76 \times 13.67 \times 981 \times 22400}{273}$$

$$= 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

Since, 1 joule = 10^7 erg, so

$$R = 8.314 \text{ joule K}^{-1} \text{ mol}^{-1}$$

Since, 1 calorie = 4.184×10^7 erg, so

$$R = \frac{8.314 \times 10^7}{4.184 \times 10^7}$$

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

Note: Although, R can be expressed in different units, but for pressure-volume calculations, R must be taken in the same units of pressure and volume.

Barometric Distribution

In the case of ordinary gases, pressure in the container is unaffected by the gravitational field. But in high molecular mass polymeric gases, pressure varies with height.

Let P_0 be the pressure at ground level and P be the pressure at height ' h '; then

$$2.303 \log_{10} \left(\frac{P}{P_0} \right) = - \left\{ \frac{Mgh}{R} \right\}$$

Similarly for density and number of moles the equation may be given as:

$$2.303 \log_{10} \left(\frac{d}{d_0} \right) = - \left\{ \frac{Mgh}{R} \right\}$$

$$2.303 \log_{10} \left(\frac{n}{n_0} \right) = - \left\{ \frac{Mgh}{R} \right\}$$

These relations are valid under isothermal conditions for density, pressure and number of moles.

If temperature is not constant then the relations of barometric distribution may be given as,

$$2.303 \log_{10} \left(\frac{P}{P_0} \right) = - \frac{Mgh}{RT}$$

$$2.303 \log_{10} \left(\frac{n}{n_0} \right) = - \frac{Mgh}{RT}$$

Open vessel concept: In open vessel of a gas, pressure and volume are always constant.

$$\therefore PV = n_1 RT_1 \quad \dots (1)$$

$$PV = n_2 RT_2 \quad \dots (2)$$

Here, n_1 and n_2 are number of moles at temperatures T_1 and T_2 .

Dividing eq. (1) by (2), we get

$$n_1 T_1 = n_2 T_2$$

Dry and moist gas: If volume under moist condition is given then volume of dry gas can be determined.

$$P_{\text{moist}} V_{\text{moist}} = P_{\text{dry}} V_{\text{dry}}$$

$$P_{\text{dry}} = P_{\text{moist}} - \text{Aqueous tension or vapour pressure of water}$$

$$\text{Relative humidity} = \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}$$

Payload (Lifting Capacity of Balloon)

When a balloon is filled with lighter gas like H_2 and He (lighter than air) then it rises up due to the difference in the density of air and the gas. Payload or lifting capacity of balloon may be calculated as:

$$\text{Pay Load} = \left[\text{Mass of air filled in the balloon} \right] - \left[\text{Mass of gas filled in the balloon at same temperature and pressure} \right] - \left[\text{Mass of balloon} \right]$$

SOME SOLVED EXAMPLES

Example 1. A sample of a gas occupies 10 litre under a pressure of 1 atmosphere. What will be its volume if the pressure is increased to 2 atmosphere? Assume that the temperature of the gas sample does not change.

Solution: $V_1 = 10$ litre $V_2 = ?$

$$P_1 = 1 \text{ atm} \quad P_2 = 2 \text{ atm}$$

Applying Boyle's law,

$$P_1 V_1 = P_2 V_2$$

$$\text{So, } V_2 = \frac{P_1 V_1}{P_2} = \frac{1 \times 10}{2} = 5 \text{ litre}$$

Example 2. A sample of a gas occupies 600 mL at 27°C and 1 atm. What will be the volume at 127°C if the pressure is kept constant?

Solution: $V_1 = 600$ mL $T_1 = 27 + 273 = 300$ K

$$V_2 = ? \quad T_2 = 127 + 273 = 400 \text{ K}$$

Applying Charles' law,

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

$$V_2 = \frac{V_1}{T_1} \times T_2$$

$$= \frac{600 \times 400}{300}$$

$$= 800 \text{ mL}$$

Example 3. A gas cylinder containing cooking gas can withstand a pressure of 14.9 atmosphere. The pressure gauge of the cylinder indicates 12 atmosphere at 27°C . Due to a sudden fire in the building, the temperature starts rising. At what temperature will the cylinder explode?

Solution: Since, the gas is confined in a cylinder, its volume will remain constant.

Initial conditions

$$P_1 = 12 \text{ atm}$$

$$T_1 = 27 + 273 = 300 \text{ K}$$

Final conditions

$$P_2 = 14.9 \text{ atm}$$

$$T_2 = ?$$

Applying pressure-temperature law,

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

So,

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

$$= \frac{14.9 \times 300}{12} = 372.5 \text{ K}$$

$$\text{Temperature in } ^\circ\text{C} = (372.5 - 273) = 99.5^\circ\text{C}$$

Example 4. A 1000 mL sample of a gas at -73°C and 2 atmosphere is heated to 123°C and the pressure is reduced to 0.5 atmosphere. What will be the final volume?

Solution:

Initial conditions

$$P_1 = 2 \text{ atm}$$

$$V_1 = 1000 \text{ mL}$$

$$T_1 = -73^\circ\text{C} = (-73 + 273)$$

$$= 200 \text{ K}$$

Final conditions

$$P_2 = 0.5 \text{ atm}$$

$$V_2 = ?$$

$$T_2 = 123^\circ\text{C} = (123 + 273)$$

$$= 400 \text{ K}$$

We know that,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

So,

$$\frac{2 \times 1000}{200} = \frac{0.5 \times V_2}{400}$$

or

$$V_2 = \frac{2 \times 1000 \times 400}{200 \times 0.5}$$

$$= 8000 \text{ mL}$$

Example 5. A sample of a gas occupies a volume of 512 mL at 20°C and 74 cm of Hg as pressure. What volume would this gas occupy at STP?

Solution:

Initial conditions

$$P_1 = 74 \text{ cm}$$

$$T_1 = 20^\circ \text{C} = (20 + 273) = 293 \text{ K},$$

$$V_1 = 512 \text{ mL}$$

Final conditions (STP)

$$P_2 = 76 \text{ cm}$$

$$T_2 = 0^\circ \text{C} = 273 \text{ K}$$

$$V_2 = ?$$

We know that,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{74 \times 512}{293} = \frac{76 \times V_2}{273}$$

So,

$$V_2 = \frac{74 \times 512 \times 273}{293 \times 76}$$

$$= 464.5 \text{ mL}$$

Example 6. 3.7 g of a gas at 25°C occupied the same volume as 0.184 g of hydrogen at 17°C and at the same pressure. What is the molecular mass of the gas?

Solution: For hydrogen,

$$w = 0.184 \text{ g}; \quad T = 17 + 273 = 290 \text{ K}; \quad M = 2$$

We know that, $PV = \frac{w}{M} RT$

$$= \frac{0.184}{2} \times R \times 290 \quad \dots (i)$$

For unknown gas,

$$w = 3.7 \text{ g}; \quad T = 25 + 273 = 298 \text{ K}; \quad M = ?$$

$$PV = \frac{3.7}{M} \times R \times 298 \quad \dots (ii)$$

Equating both the equations,

$$\frac{3.7}{M} \times R \times 298 = \frac{0.184}{2} \times R \times 290$$

or

$$M = \frac{3.7 \times 298 \times 2}{0.184 \times 290} = 41.33$$

Example 7. What is the pressure of HCl gas at -40°C if its density is 8.0 kg m⁻³? ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

Solution: Equation for ideal gas,

$$PV = \frac{w}{M} RT$$

or

$$P = \frac{w}{V} \times \frac{RT}{M} = d \times \frac{RT}{M} \quad \left(\frac{w}{V} = \text{density} = d \right)$$

Given, $d = 8.0 \text{ kg m}^{-3}$; $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$;

$$T = -40 + 273 = 233 \text{ K}$$

and $M = 36.5 \text{ g mol}^{-1} = 36.5 \times 10^{-3} \text{ kg mol}^{-1}$

Substituting the values in the above equation,

$$P = \frac{8.0 \times 8.314 \times 233}{36.5 \times 10^{-3}} = 424.58 \times 10^3 \text{ Pa}$$

Example 8. A certain quantity of a gas occupies 100 mL when collected over water at 15°C and 750 mm pressure. It occupies 91.9 mL in dry state at NTP. Find the aqueous vapour pressure at 15°C.

Solution: Let the aqueous vapour pressure be p mm.

Initial conditions

$$P_1 (\text{dry gas}) = (750 - p) \text{ mm}$$

$$V_1 = 100 \text{ mL}$$

$$T_1 = 15 + 273 = 288 \text{ K}$$

NTP conditions

$$P_2 = 760 \text{ mm}$$

$$V_2 = 91.9 \text{ mL}$$

$$T_2 = 273 \text{ K}$$

Applying gas equation,

$$\frac{(750 - p) \times 100}{288} = \frac{760 \times 91.9}{273}$$

or

$$750 - p = \frac{760 \times 91.9 \times 288}{100 \times 273}$$

$$= 736.8 \text{ mm}$$

$$p = 750 - 736.8$$

$$= 13.2 \text{ mm}$$

Example 9. A balloon of diameter 20 m weighs 100 kg. Calculate its payload if it is filled with helium at 1.0 atm and 27°C. Density of air is 1.2 kg m⁻³.

$$(R = 0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})$$

(IIT 1994)

Solution:

$$\text{Volume of balloon} = \frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10)^3 = 4190.47 \text{ m}^3$$

$$\text{Mass of the air displaced} = 4190.47 \times 1.2 = 5028.56 \text{ kg}$$

$$\text{No. of moles of helium in the balloon} = \frac{PV}{RT}$$

$$= \frac{1 \times 4190.47 \times 10^3}{0.082 \times 300} = 170344$$

$$\text{Mass of helium} = 4 \times 170.344 \times 10^3 \text{ g} = 681.376 \text{ kg}$$

$$\text{Mass of filled balloon} = 681.376 + 100 = 781.376 \text{ kg}$$

$$\text{Payload} = \text{Mass of air displaced} - \text{Mass of filled balloon}$$

$$= 5028.56 - 781.376 = 4247.184 \text{ kg}$$

Example 10. The density of a gas is 0.259 g L^{-1} at 400 K and 190 torr . Find its molar mass.

Solution: $760 \text{ torr} = 1 \text{ atm}$

So, $190 \text{ torr} = \frac{190}{760} \text{ atm}$

We know that, $P = \frac{d}{M} RT$

or $M = \frac{d}{P} RT$

Given, $d = 0.259 \text{ g L}^{-1}$; $P = \frac{190}{760} \text{ atm}$;

$R = 0.0821 \text{ L-atm K}^{-1} \text{ mol}^{-1}$; $T = 400 \text{ K}$

$M = \frac{0.259 \times 0.0821 \times 400 \times 760}{190} = 34.02 \text{ g mol}^{-1}$

Example 11. The density of phosphorus vapour at 310°C and 775 torr is 2.64 g dm^{-3} . What is the molecular formula of phosphorus?

Solution: We know that, $P = \frac{d}{M} RT$ or $M = \frac{d}{P} RT$

Given, $d = 2.64 \text{ g dm}^{-3}$; $P = \frac{775}{760} \text{ atm}$;

$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$

and $T = 310 + 273 = 583 \text{ K}$

So, $M = \frac{2.64 \times 0.0821 \times 583 \times 760}{775} = 123.9 \text{ g mol}^{-1}$

Atomic mass of P = 31 g mol^{-1}

No. of P atoms in a molecule = $\frac{123.9}{31} = 3.997 \approx 4$

Hence, molecular formula of phosphorus = P_4

Example 12. What percentage of a sample of nitrogen must be allowed to escape if its temperature, pressure and volume are changed from 220°C , 3.0 atm and 1.65 L to 110°C , 0.7 atm and 1.0 L respectively?

Solution: Applying the formula, m (mass of the gas) $= \frac{PV \times M}{RT}$, under both the conditions,

Mass of gas before escaping = $\frac{3.0 \times 1.65 \times 28}{0.0821 \times 493} = 3.42 \text{ g}$

Mass of gas after escaping = $\frac{0.7 \times 1.0 \times 28}{0.0821 \times 383} = 0.62 \text{ g}$

Percentage of nitrogen allowed to escape $= \frac{(3.42 - 0.62)}{3.42} \times 100 = 81.87$

Example 13. The density of oxygen is 1.43 g L^{-1} at STP. Determine the density of oxygen at 17°C and 800 torr .

Solution: Applying the formula $d = \frac{MP}{RT}$

At STP, $d_1 = \frac{MP_1}{RT_1}$

$[P_1 = 760 \text{ torr}; T_1 = 273 \text{ K}; d_1 = 1.43 \text{ g L}^{-1}]$

At given conditions, $d_2 = \frac{MP_2}{RT_2}$

$[P_2 = 800 \text{ torr}; T_2 = 290 \text{ K}; d_2 = ?]$

So, $\frac{d_2}{d_1} = \frac{P_2}{P_1} \times \frac{T_1}{T_2}$

or $d_2 = \frac{P_2}{P_1} \times \frac{T_1}{T_2} \times d_1$
 $= \frac{800}{760} \times \frac{273}{290} \times 1.43$
 $= 1.417 \text{ g L}^{-1}$

Example 14. A car tyre has a volume of 10 litre when inflated. The tyre is inflated to a pressure of 3 atm at 17°C with air. Due to driving the temperature of the tyre increases to 47°C . (a) What would be the pressure at this temperature? (b) How many litres of air measured at 47°C and pressure of 1 atm should be let out to restore the tyre to 3 atm at 47°C ?

Solution: (a) At constant volume,

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

or $\frac{3}{290} = \frac{P_2}{320}$

or $P_2 = \frac{320 \times 3}{290} = 3.31 \text{ atm}$

(b) Pressure to be decreased in tyre

$= 3.31 - 3.0 = 0.31 \text{ atm}$

Let the volume of the gas to be taken out at $1 \text{ atmospheric pressure}$ be V . As the temperature remains constant, i.e., 47°C , Boyle's law can be applied to determine V .

$1 \times V = 0.31 \times 10$

or $V = 3.1 \text{ litre}$

Example 15. Oxygen is present in a one litre flask at a pressure of $7.6 \times 10^{-10} \text{ mm of Hg}$. Calculate the number of oxygen molecules in the flask at 0°C .

Solution: $n = \frac{PV}{RT}$... (i)

$P = \frac{7.6 \times 10^{-10}}{760} = 10^{-12} \text{ atm}$

$V = 1 \text{ L}, T = 273 \text{ K}, R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$

From eq. (i) $n = \frac{10^{-12} \times 1}{0.0821 \times 273}$

Number of molecules = $n \times 6.023 \times 10^{23}$

$$= \frac{10^{-12}}{0.0821 \times 273} \times 6.023 \times 10^{23}$$

$$= 2.68 \times 10^{10}$$

Example 16. An open flask contains air at 27°C. Calculate the temperature at which it should be heated so that 1/3 rd of air measured at 27°C escapes out.

Solution: Let the initial number of moles of air at 27°C (300 K) be = n

Number of moles of air left when the air is heated to

the temperature T K = $n - \frac{n}{3} = \frac{2n}{3}$

At constant pressure and constant volume,

$$n_1 T_1 = n_2 T_2$$

or $n \times 300 = \frac{2n}{3} \times T$

or $T = 450 \text{ K} = (450 - 273) = 177^\circ \text{C}$

Example 17. A mixture of CO and CO₂ is found to have a density of 1.5 g L⁻¹ at 30°C and 730 torr. What is the composition of the mixture?

Solution: Let the average molecular mass be M .

$$M = \frac{dRT}{P} = \frac{1.5 \times 0.0821 \times 303 \times 760}{730} = 38.85$$

Let x mole of CO and $(1-x)$ mole of CO₂ be present.

$$x \times 28 + (1-x) \times 44 = 38.85$$

$$x = 0.3218$$

$$\text{mole \% of CO} = 32.18 \text{ and mole \% of CO}_2 = 67.82$$

Example 18. Calculate the value of molar gas constant, 'R' in (i) cc atm K⁻¹ mol⁻¹ (ii) torr cc K⁻¹ mol⁻¹ (iii) kPa litre K⁻¹ mol⁻¹.

Solution: (i) When the pressure is expressed in atmosphere and volume in cc.

$$P = 1 \text{ atm}; V = 22400 \text{ cc}$$

$$R = \frac{PV}{nT} = \frac{1 \times 22400}{1 \times 273} = 82.1 \text{ cc atm K}^{-1} \text{ mol}^{-1}$$

(ii) When the pressure is expressed in torr and volume in cc.

$$P = 760 \text{ torr}; V = 22400 \text{ cc}$$

$$R = \frac{760 \times 22400}{1 \times 273} = 62360 \text{ torr cc K}^{-1} \text{ mol}^{-1}$$

(iii) When the pressure is expressed in k Pascal and volume in litre.

$$P = 101.3 \text{ kPa}; V = 22.4 \text{ litre}$$

$$R = \frac{PV}{nT} = \frac{101.3 \times 22.4}{1 \times 273} = 8.31 \text{ kPa litre K}^{-1} \text{ mol}^{-1}$$

Example 19. The pressure exerted by 12 g of an ideal gas at temperature $t^\circ \text{C}$ in a vessel of V litre is one atmosphere. When

the temperature is increased by 10°C at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V (Molecular mass of the gas = 120). (IIT 1999)

Solution: As the volume is constant, pressure law can be applied, i.e.,

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

or

$$\frac{1}{1.1} = \frac{t + 273}{t + 283}$$

or

$$t = -173^\circ \text{C} = 100 \text{ K}$$

Now, applying gas equation,

$$PV = nRT$$

or

$$V = \frac{n}{P} RT = \frac{12 \times 0.082 \times 100}{120 \times 1} = 0.82 \text{ litre}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. 2.5 L of a sample of a gas at 27°C and 1 bar pressure is compressed to a volume of 500 mL keeping the temperature constant, the percentage increase in the pressure is:

(a) 100% (b) 400% (c) 500% (d) 80%

[Ans. (b)]

[Hint: $P_1 V_1 = P_2 V_2$

$$1 \times 2.5 = P_2 \times \frac{1}{2}$$

$$P_2 = 5 \text{ bar}$$

$$\% \text{ Increase} = \frac{\text{Increase in pressure}}{\text{Initial pressure}} \times 100$$

$$= \frac{4}{1} \times 100 = 400\%$$

2. Which of the following gases will have density of 1.8 g L⁻¹ at 760 torr pressure and 27°C?

(a) O₂ (b) CO₂ (c) NH₃ (d) SO₂

[Ans. (b)]

[Hint: $Pm = dRT$

$$m = \frac{dRT}{P} = \frac{1.8 \times 0.0821 \times 300}{1} = 44$$

∴ The gas will be CO₂]

3. 10 g C₂H₆ is filled in a bulb of 1 litre capacity which can withstand a maximum pressure of 10 atm. At what temperature will the pressure of gas reach the bursting limit?

(a) 76°C (b) 361.4°C (c) 92.4°C (d) 120°C

[Ans. (c)]

[Hint: $T = \frac{PV}{nR} = \frac{10 \times 1}{(10/30) \times 0.0821} = 365.4 \text{ K} = 92.4^\circ \text{C}$

4. The vapour of phosphine gas at 27°C and 3 bar pressure has density:

(a) 4.09 g mL⁻¹

(b) 4.14 g L⁻¹

(c) 2.04 kg L⁻¹

(d) 2.04 g L⁻¹

[Ans. (b)]

[Hint: $d = \frac{Pm}{RT} = \frac{3 \times 34}{0.0821 \times 300} = 4.14 \text{ g L}^{-1}$]

5. Coefficient of volume expansion of a gas is:

- (a) $\frac{1}{273}$ (b) $\frac{2}{273}$
(c) $\frac{3}{273}$ (d) $\frac{4}{273}$

[Ans. (a)]

[Hint: According to Charles' law,

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

$$V_t = V_0 (1 + \alpha t)$$

$$\alpha = \frac{1}{273} = \text{Coefficient of volume expansion}$$

Here, V_0 = Volume at 0°C and V_t = Volume at $t^\circ\text{C}$

6. A gas has a vapour density 11.2. The volume occupied by 1 gram of the gas at STP will be:

- (a) 11.2 L (b) 22.4 L (c) 1 L (d) 10 L

[Ans. (c)]

$$\begin{aligned} \text{[Hint: Number of moles} &= \frac{\text{Mass}}{\text{Molar mass}} \\ &= \frac{\text{Mass}}{2 \times \text{Vapour density}} \\ &= \frac{1}{2 \times 11.2} = \frac{1}{22.4} \end{aligned}$$

$$\begin{aligned} \text{Volume of gas} &= n \times 22.4 \text{ L} \\ &= \frac{1}{22.4} \times 22.4 \text{ L} = 1 \text{ L} \end{aligned}$$

7. When a gas is heated from 25°C to 50°C at constant pressure of 1 bar, its volume:

- (a) increases from V to $2V$
(b) increases from V to $1.5V$
(c) increases from V to $1.084V$
(d) increases from V to $1.8V$

[Ans. (c)]

$$\begin{aligned} \text{[Hint: } \frac{V_1}{T_1} &= \frac{V_2}{T_2} \\ \frac{V}{298} &= \frac{V_2}{323} \end{aligned}$$

$$V_2 = V \times \frac{323}{298} = 1.084 V$$

8. The molecular weights of two ideal gases A and B are respectively 100 and 200. One gram of A occupies V litre of volume at STP. What is the volume (in litre) occupied by one gram of B at STP? (EAMCET 2006)

- (a) $\frac{V}{2}$ (b) V (c) V^2 (d) $2V$

[Ans. (a)]

[Hint: Under identical conditions of temperature and pressure:

$$\frac{V_A}{V_B} = \frac{n_A}{n_B}$$

$$\frac{V}{V_B} = \frac{1/100}{1/200}$$

$$V_B = \frac{V}{2}$$

9. A bubble of volume V_1 is at the bottom of a pond at 15°C and 1.5 atm pressure. When it comes at the surface, it observes a pressure of 1 atm at 25°C and has volume V_2 ; give $\left(\frac{V_2}{V_1} \right)$:

(DCE 2006)

- (a) 15.5 (b) 0.155 (c) 155.0 (d) 1.55

[Ans. (d)]

$$\begin{aligned} \text{[Hint: } \frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} \\ \frac{V_2}{V_1} &= \frac{P_1 T_2}{P_2 T_1} \\ &= \frac{1.5 \times 288}{1 \times 298} = 1.5 \end{aligned}$$

4.5 DALTON'S LAW OF PARTIAL PRESSURES

When different gases that do not react chemically with each other are enclosed in the same container, they intermix rapidly and exert a definite pressure. Again, each of the gas in the mixture exerts its own individual pressure if it is present only in the same container at the same temperature. **John Dalton**, in 1801, established the relation between the pressure of the mixture of gases and individual pressures of the constituent gases. This relationship is known as **Dalton's law of partial pressures**. It states that,

At a given temperature, the total pressure exerted by two or more non-reacting gases occupying a definite volume is equal to the sum of the partial pressures of the component gases. Mathematically,

$$P = p_A + p_B + p_C + \dots$$

when P is the total pressure and $p_A, p_B, p_C, \dots$ are the partial pressures of the component gases A, B, C, ... respectively. *The pressure that a component gas of the gaseous mixture would exert if it were only present in the volume under consideration at a given temperature, is the partial pressure of the component.*

Derivation of Dalton's Law

Let n_1 and n_2 be the no. of moles of two non-reacting gases 'A' and 'B' filled in a vessel of volume 'V' at temperature T .

Total pressure in the vessel 'P' may be calculated as,

$$PV = (n_1 + n_2) RT \quad \dots (i)$$

Individual or partial pressure may be calculated as,

$$p_A V = n_1 RT \quad \dots (ii)$$

$$p_B V = n_2 RT \quad \dots (iii)$$

Adding eqs. (ii) and (iii), we get

$$(p_A + p_B) V = (n_1 + n_2) RT \quad \dots (iv)$$

Comparing equations (i) and (iv), we get

$$P = p_A + p_B \quad (\text{Dalton's expression})$$

Dividing eq. (ii) by (i), we get

$$\frac{p_A}{P} = \frac{n_1}{n_1 + n_2} = x_A$$

$$p_A = x_A \times P$$

where, x_A = mole fraction of 'A'.

Similarly, dividing eq. (iii) by (i), we get

$$p_B = x_B \times P$$

i.e., Partial pressure of a component

$$= \text{Mole fraction} \times \text{Total pressure}$$

Relationship between Total Pressure and Individual Pressure (before Mixing) of the Constituent Gases at Constant Temperature

At constant temperature, let V_1 volume of a gas A at a pressure p_1 be mixed with V_2 volume of gas B at a pressure p_2 . Both these gases do not react chemically.

$$\text{Total volume} = V_1 + V_2$$

Let the total pressure be P and partial pressures of A and B be p_A and p_B respectively. Applying Boyle's law,

$$p_A (V_1 + V_2) = p_1 V_1 \quad \dots (i)$$

and

$$p_B (V_1 + V_2) = p_2 V_2 \quad \dots (ii)$$

Adding eqs. (i) and (ii),

$$p_A + p_B = \frac{p_1 V_1}{V_1 + V_2} + \frac{p_2 V_2}{V_1 + V_2} = \frac{p_1 V_1 + p_2 V_2}{V_1 + V_2}$$

or

$$P = \frac{p_1 V_1 + p_2 V_2}{V_1 + V_2}$$

In the laboratory, it is often convenient to collect a gas over water. When a gas is collected over water, the observed pressure of the gas is equal to the sum of the pressure of dry gas and the pressure of water vapour.

Therefore, the pressure of dry gas

$$= \text{pressure of moist gas} - \text{pressure of water vapour}$$

$$= \text{pressure of moist gas} - \text{aqueous tension}$$

Amagat Law of Partial Volume

Total volume of a mixture of gases which does not react at constant temperature and pressure is equal to sum of individual volumes (partial volumes) of constituent gases.

$$V = \Sigma V_i = V_1 + V_2 + V_3 + \dots + V_n$$

4.6 DIFFUSION OF GASES AND GRAHAM'S LAW OF DIFFUSION

When two or more non-reacting gases are kept side by side, they have the tendency to mix with one another spontaneously and form a homogeneous mixture. This can occur also if two gases have different densities. The heavier gas moves up and the lighter one comes down even against the action of gravity. Such a phenomenon is due to the fact that gas particles are moving at random with very high velocities and there is much intermolecular empty space in the volume of any gas. When two gases are brought together, they mix with each other in no time.

This ability of a gas to mix spontaneously and to form a homogeneous mixture is known as diffusion. It is due to this phenomenon that we can readily detect the fragrance of a flower or a perfume or bad smell of hydrogen sulphide, sulphur dioxide, chlorine, etc., when these are evolved or used in any work in laboratory or in industry.

Effusion

It is a process in which a gas is allowed to escape under pressure through a fine orifice or a small aperture made in the wall of a closed container. The difference between diffusion and effusion is that in the former case, the gas spontaneously streams through a porous partition while in the case of effusion, the gas is forced out through a small hole by applying some external pressure. However, both the processes are essentially the same.

Instantaneous rate of effusion is directly proportional to the instantaneous gas pressure and inversely proportional to the square root of molar mass.

$$\begin{aligned} -\frac{dP}{dt} &= \frac{KP}{\sqrt{M}} \\ -\int_{P_1}^{P_2} \frac{dP}{P} &= \frac{K}{\sqrt{M}} \int_0^t dt \\ \ln \left(\frac{P_1}{P_2} \right) &= \frac{Kt}{\sqrt{M}} \\ \ln P_2 &= \ln P_1 - \frac{Kt}{\sqrt{M}} \\ P_2 &= P_1 e^{-Kt/\sqrt{M}} \end{aligned}$$

Hence, partial pressure decreases exponentially with time as

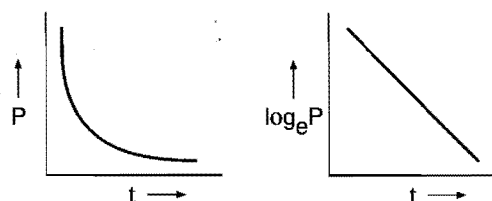


Fig. 4.4 Variation of partial pressure of gas with time, in the process of effusion.

Graham's Law of Diffusion or Effusion

This law was presented by Thomas Graham in 1833. The law states that "At constant pressure and temperature, the rate of diffusion or effusion of a gas is inversely proportional to the square root of its density."

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{d}}$$

If r_1 and r_2 represent the rates of diffusion of two gases and d_1 and d_2 are their respective densities, then

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

This equation can be written as:

$$\frac{r_1}{r_2} = \frac{\frac{\text{density of gas II}}{\text{density of hydrogen}}}{\frac{\text{density of gas I}}{\text{density of hydrogen}}} = \sqrt{\frac{\text{VD gas II}}{\text{VD gas I}}}$$

$$= \sqrt{\frac{2 \text{ VD gas II}}{2 \text{ VD gas I}}} = \sqrt{\frac{\text{Mol. mass gas II}}{\text{Mol. mass gas I}}} = \sqrt{\frac{M_2}{M_1}}$$

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

i.e., the volume which diffuses in unit time.

(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

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

or

$$\frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

(ii) **Comparison of the volumes of the gases that diffuse in same time:** Let V_1 and V_2 be the volumes of two gases that diffuse in the same time t . Then

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

(iii) **Effect of pressure on rate of diffusion:** When pressure is not constant then rate of effusion may be taken proportional to pressure.

$$r \propto \frac{1}{\sqrt{M}} \quad r \propto P$$

Combination of these equations gives:

$$r \propto \frac{P}{\sqrt{M}}$$

or

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

How to Determine Rate of Diffusion?

(a) Rate of diffusion is equal to distance travelled by gas per unit time through a tube of uniform cross-section.

(b) Number of moles effusing per unit time is also called rate of diffusion.

(c) Decrease in pressure of a cylinder per unit time is called rate of effusion of gas.

Application of Graham's Law of Diffusion

According to Graham's law of diffusion, the ratio of rate of diffusion of two gases may be given as:

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

where, M_1 and M_2 are respective molar masses of the gases.

The factor $\left(\frac{M_2}{M_1} \right)^{1/2}$ is called enrichment factor; this tells

about the preferential effusion of lighter species relative to the heavier ones. This enrichment can be applied to separate isotopes. For example, the isotope U^{235} , the active component in atomic weapons and in nuclear power generation, has a natural abundance of only 0.7% while U^{238} is far more abundant. By reaction of the isotopic mixture with fluorine, gaseous UF_6 is produced and can be enriched by passing it through a porous barrier. The process of diffusion through the porous barrier is repeated many times to achieve sufficient enrichment.

$$\text{Separation factor 'f'} = \frac{n'_1 / n'_2}{n_1 / n_2}$$

where, n_1, n_2 and n'_1, n'_2 are the concentration of two isotopes before and after diffusion.

$$\text{Theoretical separation factor for single step } f' = \sqrt{\frac{M_2}{M_1}}$$

Let enrichment of species '1' is achieved after 'n' times then

$$(f')^n = \frac{n'_1 / n'_2}{n_1 / n_2} = f$$

$$n \log f' = \log \left(\frac{n'_1 / n'_2}{n_1 / n_2} \right)$$

$$n \log \sqrt{\frac{M_2}{M_1}} = \log \left(\frac{n'_1 / n'_2}{n_1 / n_2} \right)$$

$$\frac{n}{2} \log \left(\frac{M_2}{M_1} \right) = \log \left(\frac{n'_1 / n'_2}{n_1 / n_2} \right)$$

$$n = \frac{2 \log \left(\frac{n'_1 / n'_2}{n_1 / n_2} \right)}{\log (M_2 / M_1)} = \frac{2 \log (f)}{\log \left(\frac{M_2}{M_1} \right)}$$

SOME SOLVED EXAMPLES

Example 20. A 10 litre flask contains 0.2 mole of methane, 0.3 mole of hydrogen and 0.4 mole of nitrogen at 25°C. What is the partial pressure of each component and what is the pressure inside the flask?

Solution:

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

$$\text{Partial pressure of methane} = \frac{0.2 \times 0.0821 \times 298}{10} = 0.489 \text{ atm}$$

$$\text{Partial pressure of hydrogen} = \frac{0.3 \times 0.0821 \times 298}{10} = 0.734 \text{ atm}$$

$$\text{Partial pressure of nitrogen} = \frac{0.4 \times 0.0821 \times 298}{10} = 0.979 \text{ atm}$$

$$\begin{aligned}\text{Total pressure} &= (0.489 + 0.734 + 0.979) \text{ atm} \\ &= 2.202 \text{ atm}\end{aligned}$$

Alternative solution: Total number of moles
 $= 0.2 + 0.3 + 0.4 = 0.9$

Let the total pressure be P .

We know that,

$$P = \frac{\text{total number of moles}}{V} \cdot RT$$

$$V = 10 \text{ litre}, R = 0.0821 \text{ L atm K}^{-1}, T = (25 + 273) = 298 \text{ K}$$

$$P = \frac{0.9}{10} \times 0.0821 \times 298 = 2.20 \text{ atm}$$

$$\begin{aligned}\text{Partial pressure of CH}_4 &= \text{Mole fraction of methane} \\ &\quad \times \text{total pressure} \\ &= \frac{0.2}{0.9} \times 2.20 = 0.489 \text{ atm}\end{aligned}$$

$$\begin{aligned}\text{Partial pressure of H}_2 &= \text{Mole fraction of H}_2 \times \text{total pressure} \\ &= \frac{0.3}{0.9} \times 2.20 = 0.733 \text{ atm}\end{aligned}$$

$$\begin{aligned}\text{Partial pressure of N}_2 &= \text{Mole fraction of N}_2 \times \text{total pressure} \\ &= \frac{0.4}{0.9} \times 2.20 = 0.978 \text{ atm}\end{aligned}$$

Example 21. If 200 mL of N_2 at 25°C and a pressure of 250 mm are mixed with 350 mL of O_2 at 25°C and a pressure of 300 mm so that, the volume of resulting mixture is 300 mL, what would be the final pressure of the mixture at 25°C ?

Solution: In the case of nitrogen, volume increases, its pressure must decrease. Let the new pressure be P_{N_2} .

$$P_{N_2} = \frac{250 \times 200}{300} = 166.6 \text{ mm} \quad (\text{Applying Boyle's law})$$

In the case of oxygen, volume decreases, its pressure must increase. Let the new pressure be P_{O_2} .

$$P_{O_2} = \frac{300 \times 350}{300} = 350 \text{ mm} \quad (\text{Applying Boyle's law})$$

$$\text{Total pressure} = P_{N_2} + P_{O_2} = (166.6 + 350) = 516.6 \text{ mm}$$

Example 22. 1.22 g of a gas measured over water at 15°C and a pressure of 775 mm of mercury occupied 900 mL. Calculate the volume of dry gas at NTP. Vapour pressure of water at 15°C is 14 mm.

Solution: Pressure of dry gas = Pressure of moist gas
 – Aqueous tension
 $= 775 - 14$
 $= 761 \text{ mm}$

Initial conditions NTP conditions

$$V_1 = 900 \text{ mL} \quad V_2 = ?$$

$$P_1 = 761 \text{ mm} \quad P_2 = 760 \text{ mm}$$

$$T_1 = (273 + 15) = 288 \text{ K} \quad T_2 = 273 \text{ K}$$

Since,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

So,

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$\begin{aligned}&= \frac{761 \times 900 \times 273}{288 \times 760} \\ &= 854.2 \text{ mL}\end{aligned}$$

Example 23. When 2 g of a gaseous substance A is introduced into an initially evacuated flask at 25°C , the pressure is found to be 1-atmosphere. 3 g of another gaseous substance B is then added to it at the same temperature and pressure. The final pressure is found to be 1.5 atmosphere. Calculate the ratio of molecular masses of A and B assuming ideal gas behaviour.

Solution: Let the molecular masses of A and B be M_A and M_B respectively.

Pressure exerted by the gas B = $(1.5 - 1.0) = 0.5 \text{ atm}$. Volume and temperature are same in both the gases.

$$\text{For gas A: } P = 1 \text{ atm, } w = 2 \text{ g, } M = M_A$$

$$\text{We know that, } PV = \frac{w}{M} RT$$

$$1 \times V = \frac{2}{M_A} \cdot RT \quad \text{or} \quad M_A = \frac{2RT}{V} \quad \dots (i)$$

$$\text{For gas B: } P = 0.5 \text{ atm, } w = 3 \text{ g, } M = M_B$$

$$0.5 \times V = \frac{3}{M_B} \cdot RT \quad \text{or} \quad M_B = \frac{3RT}{0.5 \times V} \quad \dots (ii)$$

Dividing Eq. (i) by Eq. (ii),

$$\begin{aligned}\frac{M_A}{M_B} &= \frac{2RT}{V} \times \frac{0.5 \times V}{3RT} \\ &= \frac{2 \times 0.5}{3} = \frac{1}{3}\end{aligned}$$

$$\text{Thus, } M_A : M_B = 1 : 3$$

Example 24. Find the total pressure exerted by 1.6 g methane and 2.2 g CO_2 contained in a four litre flask at 27°C .

Solution: $PV = (n_1 + n_2)RT$

$$P \times 4 = \left(\frac{1.6}{16} + \frac{2.2}{44} \right) \times 0.0821 \times 300$$

$$P = 0.9236 \text{ atm}$$

Example 25. 1500 mL flask contains 400 mg O_2 and 60 mg H_2 at 100°C .

(a) What is the total pressure in the flask?

(b) If the mixture is permitted to react to form water vapour at 100°C , what will be left and what will be their partial pressures?

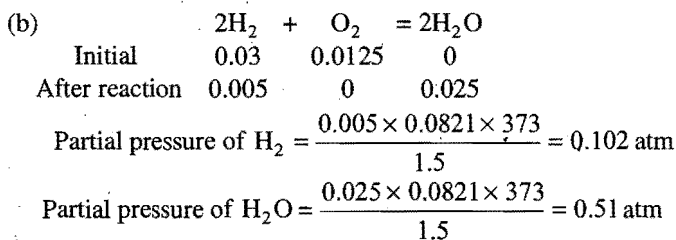
Solution: (a) No. of moles of $O_2 = \frac{400}{1000 \times 32} = 0.0125$

$$\text{No. of moles of } H_2 = \frac{60}{1000 \times 2} = 0.03$$

$$\text{Partial pressure of } O_2 = \frac{0.0125 \times 0.0821 \times 373}{1.5} = 0.255 \text{ atm}$$

$$\text{Partial pressure of } H_2 = \frac{0.03 \times 0.0821 \times 373}{1.5} = 0.612 \text{ atm}$$

$$\text{Total pressure} = 0.255 + 0.612 = 0.867 \text{ atm}$$



Example 26. 20 dm^3 of SO_2 diffuse through a porous partition in 60 s. What volume of O_2 will diffuse under similar conditions in 30 s? (IIT 1996)

Solution: Rate of diffusion of $\text{SO}_2 = \frac{20}{60} \text{ dm}^3 \text{ s}^{-1}$

Rate of diffusion of $\text{O}_2 = \frac{V}{30} \text{ dm}^3 \text{ s}^{-1}$

According to Graham's law of diffusion,

$$\frac{(V/30)}{(20/60)} = \sqrt{\frac{M_{\text{SO}_2}}{M_{\text{O}_2}}} = \sqrt{\frac{64}{32}}$$

$$V = 14.1 \text{ dm}^3$$

Example 27. 50 volume of hydrogen take 20 minute to diffuse out of a vessel. How long will 40 volume of oxygen take to diffuse out from the same vessel under the same conditions?

Solution: Rate of diffusion for hydrogen, $r_1 = \frac{50}{20}$

Rate of diffusion for oxygen, $r_2 = \frac{40}{t}$

Mol. mass of hydrogen = 2

Mol. mass of oxygen = 32

So $\frac{50/20}{40/t} = \sqrt{\frac{32}{2}}$

or $\frac{50}{20} \times \frac{t}{40} = 4$

$$t = 64 \text{ minute}$$

Example 28. Calculate the relative rates of diffusion of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ in the gaseous state (At. mass of F = 19).

Solution: Mol. mass $^{235}\text{UF}_6 = 235 + 6 \times 19 = 349$

Mol. mass $^{238}\text{UF}_6 = 238 + 6 \times 19 = 352$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{352}{349}} = 1.0043$$

$$r_1 : r_2 :: 1.0043 : 1.0000$$

Example 29. 180 mL of a hydrocarbon diffuses through a porous membrane in 15 minutes while 120 mL of SO_2 under identical conditions diffuses in 20 minutes. What is the molecular mass of the hydrocarbon?

Solution:

$$r_1 = \text{rate of diffusion of hydrocarbon} = \frac{180}{15} \text{ mL min}^{-1}$$

$$r_2 = \text{rate of diffusion of } \text{SO}_2 = \frac{120}{20} \text{ mL min}^{-1}$$

$$\frac{r_1}{r_2} = \frac{M_{\text{SO}_2}}{M}$$

Thus,

$$\frac{180/15}{120/20} = \sqrt{\frac{64}{M}}$$

$$2 = \sqrt{\frac{64}{M}}$$

$$M = 16$$

So,

Example 30. The reaction between gaseous NH_3 and HBr produces a white solid NH_4Br . Suppose a small quantity of gaseous NH_3 and gaseous HBr are introduced simultaneously into opposite ends of an open tube which is one metre long. Calculate the distance of white solid formed from the end which was used to introduce NH_3 .

Solution: Let the distance of white solid from NH_3 end = x cm.

The distance of white solid from HBr end = $(100 - x)$ cm.

Rates of diffusion shall be proportional to these distances.

$$\frac{r_1}{r_2} = \frac{x}{(100 - x)} = \sqrt{\frac{M_{\text{HBr}}}{M_{\text{NH}_3}}}$$

$$\text{Mol. mass of HBr} = 1 + 80 = 81$$

$$\text{Mol. mass of NH}_3 = 14 + 3 = 17$$

So, $\frac{x}{(100 - x)} = \sqrt{\frac{81}{17}}$

or, $\frac{x}{(100 - x)} = 2.18$

So, $x = 100 \times 2.18 - 2.18x$

or, $3.18x = 100 \times 2.18$

So, $x = \frac{100 \times 2.18}{3.18}$
 $= 68.55 \text{ cm}$

Example 31. At 27°C , hydrogen is leaked through a tiny hole into a vessel for 20 minute. Another unknown gas at the same temperature and pressure as that of hydrogen leaked through the same hole for 20 minute. After the effusion of the gases the mixture exerts a pressure of 6 atmosphere. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litre, what is the molecular mass of the unknown gas? (IIT 1992)

Solution: Let p_{H_2} and p_{un} be the partial pressures of hydrogen and unknown gas respectively and w be the number of moles of unknown gas.

$$p_{\text{H}_2} = \frac{0.7}{3} \times 0.0821 \times 300$$

$$p_{\text{un}} = \frac{w}{3} \times 0.0821 \times 300$$

Adding both,

$$p_{\text{H}_2} + p_{\text{un}} = 6 = (1/3) \times 0.0821 \times 300(0.7 + w)$$

$$w = 0.0308 \text{ mole}$$

Applying law of diffusion,

$$\frac{0.7/20}{0.0308/20} = \sqrt{\frac{M}{2}} \text{ or } M = 1033$$

Example 32. The ratio of velocities of diffusion of gases A and B is 1:4. If the ratio of their masses present in the mixture is 2:3, calculate the ratio of their mole fractions. [CEE (Bihar) 1990]

Solution:

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} = \frac{1}{4}$$

or,

$$\frac{M_B}{M_A} = \frac{1}{16}$$

Let masses W_A and W_B of A and B be present respectively.

$$\text{Mole fraction of A} = \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$\text{Mole fraction of B} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$\text{Ratio} = \frac{W_A}{M_A} \times \frac{M_B}{W_B}$$

$$\text{or } \frac{W_A}{W_B} \times \frac{M_B}{M_A} = \frac{2}{3} \times \frac{1}{16} = \frac{1}{24}$$

Example 33. A space capsule is filled with neon gas at 1.00 atm and 290 K. The gas effuses through a pin hole into outer space at such a rate that pressure drops by 0.30 torr per second.

(a) If the capsule is filled with ammonia at the same temperature and pressure, what would be rate of pressure drop?

(b) If the capsule is filled with 30.0 mol % helium, 20.0 mol % oxygen and 50.0 mol % nitrogen at a total pressure of 1.0 atm and a temperature of 290 K, what would be the corresponding rate of pressure drop?

Solution: (a) The rate of pressure drop is directly proportional to rate of effusion.

$$\frac{r_{\text{Ne}}}{r_{\text{NH}_3}} = \sqrt{\frac{M_{\text{NH}_3}}{M_{\text{Ne}}}} = \sqrt{\frac{17.0}{20}} = 0.92$$

$$r_{\text{NH}_3} = \frac{r_{\text{Ne}}}{0.92} = \frac{0.30}{0.92} = 0.326 \text{ torr / second}$$

(b) The average molecular mass of the gaseous mixture is

$$0.3 \times 4 + 0.2 \times 32 + 0.5 \times 28 = 21.6$$

$$\text{Rate of drop of pressure} = \sqrt{\frac{20}{21.6}} \times 0.30$$

$$= 0.29 \text{ torr / second}$$

Example 34. One mole of nitrogen gas at 0.8 atm takes 38 second to diffuse through a pin hole whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 second to diffuse through the same hole. Calculate the molecular formula of the compound. [IIT 1999]

Solution:

$$\frac{r_{\text{N}_2}}{r_{\text{XeF}_n}} = \frac{P_{\text{N}_2}}{P_{\text{XeF}_n}} \sqrt{\frac{M_{\text{XeF}_n}}{M_{\text{N}_2}}}$$

Molar volume

$$\frac{r_{\text{N}_2}}{r_{\text{XeF}_n}} = \frac{t_{\text{N}_2}}{\text{Molar volume}} = \frac{t_{\text{XeF}_n}}{t_{\text{N}_2}} = \frac{57}{38}$$

$$\frac{57}{38} = \frac{0.8}{1.6} \sqrt{\frac{M_{\text{XeF}_n}}{28}}$$

$$M_{\text{XeF}_n} = \left(\frac{57}{38}\right)^2 \times \left(\frac{1.6}{0.8}\right)^2 \times 28 = 252$$

$$\text{Xe} + n\text{F} = 252$$

$$131 + n \times 19 = 252$$

$$n = 6$$

$$\text{Molecular formula} = \text{XeF}_6$$

Example 35. 100 cm³ of NH₃ diffuses through a pin hole in 32.5 second. How much time will 60 cc of N₂ take to diffuse under the same conditions?

Solution:

$$\frac{r_{\text{NH}_3}}{r_{\text{N}_2}} = \sqrt{\frac{M_{\text{N}_2}}{M_{\text{NH}_3}}}$$

$$\frac{100/32.5}{60/t} = \sqrt{\frac{28}{17}}$$

$$\frac{100 \times t}{60 \times 32.5} = \sqrt{\frac{28}{17}}$$

$$t = 25 \text{ second}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

10. A gas with molecular formula $\text{C}_n\text{H}_{2n+2}$ diffuses through a porous plug at a rate 1/6th of the rate of diffusion of hydrogen gas under similar conditions. The formula of the gas is:

(a) C_2H_6 (b) $\text{C}_{10}\text{H}_{22}$ (c) C_5H_{12} (d) C_6H_{14}

[Ans. (c)]

$$\text{[Hint: } \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}]$$

$$\frac{r_1}{r_1/6} = \sqrt{\frac{M_2}{2}}$$

$$M_2 = 72$$

∴ The formula of gas will be C_5H_{12} .

11. Under similar conditions which of the following gases will diffuse four times as quickly as oxygen?

(a) He (b) H₂ (c) N₂ (d) D₂

[Ans. (b)]

$$\text{[Hint: } \frac{r_{\text{gas}}}{r_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{gas}}}}]$$

$$4 = \sqrt{\frac{32}{M_{\text{gas}}}} \text{ or } 16 = \frac{32}{M_{\text{gas}}}$$

$$\text{or } M_{\text{gas}} = \frac{32}{16} = 2, \text{ i.e., } \text{H}_2]$$

12. The rates of diffusion of hydrogen and deuterium are in the ratio:

(a) 1:1 (b) $\sqrt{2}$:1 (c) 4:1 (d) 1:4

[Ans. (b)]

[Hint: $\frac{r_{\text{H}_2}}{r_{\text{D}_2}} = \sqrt{\frac{M_{\text{D}_2}}{M_{\text{H}_2}}}$

$$\frac{r_{\text{H}_2}}{r_{\text{D}_2}} = \sqrt{\frac{4}{2}}$$

$$r_{\text{H}_2} = \sqrt{2} r_{\text{D}_2}]$$

13. The time taken for effusion of 64 mL of oxygen will be same as the time taken for the effusion of which of the following gases under identical conditions?

(a) 64 mL of H_2 (b) 100 mL of N_2
(c) 64 mL of CO_2 (d) 45.24 mL of SO_2

[Ans. (d)]

[Hint: $\frac{r_{\text{O}_2}}{r_{\text{gas}}} = \sqrt{\frac{M_{\text{gas}}}{M_{\text{O}_2}}}$

$$\frac{64}{V} = \sqrt{\frac{64}{32}} \text{ or } V = \frac{64}{\sqrt{2}} = 45.25 \text{ mL}]$$

14. Which of the following pairs of gases will have identical rate of effusion under similar conditions?

(a) Diprotium and dideuterium
(b) Carbon dioxide and ethane
(c) Dideuterium and helium
(d) Ethene and ethane

[Ans. (c)]

[Hint: Dideuterium and helium have same molar mass, hence they will diffuse with identical rate under identical conditions.]

15. Two gas bulbs A and B are connected by a tube having a stopcock. Bulb A has a volume of 100 mL and contains hydrogen. After opening the gas from A to the evacuated bulb B, the pressure falls down to 40%. The volume (mL) of B must be: [PET (Kerala) 2006]

(a) 75 (b) 150 (c) 125 (d) 200
(e) 250

[Ans. (b)]

[Hint: $P_1 V_1(A) + P_2 V_2(B) = P_R (V_1 + V_2)$

$$100 \times 100 + 0 \times V_2 = 40(100 + V_2)$$

$$V_2 = 250 - 100 = 150 \text{ mL}]$$

4.7 KINETIC THEORY OF GASES

This theory was a generalization for about ideal gases. It was presented by Bernoulli in 1738 and developed in 1860 by Clausius, Maxwell, Kronig and Boltzmann. Postulates of kinetic theory of gases are:

(1) Gases are made up of small structural units called atoms or molecules. Volume of individual atom or molecule is considered negligible.

(2) Gas molecules are always in rapid random motion colliding with each other and with the wall of container.

(3) Collision among gas molecules is perfectly elastic, i.e., there is no loss in kinetic energy and momentum during such collision.

(4) Gas molecules neither attract nor repel each other.

(5) Pressure exerted by gas is due to collisions of gas molecules with the wall of the container.

Pressure $\propto$ Number of collisions per unit time per unit area by the molecules on the wall of the container

(6) Kinetic energy of gas molecules depends only on absolute temperature.

Kinetic energy $\propto$ absolute temperature

(7) The force of gravity has no effect on the speed of gas molecules.

Derivation of Kinetic Gas Equation

On the basis of the postulates of kinetic theory of gases, it is possible to derive the mathematical expression, commonly known as kinetic gas equation, i.e.,

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

where, P = pressure of the gas, V = volume of the gas, m = mass of a molecule, n = number of molecules present in the given amount of a gas and c = root mean square speed.

The root mean square speed (rms speed) may be defined as the square root of the mean of squares of the individual speed of all the molecules.

$$\text{rms speed} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n}}$$

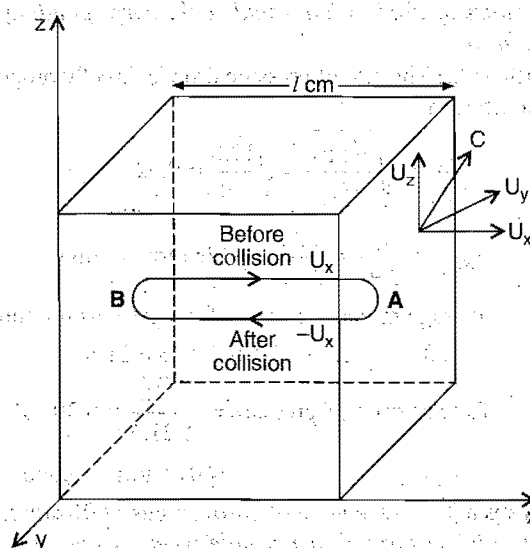


Fig. 4.5

Consider a certain mass of a gas enclosed in a cubical vessel of side ' l ' cm. Let the total number of gas molecules be ' n ' and mass of each molecule be ' m '. Let c be the root mean square speed. Speed can be resolved into three components, i.e., U_x , U_y and U_z parallel to the edges of the container (i.e., parallel to three axes x , y and z).

$$c^2 = U_x^2 + U_y^2 + U_z^2$$

Consider the movement of a single molecule between opposite faces A and B parallel to x -axis. When the molecule strikes with one wall of the container, it bounces back with the same speed and subsequently strikes the opposite wall.

The momentum of the molecule before collision with face $A = mU_x$.

The momentum of the molecule after collision = $-mU_x$

The change in momentum in one collision = $mU_x - (-mU_x)$
 $= 2mU_x$

After collision, the molecule must move a distance $2l$ cm along x -axis before making another impact on this wall. Since the velocity ' U_x ' remains unchanged, the time taken to travel a distance $2l$ cm = $\frac{2l}{U_x}$ second.

So, the number of collisions by the gas molecule in one second
 $= \frac{1}{\frac{2l}{U_x}} = \frac{U_x}{2l}$

Change of momentum per second = $2mU_x \times \frac{U_x}{2l} = m \frac{U_x^2}{l}$

The change of momentum on both the opposite faces A and B along x -axis per second would be double, i.e., $\frac{2mU_x^2}{l}$

Similarly,

Change in momentum per second along y -axis = $\frac{2mU_y^2}{l}$

and change in momentum per second along z -axis = $\frac{2mU_z^2}{l}$

Hence, total change of momentum per second on all faces will be

$$\begin{aligned} &= \frac{2mU_x^2}{l} + \frac{2mU_y^2}{l} + \frac{2mU_z^2}{l} \\ &= \frac{2m}{l} (U_x^2 + U_y^2 + U_z^2) \\ &= \frac{2m}{l} c^2 \end{aligned}$$

Change of momentum per second = Force

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

Pressure created by one molecule = $\frac{2m}{l} \frac{c^2}{6l^2}$

Pressure created by n molecules = $\frac{2mnc^2}{6l^3}$

$$P = \frac{1}{3} \frac{mnc^2}{V} \quad [V^3 = V]$$

or

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

This equation is called kinetic gas equation.

For one gram mole of the gas,

$$n = N \quad (\text{Avogadro's number}) \\ = 6.02 \times 10^{23}$$

$m \times N = M$ = molecular mass of the gas

The above kinetic equation can be written as:

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

or

$$c^2 = \frac{3PV}{M}$$

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

$$= \sqrt{\frac{3P}{d}}$$

[d = density]

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

Thus,

$$c = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

The value of R should be taken in $\text{erg K}^{-1} \text{mol}^{-1}$, e.g.,

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{mol}^{-1}$$

$$c = \sqrt{\frac{3 \times 8.314 \times 10^7 \times T}{M}} = 1.58 \sqrt{\frac{T}{M}} \times 10^4 \text{ cm/sec}$$

Calculation of Kinetic Energy

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

For one gram mole of the gas,

$$PV = RT \quad \text{and} \quad n = N$$

$$\frac{1}{3} mNc^2 = RT$$

$$\text{or} \quad \frac{2}{3} \cdot \frac{1}{2} mNc^2 = RT \quad \left(\frac{1}{2} mNc^2 = \text{KE per mol} \right)$$

$$\frac{2}{3} \cdot \text{KE} = RT$$

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

Average kinetic energy per mol does not depend on the nature of the gas but depends only on temperature. Thus, when two gases are mixed at the same temperature, there will be no rise or decrease in temperature unless both react chemically.

Average kinetic energy per molecule = $\frac{\text{Average KE per mole}}{N}$

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

k = Boltzmann constant

The ratio R/N is constant and is known as Boltzmann constant. Its numerical value is 1.38×10^{-16} erg K^{-1} molecule $^{-1}$.

4.8 MAXWELL-BOLTZMANN DISTRIBUTION OF MOLECULAR SPEEDS

The gas molecules are moving in all possible directions. They collide with one another and also with the walls of the container. As a result of collisions, the speed and direction of the gas molecules are ever changing, i.e., all the molecules in a given sample of gas do not have the same speed.

The distribution of gas molecules among different possible speeds was studied by **Maxwell** and **Boltzmann** using the theory of probability. The results are mathematically expressed as,

$$dNu = 4\pi N \left[\frac{M}{2\pi RT} \right]^{3/2} e^{-\frac{Mu^2}{2RT}} u^2 du$$

$$= 4\pi N \left[\frac{m}{2\pi kT} \right]^{3/2} e^{-\frac{mu^2}{2kT}} u^2 du$$

Here, N = Total number of molecules, M = molar mass of gas. This expression gives the number of molecules (dNu) having speed between u and $(u + du)$ at temperature (T).

A plot of fraction of molecules in the speed range $(u + du)$, $\frac{1}{N} \left(\frac{dNu}{du} \right)$ against speed u is:

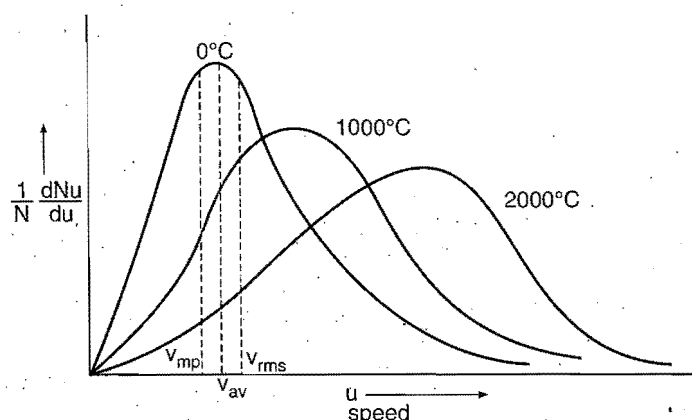


Fig. 4.6

- v_{mp} = most probable speed
- v_{av} = average speed
- v_{rms} = root mean square speed

Kinds of Molecular Speeds

Molecular speeds are of three types:

- (i) The rms speed,
- (ii) The average speed and
- (iii) The most probable speed

Note: Root mean square speed explained the non-existence of gases in the atmosphere of moon. Root mean square speed of gases exceeds the escape velocity of moon and hence gases escape from atmosphere of moon against the gravitational barrier of moon.

(i) The root mean square speed: The speed in kinetic gas equation, $PV = \frac{1}{3} mnc^2$, is the hypothetical speed possessed by all the gas molecules when the total kinetic energy is equally distributed amongst them. The total kinetic energy of the n molecules of the gas is sum of the kinetic energies of the individual molecules.

Total kinetic energy

$$= \frac{1}{2} mc_1^2 + \frac{1}{2} mc_2^2 + \frac{1}{2} mc_3^2 + \dots + \frac{1}{2} mc_n^2 \quad \dots (i)$$

Let c be the velocity possessed by each of the n molecules; then,

$$\text{total kinetic energy} = n \times \frac{1}{2} mc^2 \quad \dots (ii)$$

Equating both the equations,

$$n \times \frac{1}{2} mc^2 = \frac{1}{2} mc_1^2 + \frac{1}{2} mc_2^2 + \frac{1}{2} mc_3^2 + \dots + \frac{1}{2} mc_n^2$$

or

$$c^2 = \frac{c_1^2 + c_2^2 + c_3^2 + c_4^2 + \dots + c_n^2}{n}$$

or

$$c = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n}}$$

Thus, rms speed is defined as the square root of the mean of the squares of the speed of all the molecules present in the given sample of the gas. The value of c is determined by using the following expressions:

$$c = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

In SI units, the values of R , P , V , M and d used are given below:

- (i) $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ or $R = 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$
- (ii) V of the gas always in litre
- (iii) P of the gas in kilopascal (kPa). $1 \text{ atm} = 101.3 \text{ kPa}$ and $1 \text{ torr} = 0.133 \text{ kPa}$
- (iv) M in kg mol^{-1}
- (v) d in kg m^{-3}

(ii) Average speed: It is the arithmetic mean of the various speeds of the molecules.

$$\text{Average speed} = \frac{c_1 + c_2 + c_3 + \dots + c_n}{n}$$

$$\text{It is equal to } \sqrt{\frac{8RT}{\pi M}}$$

It is related to rms speed by the following relationship:

$$\text{Average speed} = 0.9213 \times \text{rms speed}$$

$$\text{rms speed} = 1.085 \times \text{average speed}$$

(iii) Most probable speed: This is defined as the speed possessed by maximum number of molecules of a gas at a given temperature.

It is equal to $\sqrt{\frac{2RT}{M}}$

This is related to rms speed by the following relationship:

$$\text{Most probable speed} = \left\{ \sqrt{\frac{2}{3}} \right\} \text{rms} = 0.816 \text{ rms}$$

or $\text{rms} = 1.224 \text{ most probable speed}$

The three kinds of molecular speeds are related to each other as:

Most probable speed : Average speed : rms speed

$$\begin{aligned} &= \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} \\ &= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} \\ &= 1 : 1.128 : 1.224 \end{aligned}$$

rms speed at any temperature $t^\circ\text{C}$ may be related to its value at STP as:

$$c_t = c_0 \sqrt{\frac{(273+t)}{273}} \quad \dots (i)$$

$$c_0 = \sqrt{\frac{3P}{d}} \quad \dots (ii)$$

From eqs. (i) and (ii), we get

$$\begin{aligned} c_t &= \sqrt{\frac{3P}{d}} \sqrt{\frac{(273+t)}{273}} \\ &= \sqrt{\frac{3P(273+t)}{273d}} \end{aligned}$$

Some Essential Points for Distribution of Molecular Speed

(i) The fraction of molecules with very low or very high speeds is very small. Maximum fraction of molecules have speed near to the most probable speed v_{mp} .

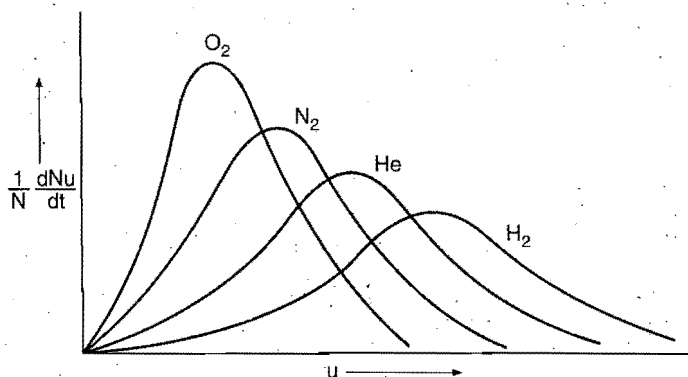


Fig. 4.7 Distribution of molecular speeds of various gases at a constant temperature

(ii) Total area under the curve is a measure of total number of molecules in the collection. Thus, area under the curve remains constant at different temperature.

(iii) Distribution of molecular speed also depends upon the molecular mass of the gas. At similar temperature a heavier gas molecule has a narrow distribution of speed than those of lighter gas molecules.

(iv) The fraction of molecules having speeds greater than minimum goes on increasing with increase in speed. It reaches to a maximum value and then begins to decrease.

(v) As long as temperature of the gas is constant, the fraction having a particular speed remains the same inspite of the fact that the molecules change their speeds due to collisions.

The increase in the temperature of the gas increases the molecular speed. As a result, the most probable speed increases with the increase of temperature and the distribution curve shifts towards right. The general shape of the curve remains the same but the maxima of the curve becomes somewhat flat at a higher temperature, i.e., there is a wider distribution of molecular speeds and the fraction of the molecules having high speeds increases. However, the fraction of molecules possessing most probable speeds decreases with increase in temperature.

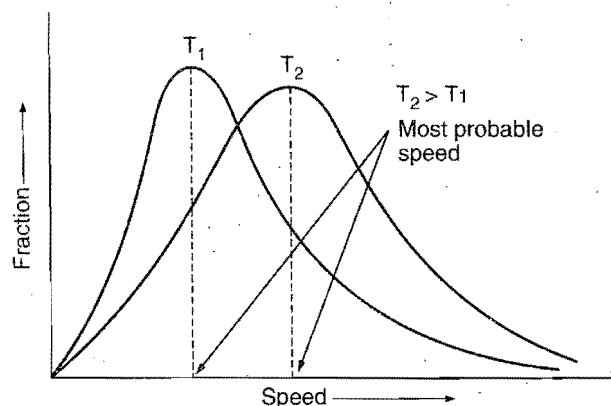


Fig. 4.8

SOME SOLVED EXAMPLES

Example 36. Calculate the kinetic energy in joule of 8.00 g of methane at 27°C .

Solution: Number of gram moles of methane $= \frac{8}{16} = \frac{1}{2}$

$$T = (27 + 273) = 300 \text{ K}$$

$$R = 8.32 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Kinetic energy for one gram mole} = \frac{3}{2} RT$$

$$= \frac{3}{2} \times 8.32 \times 300 \text{ J}$$

Thus,

$$\text{kinetic energy for } \frac{1}{2} \text{ gram mole} = \frac{1}{2} \times \frac{3}{2} \times 8.32 \times 300 = 1872 \text{ J}$$

Example 37. Calculate the average and total kinetic energy of 0.5 mole of an ideal gas at 0°C .

Solution: Average kinetic energy per molecule of the gas

$$= \frac{3}{2} \frac{R}{N} T$$

$$= \frac{3}{2} \times \frac{8.314 \times 10^7}{6.023 \times 10^{23}} \times 273$$

$$= 5.65 \times 10^{-14} \text{ erg} = 5.65 \times 10^{-21} \text{ J}$$

Total kinetic energy of 0.5 mole of the gas

$$= \frac{3}{2} RT \times 0.5$$

$$= \frac{3}{2} \times 8.314 \times 10^7 \times 273 \times 0.5$$

$$= 1.702 \times 10^{10} \text{ erg} = 1.702 \text{ kJ}$$

Example 38. Calculate the pressure exerted by 10^{23} gas molecules each of mass 10^{-22} g in a container of volume 1 litre, the rms speed is 10^5 cm s^{-1} .

Solution: Using kinetic gas equation,

$$P = \frac{1}{3} \frac{mnc^2}{V}$$

Given, $V = 1 \text{ litre} = 1000 \text{ mL} = 1000 \text{ cm}^3$; $n = 10^{23}$; $m = 10^{-22} \text{ g}$ and $c = 10^5 \text{ cm s}^{-1}$.

Substituting the values in the above equation,

$$P = \frac{1}{3} \times \frac{10^{-22} \times 10^{23} \times 10^{10}}{1000} = 3.33 \times 10^7 \text{ dyne cm}^{-2}$$

Example 39. Calculate the root mean square speed of an oxygen molecule at 288 K in SI units.

Solution: $c = \sqrt{\frac{3RT}{M}}$

$$R = 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}, T = 288 \text{ K}$$

and $M = 0.032 \text{ kg mol}^{-1}$

Substituting the values in above equation

$$c = \sqrt{\frac{3 \times 8.314 \times 288}{0.032}} = 473.79 \text{ ms}^{-1}$$

Example 40. Calculate the root mean square speed of hydrogen molecule at STP.

Solution: $c = \sqrt{\frac{3PV}{M}}$

$$P = 1 \text{ atm} = 101.3 \text{ kPa}$$

$$V = 22.4 \text{ dm}^3$$

$$M = 2 \text{ g mol}^{-1} = 0.002 \text{ kg mol}^{-1}$$

Substituting the values,

$$c = \sqrt{\frac{3 \times 101.3 \times 22.4}{0.002}} = 1844.91 \text{ ms}^{-1}$$

Alternative method:

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

$$R = 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}, T = 273 \text{ K},$$

$$M = 0.002 \text{ kg mol}^{-1}$$

Substituting the values,

$$c = \sqrt{\frac{3 \times 8.314 \times 273}{0.002}} = 1845.15 \text{ ms}^{-1}$$

Example 41. Oxygen at 1 atmosphere and 0°C has a density of 1.4290 g L^{-1} . Find the rms speed of oxygen molecule.

Solution: $P = 1 \text{ atm} = 101.3 \times 10^3 \text{ Pa}$

$$d = 1.4290 \text{ g L}^{-1} = 1.4290 \text{ kg m}^{-3}$$

We know that,

$$c = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 101.3 \times 10^3}{1.4290}} = 461.15 \text{ ms}^{-1}$$

Example 42. At what temperature will hydrogen molecules have the same root mean square speed as nitrogen molecules at 27°C ?

Solution: $\sqrt{\frac{3RT}{M_H}} = \sqrt{\frac{3R \times 300}{M_N}}$

$$\text{or } \frac{T}{M_H} = \frac{300}{M_N} \text{ or } T = \frac{300}{28} \times 2 = 21.43 \text{ K}$$

Example 43. Calculate the root mean square, average and most probable speed of oxygen at 27°C .

Solution: $27^\circ\text{C} = 300 \text{ K}$

$$\text{Root mean square speed} = \sqrt{\frac{3RT}{M}}$$

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}; M = 32 \text{ g mol}^{-1}; T = 300 \text{ K}$$

Substituting the values,

$$= \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{32}}$$

$$= 48356 \text{ cm/sec}$$

$$= 483.56 \text{ m/sec}$$

$$\text{Average speed} = \sqrt{\frac{8RT}{\pi M}}$$

$$= \sqrt{\frac{8 \times 8.314 \times 10^7 \times 300 \times 7}{22 \times 32}}$$

$$= 44542 \text{ cm/sec}$$

$$= 445.42 \text{ m/sec}$$

$$\text{Most probable speed} = \sqrt{\frac{2 \times R \times T}{M}}$$

$$= \sqrt{\frac{2 \times 8.314 \times 10^7 \times 300}{32}}$$

$$= 39483 \text{ cm/sec}$$

$$= 394.83 \text{ m/sec}$$

Example 44. Calculate the average kinetic energy per mole of CO_2 gas at 27°C in different units.

Solution: $KE = \frac{3}{2} nRT$
 $= \frac{3}{2} \times 1 \times 1.987 \times 300 = 894.15 \text{ cal}$

$KE = \frac{3}{2} nRT$
 $= \frac{3}{2} \times 1 \times 8.314 \times 300$
 $= 3741 \text{ J}$
 $= 3.741 \times 10^{10} \text{ erg}$

Example 45. A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of $7.57 \times 10^3 \text{ N m}^{-2}$. Calculate the root mean square speed and temperature of the gas molecules. If the ratio of most probable speed to the root mean square speed is 0.82, calculate the most probable speed of these molecules at this temperature.

(IIT 1993)

Solution: Amount of the gas = $\frac{2.0 \times 10^{21}}{6.023 \times 10^{23}} \text{ mole}$

Given, $V = 1 \text{ litre} = 10^{-3} \text{ m}^3$; $P = 7.57 \times 10^3 \text{ N m}^{-2}$,
 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

Applying $PV = nRT$ or $T = \frac{PV}{nR}$

$T = \frac{10^{-3} \times 7.57 \times 10^3}{\frac{2.0 \times 10^{21}}{6.023 \times 10^{23}} \times 8.314} = 274.2 \text{ K}$

rms speed = $\sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 274.2}{28 \times 10^{-3}}} = 494.22 \text{ ms}^{-1}$

Most probable speed = $0.8 \times \text{rms}$
 $= 0.8 \times 494.22 \text{ ms}^{-1} = 395.376 \text{ ms}^{-1}$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

16. At what temperature is the root mean square speed of N_2 gas equal to that of propane gas at STP?

(a) 173.7°C (b) 173.7 K (c) 273 K (d) -40°C

[Ans. (b)]

[Hint: $v_{\text{rms}}(\text{N}_2) = v_{\text{rms}}(\text{C}_3\text{H}_8)$

$\sqrt{\frac{3RT}{28}} = \sqrt{\frac{3R \cdot 273}{44}}$
 $T = 173.7 \text{ K}]$

17. At what temperature is the kinetic energy of a gas molecule half of its value at 327°C ?

(a) 13.5°C (b) 150°C (c) 27°C (d) -123°C

[Ans. (c)]

[Hint: $KE = \frac{3}{2} RT$

$\frac{E_1}{E_2} = \frac{\frac{3}{2} RT_1}{\frac{3}{2} RT_2}$
 $\frac{1}{1/2} = \frac{600}{T_2}$

$T_2 = 300 \text{ K}$

$(= 27^\circ\text{C})$

18. The root mean square speed of molecules of nitrogen gas is v at a certain temperature. When the temperature is doubled, the molecules dissociate into individual atoms. The new rms speed of the atom is:

(a) $\sqrt{2}v$ (b) $2v$ (c) v (d) $4v$

[Ans. (b)]

[Hint: $v_1 = \sqrt{\frac{3RT}{M}}$

$T_2 = 2T, M_2 = M/2$

$v_2 = \sqrt{\frac{3R \times 2T}{M/2}} = 2v_1]$

19. The translational kinetic energy of an ideal gas depends only on its:

(a) pressure (b) force
 (c) temperature (d) molar mass

[Ans. (c)]

[Hint: $KE = \frac{3}{2} RT \therefore$ Kinetic energy depends on temperature.]

20. At what temperature is the rms speed of H_2 molecules the same as that of oxygen molecules at 1327°C ?

(a) 173 K (b) 100 K (c) 400 K (d) 523 K

[Ans. (b)]

[Hint: $\left(\sqrt{\frac{3RT_1}{M_1}}\right)_{\text{H}_2} = \left(\sqrt{\frac{3RT_2}{M_2}}\right)_{\text{O}_2}$

$\sqrt{\frac{T_1}{2}} = \sqrt{\frac{1600}{32}}$

$T_1 = 100 \text{ K}]$

21. If the temperature of 1 mole of a gas is increased by 50°C , calculate the change in kinetic energy of the system:

(DCE 2006)

(a) 62.32 J (b) 6.235 J (c) 623.5 J (d) 6235.0 J

[Ans. (c)]

[Hint: $E = \frac{3}{2} RT$ (Kinetic energy of 1 mole gas)

$\Delta E = \frac{3}{2} R(T + 50) - \frac{3}{2} RT$
 $= \frac{3}{2} R \times 50 = \frac{3}{2} \times 8.314 \times 50$
 $= 623.55 \text{ J}]$

22. At same temperature, calculate the ratio of average velocity of SO_2 to CH_4 :

(DCE 2006)

(a) $2:3$ (b) $3:4$ (c) $1:2$ (d) $1:6$

[Ans. (c)]

[Hint: $v_{\text{av}} = \sqrt{\frac{8RT}{\pi m}}$

$$\frac{v_{\text{SO}_2}}{v_{\text{CH}_4}} = \sqrt{\frac{m_{\text{CH}_4}}{m_{\text{SO}_2}}} = \sqrt{\frac{16}{64}} = \frac{1}{2}$$

4.9 VAN DER WAALS' EQUATION

The gas which conforms to all of the postulates of kinetic theory or which obeys Boyle's law and Charles' law rigidly for all values of temperature and pressure or which strictly follows the general gas equation ($PV = nRT$) is called **ideal** or **perfect gas**. Actually no gas is ideal or perfect in nature. Under ordinary conditions, only those gases nearly behave as ideal or perfect which have very low boiling points such as nitrogen, hydrogen, etc.

At low pressure and moderately high temperature, the real gases approach ideal behaviour (see fig.).

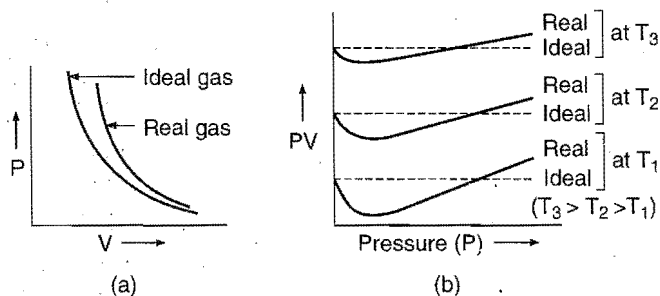


Fig. 4.9 (a) Ideal and real gas, (b) Ideal and real gas (real gas is approaching ideal behaviour with rise in temperature)

It is observed that deviations from gas laws are high under high pressure and low temperature. van der Waals suggested that these deviations are due to the following two faulty assumptions in the kinetic theory of gases:

- Actual volume of the gas molecules is negligible as compared to the total volume of the gas.
- Intermolecular attractions are not present in gases.

van der Waals pointed out that in the case of real gases, molecules do have a volume and also exert intermolecular attractions especially when the pressure is high and temperature is low. He applied two corrections:

(a) Volume correction: van der Waals assumed that molecules of a real gas are rigid spherical particles which possess a definite volume. Thus, the volume of a real gas, i.e., volume available for compression or movement is, therefore, actual volume minus the volume occupied by gas molecules. If b is the effective volume of the molecules per mol of the gas, the ideal volume for the gas equation is $(V - b)$ and not V , i.e.,

corrected volume ' V_i ' = $V - b$ for one mole of the gas
and for n mole of the gas, ' V_i ' = $V - nb$.

b is termed the excluded volume which is constant and characteristic for each gas. The excluded volume ' b ' is actually four times the actual volume of the gas molecules.

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

where ' r ' = radius of gas molecule

N = Avogadro's number

(b) Pressure correction: A molecule in the interior of the gas is attracted by other molecules on all sides. These forces, thus, are not effective, as equal and opposite forces cancel each other. However, a gas molecule which is just going to strike the wall of the vessel experiences an inward pull due to unbalanced attractive forces. Therefore, it strikes the wall with less momentum and the observed pressure will be less than the ideal pressure.

$$P_{\text{ideal}} = P_{\text{obs}} + P'$$

where P' is the pressure correction.

Pressure Correction Depends upon Two Factors

(i) The attractive force exerted on a single molecule about to strike the wall is proportional to the number of molecules per unit volume in the bulk of the gas.

(ii) The number of molecules striking the wall which is also proportional to the number of molecules per unit volume of the gas.

Both these factors are proportional to the density of the gas. Therefore, the attractive force is proportional to the square of the density of the gas.

$$P' \propto \text{total attractive force}$$

$$\propto d^2$$

$$\propto \frac{1}{V^2}$$

or

$$P' = \frac{a}{V^2}$$

where ' a ' is a constant depending upon the nature of the gas and V is the volume of 1 mole of the gas.

$$\text{Thus, corrected pressure, } P_{\text{ideal}} = P_{\text{obs}} + \frac{a}{V^2}$$

Making both the corrections, the general gas equation $PV = RT$ may be written as:

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

The equation is called van der Waals' equation. van der Waals' equation for n moles of the gas is:

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

van der Waals' equation is obeyed by real gases over a wide range of temperature and pressure and hence this equation is called equation of state for the real gases. The constants ' a ' and ' b ' are called van der Waals' constants and they are characteristic of each gas.

Unit of van der Waals' Constants

a and b are expressed in terms of the units of P and V .

$$\text{Pressure correction } P' = \frac{n^2 a}{V^2}$$

$$a = \frac{P' V^2}{n^2} = \frac{\text{Pressure correction} \times (\text{Volume})^2}{(\text{Mole})^2}$$

Thus, if pressure and volume are expressed in atmosphere and litre respectively, the units of constant ' a ' will be atmosphere litre² mol⁻².

$$\text{SI unit, 'a' = Nm}^4 \text{ mol}^{-2}$$

' b ' is the effective volume of the gas molecules in one gram mole of the gas. Thus, the unit of ' b ' is the same as for the volume, i.e., litre mol⁻¹.

$$\text{SI unit, 'b' = m}^3 \text{ mol}^{-1}$$

Boyle temperature: The temperature at which real gas behaves like ideal gas and obeys the gas laws over a wide range of pressure is called Boyle temperature ' T_b '. At this temperature, PV remains constant for an appreciable range of pressure

$$T_b = \frac{a}{Rb} = \frac{1}{2T_i}$$

where, T_i = inversion temperature

a, b = van der Waals' constants

At Boyle temperature, $\frac{\partial PV}{\partial P} \approx 0$ when P approaches zero.

4.10 CRITICAL PHENOMENON AND LIQUEFACTION OF GASES

During the early part of nineteenth century, a number of gases such as carbon dioxide, sulphur dioxide, ammonia, etc. were liquefied by subjecting the gas to low temperature and high pressure. On cooling, the kinetic energy of the gas molecules decreases. The slow moving molecules come nearer to each other due to forces of attraction and, thus, aggregate and are converted into liquid. The increase of pressure can also bring the gas molecules closer to each other and, thus, is helpful in converting a gas into liquid. The effect of temperature is rather more important than that of pressure. The essential conditions for liquefaction of gases were discovered by **Andrews** in 1869 as a result of his study of Pressure-Volume-Temperature ($P-V-T$) relationship for carbon dioxide. It was found that above a certain temperature, it was impossible to liquefy a gas whatever the pressure was applied. **The temperature below which the gas can be liquefied by the application of pressure alone is called critical temperature (T_c).** The pressure required to liquefy a gas at this temperature is called the **critical pressure (P_c)**. The volume occupied by one mole of the substance at the critical temperature and pressure is called **critical volume (V_c)**.

The results of Andrews experiments are shown in the following Figure. 4.10(a) in which the pressure is plotted against volume at various temperatures for carbon dioxide. Each pressure-volume plot is called isotherm.

Let us consider an isotherm at 13.1°C. At low pressure, carbon dioxide is entirely gaseous and is represented by the point (A) in the isotherm. On increasing pressure, volume decreases as shown by the portion AX of the isotherm, approximately in accordance with Boyle's law. At X, deviations from Boyle's law begin to appear and the volume decreases rapidly as the gas is converted into liquid. At point Y, carbon dioxide has been completely liquefied. Between X and Y, pressure remains constant and both the gas and liquid phases are in equilibrium. The pressure corresponding to the horizontal portion XY of the isotherm is the vapour pressure of the liquid at the temperature of the isotherm.

The isotherm at 21.5°C shows a similar behaviour except that liquefaction starts at higher pressure and the horizontal portion MN is shorter. As the temperature is raised, the horizontal portion

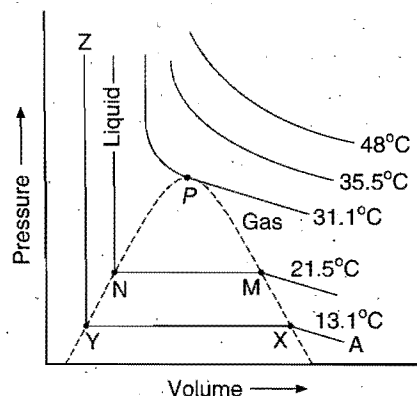


Fig. 4.10 (a) Isotherms of carbon dioxide showing critical region

of the isotherm becomes smaller and smaller until at 31.1°C at which it reduces to a point P. Point P is called **critical point**; at this point the boundary between liquid and gas phase (meniscus) disappears indicating that both the phases have identical characteristics. Above 31.1°C, there is no indication of liquefaction. The isotherm at critical temperature 31.1°C is called **critical isotherm**. The tangent at critical point P is horizontal, so that, $\frac{dP}{dV}$ at critical point will be zero. Thus, the point 'P' is also called the **point of inflection**.

It may be concluded from this explanation that in the area to the left of the dotted line below the critical isotherm, only liquid carbon dioxide exists. To the right of the dotted line, only gaseous carbon dioxide exists. The horizontal portion, within the dotted line shows the equilibrium between gas and liquid phase.

The van der Waals' Equation and the Critical Constants

The van der Waals' equation for 1 mole of a gas is given by:

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

This equation may be written as,

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

$$\text{or } PV^3 + aV - PbV^2 - ab - RTV^2 = 0$$

Dividing above equation by 'P', we get

$$V^3 + \frac{aV}{P} - bV^2 - \frac{ab}{P} - \frac{RTV^2}{P} = 0$$

Arranging in descending powers of V, we get

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{aV}{P} - \frac{ab}{P} = 0 \quad \dots (i)$$

Equation (i) is a cubic equation in 'V' and therefore for any value of P and T, it will have three values of V, all of which may be real or one may be real and the other two imaginary. When pressure *versus* volume plots are constructed using equation (i) we get the curves as shown in Fig. 4.10(b).

It is evident from the Fig. 4.10 (b) that the curves at and above the critical temperature are similar to those in Fig. 4.10 (a). However, below critical temperature, the horizontal portion determining the coexistence of gas and liquid is replaced by a (~) shaped curve ABC in Fig. 4.10(b). Thus, this curve predicts that there are three values of V corresponding to the points A, B and C. At the critical point 'P', the three roots of van der Waals' equation are not only real and positive but also identical and equal to the critical value V_c . This condition may be expressed as,

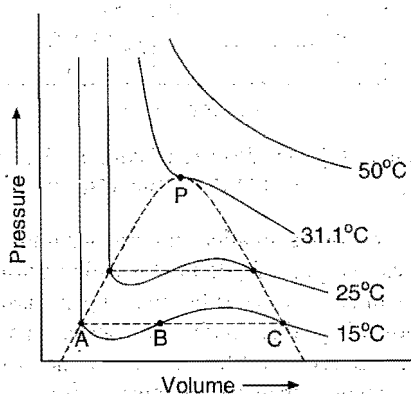


Fig. 4.10 (b) Isotherms of carbon dioxide according to van der Waals' equation

$$V = V_c$$

$$\text{or } V - V_c = 0$$

$$(V - V_c)^3 = 0$$

$$\therefore V^3 - 3V_c V^2 + 3V V_c^2 - V_c^3 = 0 \quad \dots (ii)$$

At critical point, equations (i) and (ii) must be identical. Comparing and equating the coefficients of like powers of V gives:

$$3V_c = b + \frac{RT_c}{P_c} \quad \dots (iii)$$

$$3V_c^2 = \frac{a}{P_c} \quad \dots (iv)$$

$$V_c^3 = \frac{ab}{P_c} \quad \dots (v)$$

In above equations, $T = T_c$, $P = P_c$ at critical state.

Dividing equation (v) by (iv), we get,

$$\frac{V_c}{3} = b$$

$$\text{i.e., } V_c = 3b \quad \dots (vi)$$

Substituting the value of V_c from eq. (vi) in (v), we get

$$(3b)^3 = \frac{ab}{P_c}$$

$$P_c = \frac{a}{27b^2} \quad \dots (vii)$$

Finally, substituting the values of P_c and V_c in eq. (iii), we get

$$T_c = \frac{8a}{27Rb} \quad \dots (viii)$$

We can express the constants a, b and R in terms of critical constants as:

$$b = \frac{V_c}{3}$$

$$a = 3P_c V_c^2$$

$$R = \frac{8P_c V_c}{3T_c}$$

$$P_c V_c = \frac{3}{8} RT_c \quad \dots (ix)$$

Equation (ix) is called equation of critical state. Critical compressibility factor of a gas may be calculated as,

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{\left(\frac{a}{27b^2}\right)(3b)}{R\left(\frac{8a}{27Rb}\right)} = 0.375$$

Critical constants of gases

Gas	P_c (atm)	V_c ($\text{cm}^3 \text{mol}^{-1}$)	T_c (K)
He	2.3	57.8	5.3
H ₂	12.8	65	33.2
Ne	26.9	41.7	44.4
N ₂	33.6	90.1	126.1
O ₂	50.3	74.4	154.5
CO ₂	72.7	95.0	304.2
H ₂ O	218.0	55.6	647.3
NH ₃	112.0	72.0	405.5
CH ₄	45.8	99.0	191.0
C ₂ H ₆	48.2	139.0	305.5
C ₂ H ₄	50.5	124.0	417.2

4.10.1 EXPERIMENTAL METHODS FOR LIQUEFACTION OF GASES

Discovery of critical phenomenon by Andrews in 1869 showed that gases cannot be liquefied by the application of pressure alone; they must first be cooled below their critical temperatures and then subjected to adequate pressure to cause liquefaction.

Principles involved in liquefaction are:

(1) A gas must be at or below its critical temperature. Lower the temperature below the critical value, easier would be the liquefaction.

(2) The gas is cooled either by doing external work or by expanding against the internal forces of molecular attraction.

Low temperature for liquefaction of gases can be achieved by the following techniques:

- (a) Cooling by rapid evaporation of a volatile liquid.
- (b) Cooling by Joule-Thomson effect.
- (c) Cooling by adiabatic expansion involving mechanical work.

(a) Cooling by Rapid Evaporation of a Volatile Liquid

This method was first employed by **Pictet and Cailletet**. An easily volatile liquid is rapidly evaporated to cool and liquefy a less volatile liquid. This is the principle underlying the cascade process [Fig. 4.11(a)] for liquefaction of O_2 .

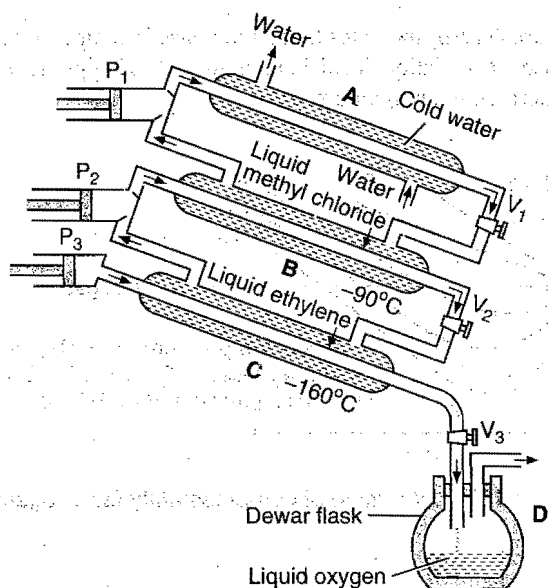


Fig. 4.11 (a) Cascade process for the liquefaction of oxygen

The apparatus consists of three compression pumps P_1 , P_2 and P_3 and three compression chambers A , B and C . The compression pumps are joined in series. The pump P_1 compresses methyl chloride gas which is cooled by cold water circulating in outer jacket of A . As the critical temperature of methyl chloride is 143°C , it is liquefied at room temperature. The liquid methyl chloride passes through valve V_1 into the outer jacket of B which is connected to the suction side of P_1 . As a result of reduced pressure, the liquid methyl chloride evaporates and the temperature in B reaches -90°C .

The inner tube of B is filled with ethylene gas which is cooled to -90°C . As the critical temperature of ethylene is 10°C , it gets liquefied and passes through valve V_2 into the outer jacket of C . Ethylene liquid is allowed to evaporate under reduced pressure with the help of pump P_2 resulting in a sharp fall in the

temperature of oxygen (-118°C) which is filled in the inner tube of C . Oxygen gets liquefied during the compression stroke of pumps P_3 and is collected in the Dewar flask D .

(b) Cooling by Joule-Thomson Effect

(Linde's process for liquefaction of air)

When a compressed gas is allowed to expand into a low pressure or vacuum under adiabatic conditions, a lowering of temperature is observed. This is known as Joule-Thomson effect. In the expansion, molecules of the gas move far apart from one another. Work is done by the gas molecules to overcome intermolecular forces. Work is done at the cost of the kinetic energy of gas molecules. Consequently a cooling effect is observed. For each gas, there is a characteristic temperature above which a gas on expansion shows a heating effect while below it the gas cools on expansion. This temperature is known as **inversion temperature** of the gas. This temperature is related to van der Waals' constant a and b by the expression:

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

where, T_i is the inversion temperature of the gas.

Gases like H_2 and He have low inversion temperatures ($T_{iH_2} = 193\text{ K}$ and $T_{iHe} = 33\text{ K}$) and they show heating effects in Joule-Thomson expansion under ordinary temperature. If these gases are cooled below their inversion temperatures, they also show cooling effects.

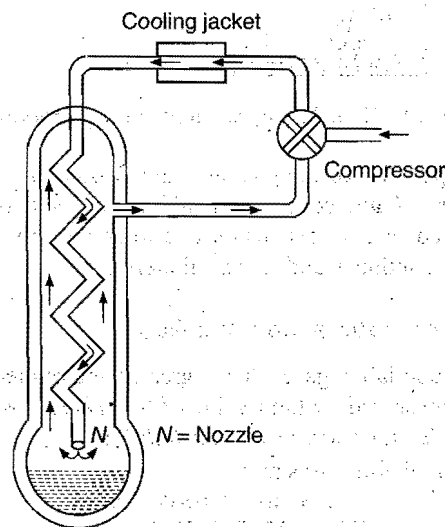


Fig. 4.11 (b) Linde's process for liquefaction of air

Joule-Thomson effect is the basis for liquefaction of air by Linde's process. The apparatus is shown in Fig. 4.11 (b).

Pure and dry air is compressed to a pressure of about 200 atm. Any heat produced during the compression is removed by passing the gas through a cooling jacket. Compressed air is allowed to expand suddenly through a nozzle (N) to a large chamber, where it gets cooled and the pressure reduced to about 1 atmosphere. The cooled air is made to pass through the outer tube and is sent back to the compressor. The incoming air further cools on expansion. The process is continued until air liquefies and is collected at the bottom.

(c) Cooling by Adiabatic Expansion Involving Mechanical Work

When a gas is allowed to expand adiabatically against a pressure, it does some external work at the cost of its kinetic energy, due to which its temperature falls. This principle is used in Claude's process for liquefaction of air. The apparatus is shown in Fig. 4.11 (c).

Pure and dry air is compressed to about 200 atmospheric pressure and then passed through the tube *T*. Compressed air divides itself into two parts at 'A' and a portion enters through 'C' fitted with an airtight piston. There, it expands, pushing the piston outward and performs some external work.

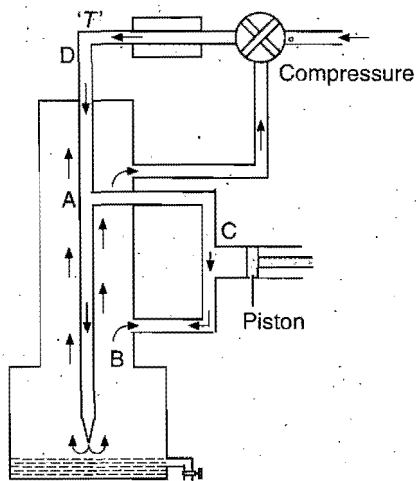


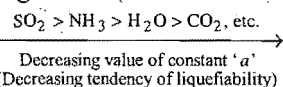
Fig. 4.11 (c) Claude's apparatus for liquefaction of air

The temperature of the gas thus falls. Cooled air then enters the chamber at *B* and cools the incoming air. The temperature of air is also reduced on expansion due to Joule-Thomson effect. The process continues until the air liquefies.

Tendency of Liquefaction of a Gas

Easily liquefiable gases have greater intermolecular force which is represented by high value of '*a*'. Thus, greater will be the value of '*a*' more will be its liquefiability.

Easily liquefiable gases are:



Above gases have higher value of '*a*' as compared to the permanent gases O_2 , N_2 , H_2 , He, Ne, etc.

Incompressibility of a Gas

van der Waals' constant '*b*' represents the excluded volume, i.e., four times the volume occupied by the gas per mole. Value of '*b*' remains constant over a wide range of temperature and pressure which implies that gas molecules are incompressible.

Compressibility factor: Mathematically, it may be defined as,

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

The extent to which a real gas departs from ideal behaviour is expressed in terms of compressibility factor.

$$Z = \frac{\text{Molar volume of real gas } (V_m)}{\text{Molar volume of ideal gas } (V_m)} = \frac{PV_m}{RT}$$

When $Z > 1$, $V_m > 22.4 \text{ L}$ at STP and when $Z < 1$, $V_m < 22.4 \text{ L}$ at STP.

(i) $Z = 1$ for ideal gas. Deviation from the unity indicates extent of imperfection or non-ideality.

(ii) Real gases have $Z \approx 1$ at low pressure and high temperature. In this case, the real gas behaves like ideal gas.

(iii) $Z > 1$ shows that it is difficult to compress the gas as compared to ideal gas. It is possible at high pressure. In this case, repulsive forces dominate.

(iv) $Z < 1$ shows that the gas is easily compressible as compared to ideal gas. It is possible at intermediate pressure. In this case, attractive forces are dominant.

Plots of Compressibility Factor against Pressure

Figure 4.12(b) indicates that an increase in temperature shows decrease in deviation ideal behaviour, i.e., *Z* approaches unity with increase in temperature.

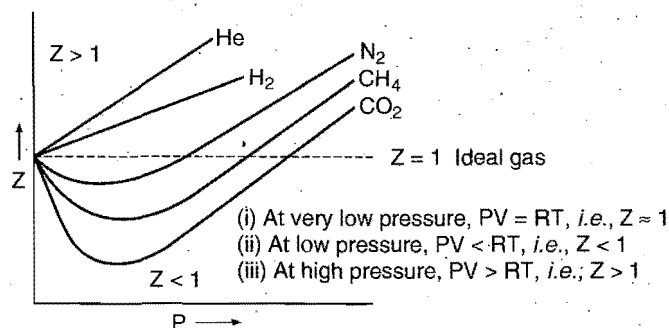


Fig. 4.12(a) Variation of compressibility factor against

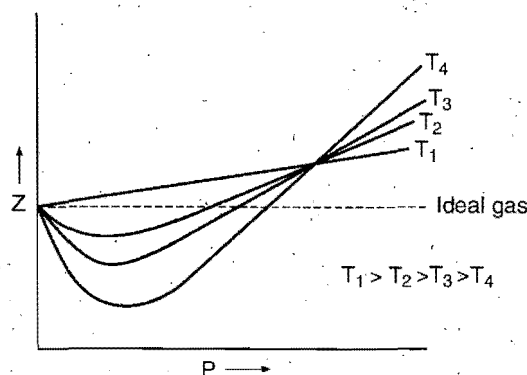


Fig. 4.12(b) Variation of compressibility factor against pressure at different temperature

Note: (i) In case of H_2 , $Z > 1$ at 273 K and *Z* increases with the pressure. When temperature is less than 273 K, H_2 has $Z < 1$.

(ii) For gases other than hydrogen, at 273 K there is decrease in '*Z*' at initial stage, with increase in pressure, value of '*Z*' approaches a minimum, with increase in pressure.

(iii) In case of easily liquefiable gas like CO_2 , Z dips largely below ideal line in low pressure region, see Fig. 4.12 (a).

Specific Heat of Gases

Amount of heat required to raise the temperature, of 1 g of a substance through 1°C is called its specific heat. It can be measured at constant pressure and at constant volume.

Molar specific heat, i.e., heat required to raise 1 gram mole of a substance through 1°C is called heat capacity.

Heat Capacity at Constant Volume

It is denoted by C_V . It may be the heat supplied to one mole of a substance to increase the temperature through 1°C at constant volume.

We know from kinetic theory that,

$$PV = \frac{1}{3} mnc^2 \quad \text{or} \quad \frac{1}{2} mnc^2 = \frac{3}{2} RT$$

Thus, kinetic energy $E = \frac{3}{2} RT$

When temperature is raised through 1°C then the increase in kinetic energy may be given as:

$$\text{Increase in kinetic energy} = \frac{3}{2} R(T+1) - \frac{3}{2} RT = \frac{3}{2} R$$

Now, $C_V = \frac{3}{2} R$ since at constant volume, heat supplied to raise the temperature is used up to increase the kinetic energy only.

$$C_V = \frac{3}{2} R \quad [\text{for monoatomic gases only, since monoatomic gases undergo translational motion only}]$$

$$C_V = \frac{3}{2} R + x \quad [\text{for di and polyatomic molecules; vibrational and rotational motions also contribute to the total kinetic energy}]$$

where factor 'x' varies from gas to gas and its value is zero for monoatomic gases.

Heat Capacity at Constant Pressure

It is denoted by C_P ; it may be defined as heat supplied to 1 mole of a substance in order to increase the temperature through 1°C at constant pressure.

Heat supplied at constant pressure will be used in:

(i) Increasing kinetic energy, which is equal to $\frac{3}{2} R + x$. For monoatomic gas increase in kinetic energy is equal to $\frac{3}{2} R$ when temperature is raised through 1°C .

(ii) Doing work due to volume expansion.

We know that, $PV = RT$ for 1 mole of gas ... (i)

When temperature changes to $(T+1)$, then

$$P(V + \Delta V) = R(T+1) \quad \dots (ii)$$

Subtracting eq. (i) from eq. (ii), we have

$$P\Delta V = R = \text{Work done due to volume expansion}$$

Thus, $C_P = \frac{3}{2} R + R = \frac{5}{2} R$ for monoatomic gases

$$C_P = C_V + R \quad \text{or} \quad C_P - C_V = R \quad (\text{general equation})$$

Ratio of Molar Heat Capacity

It is denoted as γ and it represents atomicity of the gas.

$$\text{For monoatomic gas, } (\gamma) = \frac{C_P}{C_V} = \frac{\frac{5}{2} R}{\frac{3}{2} R} = 1.66$$

$$\text{For diatomic gas, } (\gamma) = \frac{C_P}{C_V} = \frac{\frac{7}{2} R}{\frac{5}{2} R} = 1.40$$

$$\text{For triatomic gas, } (\gamma) = \frac{C_P}{C_V} = \frac{4R}{3R} = 1.33$$

Name	C_P	C_V	$C_P + C_V$	$C_P/C_V = \gamma$	Atomicity
He	5	3.01	1.99	1.661	1
N_2	6.95	4.96	1.99	1.4	2
O_2	6.82	4.83	1.99	1.4	2
CO_2	8.75	6.71	2.04	1.30	3
H_2S	8.62	6.53	2.09	1.32	3

Example 46. Specific heat of a monoatomic gas at constant volume is $315 \text{ J kg}^{-1} \text{ K}^{-1}$ and at a constant pressure is $525 \text{ J kg}^{-1} \text{ K}^{-1}$. Calculate the molar mass of the gas.

Solution: $C_P = M \times 525$ and $C_V = M \times 315$

where, M is the molecular mass.

$$C_P - C_V = R \quad (R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$M \times 525 - M \times 315 = 8.314$$

$$M(525 - 315) = 8.314$$

$$M = \frac{8.314}{210} = 0.0396 \text{ kg mol}^{-1} = 39.6 \text{ g mol}^{-1}$$

Example 47. Calculate the pressure exerted by 16 g of methane in a 250 mL container at 300 K using van der Waals' equation. What pressure will be predicted by ideal gas equation?

$$a = 2.253 \text{ atm L}^2 \text{ mol}^{-2}, \quad b = 0.0428 \text{ L mol}^{-1},$$

$$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

Solution: Given, $16 \text{ g CH}_4 = \frac{16}{16} = 1 \text{ mole}$

Applying van der Waals' equation,

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

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

Substituting $n = 1$,

$$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}; \quad T = 300 \text{ K}; \quad V = 0.250 \text{ L};$$

$$a = 2.253 \text{ atm L}^2 \text{ mol}^{-2}; \quad b = 0.0428 \text{ L mol}^{-1}$$

$$P = \frac{1 \times 0.0821 \times 300}{(0.250 - 1 \times 0.0428)} - \frac{1 \times 2.253}{(0.250)^2} = 82.822 \text{ atm}$$

The ideal gas equation predicts that,

$$P = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 300}{0.250} = 98.52 \text{ atm}$$

Example 48. Calculate the temperature of the gas if it obeys van der Waals' equation from the following data. A flask of 2.5 litre contains 10 mole of a gas under 50 atm. Given $a = 5.46 \text{ atm litre}^2 \text{ mol}^{-2}$ and $b = 0.031 \text{ litre mol}^{-1}$.

Solution: Given that,

$$P = 50 \text{ atm}; V = 2.5 \text{ litre}, n = 10; a = 5.46 \text{ atm litre}^2 \text{ mol}^{-2};$$

$$b = 0.031 \text{ litre mol}^{-1}; R = 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1}$$

Applying van der Waals' equation,

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

$$\text{or } T = \frac{\left(P + \frac{an^2}{V^2}\right)(V - nb)}{nR}$$

$$= \frac{\left(50 + \frac{5.46 \times 100}{(2.5)^2}\right)(2.5 - 10 \times 0.031)}{10 \times 0.0821} = 366.4 \text{ K}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

23. At high temperature and low pressure, the van der Waals' equation is reduced to:

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

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

[Ans. (b)]

[Hint: At high temperature and low pressure, V is large in comparison to b and $\left(\frac{a}{V^2}\right)$ is negligible in comparison to P .

Hence, the equation reduces to $PV = RT$.]

24. The constant ' a ' in van der Waals' equation is maximum in:

- (a) He (b) H_2
(c) O_2 (d) NH_3

[Ans. (d)]

[Hint: Intermolecular force of NH_3 is maximum, hence its van der Waals' constant (a) will also be maximum.]

25. The van der Waals' equation for 0.5 mol gas is:

(a) $\left(P + \frac{a}{4V^2}\right)\left(\frac{V - b}{2}\right) = \frac{2RT}{2}$

(b) $\left(P + \frac{a}{4V^2}\right)(2V - b) = RT$

(c) $\left(P + \frac{a}{4V^2}\right)(2V - 4b) = RT$

(d) $\left(P + \frac{a}{4V^2}\right) = \frac{2RT}{2(V - b)}$

[Ans. (b)]

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

For $n = \frac{1}{2}$, $\left(P + \frac{a}{4V^2}\right)\left(V - \frac{b}{2}\right) = \frac{1}{2}RT$

$\left(P + \frac{a}{4V^2}\right)(2V - b) = RT]$

26. van der Waals' constants of two gases X and Y are as given:

a (litre-atm mol^{-2}) b (litre mol^{-1})

Gas X 5.6 0.065

Gas Y 5.1 0.012

What is correct about the two gases?

(a) $T_c(X) > T_c(Y)$ (b) $T_c(X) = T_c(Y)$

(c) $V_c(X) > V_c(Y)$ (d) $V_c(Y) > V_c(X)$

[Ans. (c)]

[Hint: Gas X Gas Y

$V_c = 3b$ $3 \times 0.065 = 0.195$ $3 \times 0.012 = 0.036]$

27. Select the correct statements about van der Waals' constant ' b ':

1. It is excluded volume

2. Its unit is mol litre^{-1}

3. It depends on intermolecular force

4. Its value depends on molecular size

(a) 2, 3 (b) 1, 2, 4 (c) 2, 3, 4 (d) 3, 4

[Ans. (b)]

28. Gases X, Y, Z, P and Q have the van der Waals' constants ' a ' and ' b ' (in CGS units) as shown below:

	X	Y	Z	P	Q
a	6	6	20	0.05	30
b	0.025	0.15	0.1	0.02	0.2

The gas with the highest critical temperature is:

[PET (Kerala) 2006]

(a) P (b) Q (c) Y (d) Z

(e) X

[Ans. (e)]

[Hint: Critical temperature, $T_c = \frac{8a}{27Rb}$

∴ Greater is the value of (a/b) , more is the critical temperature of gas.

For gas X , T_c will be maximum.

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

$\frac{a}{b}$ for $X = \frac{6}{0.025} = 240$; for all other gases, $\left(\frac{a}{b}\right)$ is lesser.]

29. At high pressure, van der Waals' equation becomes:

(DPMT 2006)

(a) $PV = RT$ (b) $PV = RT + \frac{a}{V}$

(c) $PV = RT - \frac{a}{V}$ (d) $PV = RT + Pb$

[Ans. (d)]

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

$\left(P + \frac{a}{V^2}\right)(V - b) = RT$ for 1 mol gas

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

$P(V - b) = RT$

$PV = RT + Pb$

SOME SOLVED EXAMPLES

Example 49. Calculate the total pressure in a 10 litre cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 g of nitrogen at 27°C. Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behaviour of gases.

Given that, $R = 0.082 \text{ litre-atm K}^{-1} \text{ mol}^{-1}$. (IIT 1997)

Solution:

$$n_{\text{He}} = \frac{0.4}{4} = 0.1, n_{\text{O}_2} = \frac{1.6}{32} = 0.05$$

$$n_{\text{N}_2} = 1.4 / 28 = 0.05$$

$$P_{\text{He}} \times V = n_{\text{He}} \times R \times T$$

$$P_{\text{He}} \times 10 = 0.1 \times 0.0821 \times 300$$

$$P_{\text{He}} = 0.2463 \text{ atm}$$

$$P \times V = (n_{\text{He}} + n_{\text{O}_2} + n_{\text{N}_2}) RT$$

$$P \times 10 = (0.1 + 0.05 + 0.05) \times 0.0821 \times 300$$

$$P = 0.4926 \text{ atm}$$

Example 50. An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g/mL^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas. (IIT 1998)

Solution: Mass of liquid = $148 - 50 = 98 \text{ g}$

$$\text{Volume of liquid} = \frac{\text{mass}}{\text{density}} = \frac{98}{0.98} = 100 \text{ mL}$$

Volume of vessel = Volume of liquid

Mass of gas = $50.5 - 50 = 0.5 \text{ g}$

On applying ideal gas equation, we have,

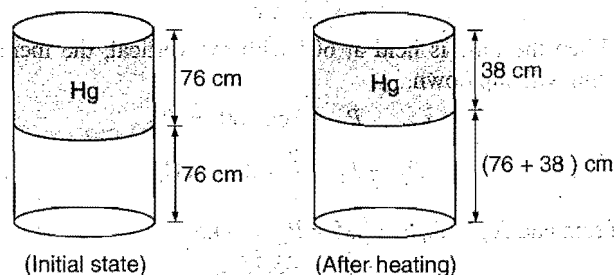
$$PV = \frac{w}{m} RT$$

$$\frac{760}{760} \times \frac{100}{1000} = \frac{0.5}{m} \times 0.0821 \times 300$$

$$m = 123$$

Example 51. A vertical hollow cylinder of height 1.52 m is fitted with a movable piston of negligible mass and thickness. The lower half of the cylinder contains an ideal gas and the upper half is filled with mercury. The cylinder is initially at 300 K. When the temperature is raised half of the mercury comes out of the cylinder. Find the temperature assuming the thermal expansion of mercury to be negligible.

Solution:



At initial stage:

Pressure of gas = Pressure of Hg + Pressure of atmospheric air

$$= 76 + 76 = 152 \text{ cm}$$

$$T = 300 \text{ K}$$

$$V = V_1 / 2 \text{ where, } V_1 \text{ is volume of cylinder.}$$

At final stage after heating:

Pressure of gas = Pressure of Hg + Pressure of atmospheric air

$$= 38 + 76 = 114 \text{ cm}$$

$$V = \frac{3V_1}{4}, T = ?$$

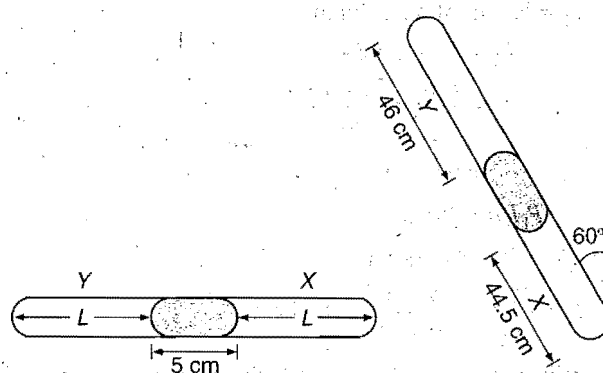
Applying gas equation, we have

$$\frac{152 \times V_1}{2 \times 300} = \frac{114 \times (3V_1 / 4)}{T}$$

$$T = \frac{114 \times 3 \times 2 \times 300}{4 \times 152}$$

$$= 337.5 \text{ K}$$

Example 52. A thin tube of uniform cross-section is sealed at both ends. It lies horizontally, the middle 5 cm containing Hg and the two equal ends containing air at the same pressure P_0 . When the tube is held at an angle 60° with the vertical, the lengths of the air column above and below the mercury are 46 and 44.5 cm respectively. Calculate pressure P_0 in cm of Hg. (The temperature of the system is kept at 30°C).



Solution: At horizontal position, let the length of air column in tube be L cm.

$$2L + 5 = 46 + 5 + 44.5 \text{ cm}$$

$$L = 45.25 \text{ cm}$$

When the tube is held at 60° with the vertical, the mercury column will slip down.

$$P_Y + 5 \cos 60^\circ = P_X$$

$$P_X - P_Y = \frac{5}{2} = 2.5 \text{ cm Hg} \quad \dots (i)$$

$$\text{From end X, } P_0 \times 45.25 = P_X \times 44.5$$

$$P_X = \frac{45.25}{44.5} P_0 \quad \dots (ii)$$

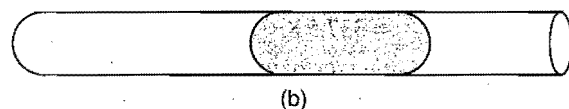
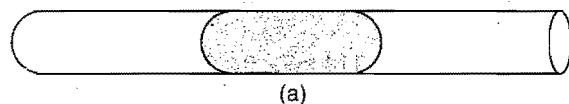
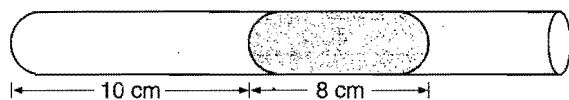
$$\text{From end Y, } P_0 \times 45.25 = P_Y \times 46$$

$$P_Y = \frac{45.25}{46} P_0 \quad \dots (iii)$$

Substituting the values of P_X and P_Y in equation (i) we get

$$P_0 = 75.4$$

Example 53. A 10 cm column of air is trapped by a column of Hg, 8 cm long, in a capillary tube horizontally fixed as shown below, at 1 atm pressure. Calculate the length of air column when the tube is fixed at the same temperature (a) vertically with open end up (b) vertically with open end down (c) at 45° with the horizontal with open end up.



Solution: (a) $P_1 V_1 = P_2 V_2$

or $P_1 l_1 a = P_2 l_2 a$

where, a = area of cross section of tube

l_1, l_2 = length of air column

$$\therefore P_2 = 76 + 8 = 84 \text{ cm}$$

$$\therefore l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{84}$$

$$= 9.04 \text{ cm}$$

$$P_1 l_1 a = P_2 l_2 a$$

$$(b) P_2 = 76 - 8 = 68 \text{ cm}$$

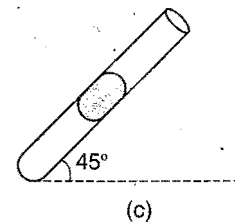
$$\therefore l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{68} = 11.17 \text{ cm}$$

(c) When the tube is held at 45° with open end up, the weight of Hg is borne partially by the gas and partially by the Hg. Vertical height of Hg is a measure of additional pressure on gas, i.e.,

$$l = \frac{8}{\sqrt{2}}$$

$$\text{Also } P_2 l_2 a = P_1 l_1 a$$

$$\begin{aligned} \therefore l_2 &= \frac{P_1 l_1}{P_2} \\ &= \frac{76 \times 10}{76 + \frac{8}{\sqrt{2}}} = 9.3 \text{ cm} \end{aligned} \quad (c)$$



Example 54. The stop cock connecting two bulbs of volume 5 litre and 10 litre containing an ideal gas at 9 atm and 6 atm respectively, is opened. What is the final pressure in the two bulbs if the temperature remains the same?

Solution: $P_1 V_1 + P_2 V_2 = P_R (V_1 + V_2)$

$$9 \times 5 + 6 \times 10 = P_R (15)$$

$$P_R = 7 \text{ atm}$$

where, P_R = resultant pressure after mixing.

Example 55. At what temperature is the average velocity of O_2 molecule equal to the root mean square velocity at 27°C ?

(BSEPT 2005)

Solution: $v_{av} = v_{rms}$

$$\sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{3RT}{M}}$$

$$\frac{8RT}{\pi M} = \frac{3R \times 300}{M}$$

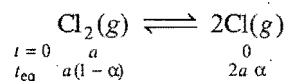
$$T = 353.57 \text{ K}$$

$$t = 80.57^\circ\text{C}$$

Example 56. The composition of the equilibrium mixture for the equilibrium $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$ at 1400 K may be determined by the rate of diffusion of mixture through a pin hole. It is found that at 1400 K, the mixture diffuses 1.16 times as fast as krypton diffuses under the same conditions. Find the degree of dissociation of Cl_2 equilibrium.

(IIT 1995)

Solution: Equilibrium of dissociation of Cl_2 may be represented as:



$$\text{Total moles} = a(1-\alpha) + 2a\alpha = a(1+\alpha)$$

$$M_{\text{mix}} = \frac{aM_{\text{Cl}_2}}{a(1+\alpha)} = \frac{M_{\text{Cl}_2}}{(1+\alpha)}$$

$$\frac{R_{\text{mix}}}{R_{\text{Kr}}} = \sqrt{\frac{M_{\text{Kr}}}{M_{\text{mix}}}}$$

$$1.16 = \frac{84(1+\alpha)}{M_{\text{Cl}_2}}$$

$$\frac{(1.16)^2 \times 71}{84} - 1 = \alpha; \alpha = 0.1374$$

Example 57. A gaseous mixture of helium and oxygen is found to have a density of 0.518 g dm^{-3} at 25°C and 720 torr. What is the per cent by mass of helium in this mixture?

Solution: We know that, $Pm = dRT$

$$\frac{720}{760} \times m = 0.518 \times 0.0821 \times 298$$

$$m = 13.37 \text{ g/mol}$$

Let mole fraction of He in mixture be α .

$$x_{\text{He}} = \alpha, x_{\text{O}_2} = (1 - \alpha)$$

$$\text{Average mw} = \alpha \times M_{\text{He}} + (1 - \alpha)M_{\text{O}_2}$$

$$13.37 = \alpha \times 4 + (1 - \alpha)32$$

$$\alpha = 0.666$$

$$\begin{aligned} \% \text{ by mass of He} &= 0.666 \times \frac{4}{0.666 \times 4 + 0.334 \times 32} \times 100 \\ &= 19.95\% \end{aligned}$$

Example 58. Find the temperature at which 3 moles of SO_2 will occupy a volume of 10 litre at a pressure of 15 atm.

$$a = 6.71 \text{ atm litre}^2 \text{ mol}^{-2}; b = 0.0564 \text{ litre mol}^{-1}$$

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

$$\left(15 + \frac{6.71 \times 9}{100}\right)(10 - 3 \times 0.0564) = 3 \times 0.082 \times T$$

$$T = 624 \text{ K}$$

Example 59. van der Waals' constant 'b' of Ar is $3.22 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. Calculate the molecular diameter of Ar.

Solution: We know that,

$$b = 4 \times \text{volume occupied by the molecules in one mole of a gas}$$

$$= 4 \times N_0 \times \left(\frac{4}{3} \pi r^3\right)$$

$$3.22 \times 10^{-5} = 4 \times 6.02 \times 10^{23} \times \frac{4}{3} \times \frac{22}{7} \times r^3$$

or
$$r = \left(\frac{3.22 \times 10^{-5} \times 3 \times 7}{4 \times 6.02 \times 10^{23} \times 4 \times 22}\right)^{1/3}$$

$$= 0.1472 \times 10^{-9} \text{ m}$$

$$\therefore \text{Diameter} = 2r = 2 \times 0.1472 \times 10^{-9}$$

$$= 0.2944 \times 10^{-9} \text{ m}$$

Example 60. The compression factor (compressibility factor) for 1 mole of a van der Waals' gas at 0°C and 100 atmospheric pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals' constant 'a'. (IIT 2001)

Solution: We know that,

$$Z = \frac{PV}{RT}$$

$$0.5 = \frac{100 \times V}{0.0821 \times 273}$$

$$V = 0.112 \text{ litre}$$

According to van der Waals' equation,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \text{for 1 mole}$$

$$\left[100 + \frac{a}{(0.112)^2}\right][0.112 - 0] = 0.0821 \times 273$$

On solving, we get $a = 1.253 \text{ L}^2 \text{ mol}^{-2} \text{ atm}$

Example 61. The density of the vapours of a substance at 1 atm pressure and 500 K is 0.36 kg m^{-3} . The vapours effuse through a small hole at a rate of 1.33 times faster than oxygen under the same conditions:

(a) Determine: (i) molecular weight, (ii) molar volume, (iii) compressibility factor (Z) of the vapours, (iv) Which forces among gas molecules are dominating, the attractive or the repulsive?

(b) If the vapours behave ideally at 1000 K, determine the average translational kinetic energy of a molecule. (IIT 2002)

Solution: (a) (i) $\frac{r_{\text{vapour}}}{r_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{vapour}}}}$

$$1.33 = \sqrt{\frac{32}{M_{\text{vapour}}}}$$

$$M_{\text{vapour}} = 18.1$$

(ii) $\text{Molar volume} = \frac{\text{Molar mass}}{\text{Density}}$

$$= \frac{18.1}{0.36} = 50.25 \times 10^{-3} \text{ m}^{-3}$$

(iii) Compressibility factor, $Z = \frac{PV}{RT} = \frac{101325 \times 50.25 \times 10^{-3}}{8.314 \times 500}$

$$= 1.225$$

(iv) $Z > 1$ shows that repulsive forces are dominant.

(b) Translational KE per molecule

$$= \frac{3}{2} \times \frac{R}{N} \times T$$

$$= \frac{3}{2} \times \frac{8.314}{6.023 \times 10^{23}} \times 1000$$

$$= 2.07 \times 10^{-20} \text{ J}$$

Example 62. The ratio of rate of diffusion of helium and methane under identical conditions of pressure and temperature will be: [IIT (S) 2005]

(a) 4 (b) 2 (c) 1 (d) 0.5

Solution: $\frac{r_{\text{CH}_4}}{r_{\text{He}}} = \sqrt{\frac{m_{\text{He}}}{m_{\text{CH}_4}}} = \sqrt{\frac{4}{16}} = \frac{1}{2}$

$$r_{\text{He}} = 2r_{\text{CH}_4}$$

SECTION 2 : LIQUID STATE

4.11 THE LIQUID STATE

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

The behaviour of liquids explained above gives some characteristic properties to the liquids such as definite volume but no definite shape, incompressibility, 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 of 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 kinetic 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 not 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 with 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

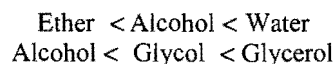
much less and their velocities are small, liquids diffuse slowly in comparison to gases.

(vi) Evaporation

The process of change 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 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 accompanied by cooling as average kinetic energy of remaining molecules decreases.

Evaporation depends on the following factors:

(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:



→ Increasing extent of hydrogen bonding

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

$$\text{Rate of evaporation} \propto \text{Surface area}$$

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

$$\text{Rate of evaporation} \propto \text{Temperature}$$

(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 liquid at constant temperature is known as heat of vaporisation or heat of evaporation. The heat of vaporisation depends on the strength of the intermolecular forces within 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 liquid 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

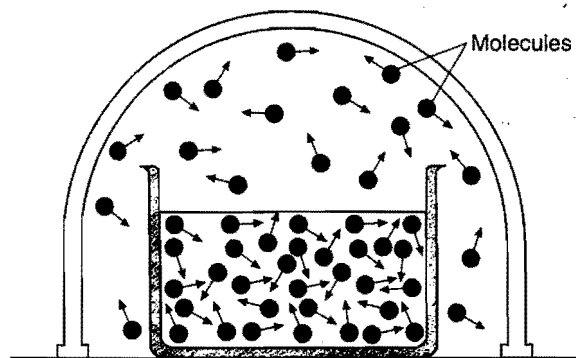


Fig. 4.13 (a) Evaporation in a closed vessel

trapped. The return of the molecules from the vapour state to 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.

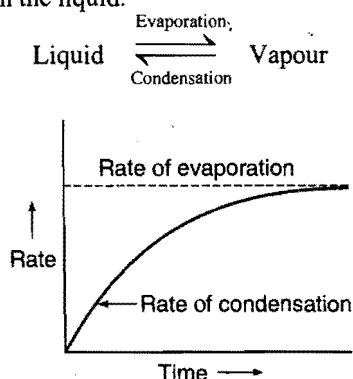


Fig. 4.13 (b)

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.

In closed vessel,

Rate of evaporation $\propto e^{-E/RT}$ (Boltzmann factor)

Thus, rate of evaporation remains constant at constant temperature.

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 pressures. 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	135.3	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 and ethyl alcohol possess fairly high vapour pressures on account of weak intermolecular forces (cohesive forces) whereas polar molecules such as water which have stronger intermolecular forces possess relatively lower vapour pressures.

The simplest method for measuring vapour pressure is the **barometric method**. It consists of two barometer tubes as shown in Fig. 4.14. A small quantity of the liquid is introduced into one of the tubes. It changes into vapour and rises into vacuum above

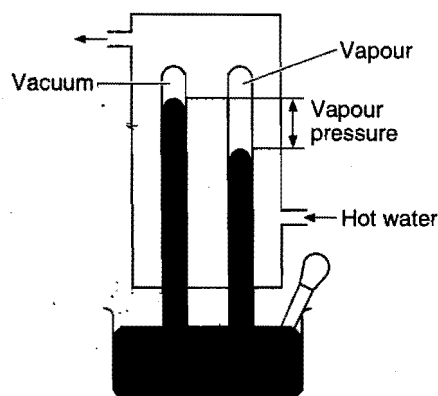


Fig. 4.14 The barometric method for measurement of vapour pressure

the mercury. Some more of the liquid is introduced and the process is continued till a small amount of the liquid is visible on the surface of mercury. The difference in the levels of mercury in the two tubes is noted and this measures the vapour pressure of the liquid at atmospheric temperature. The measurement can also be made at any desired temperature by surrounding the tubes with a jacket maintained at that temperature.

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

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

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

The actual form of Clausius-Clapeyron equation is:

$$\log_{10} P = \frac{-\Delta H_{\text{vap}}}{2.303RT} + A$$

Note : Vapour and gas: A gas can be liquefied only below critical temperature, by applying pressure. There is no characteristic critical temperature for vapours.

When ΔH_{vap} = Latent heat of vaporisation and 'A' is constant. A graph between $\log_{10} P$ and $\frac{1}{T}$ will be a straight line with negative slope.

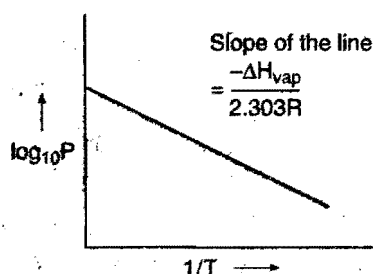


Fig. 4.15 Variation of vapour pressure with temperature

(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). Fig. 4.16 shows that normal boiling points of diethyl ether, ethyl alcohol and water are 34.6°C, 78.5°C and 100°C respectively.

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

The boiling point of a liquid changes with the change in external pressure. A liquid may boil at temperature higher than normal under external pressure greater than one atmosphere; 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 temperature below its normal boiling point of 100°C. Food cooks more slowly at higher altitudes because the temperature of 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 temperature 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 the following respects:

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

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

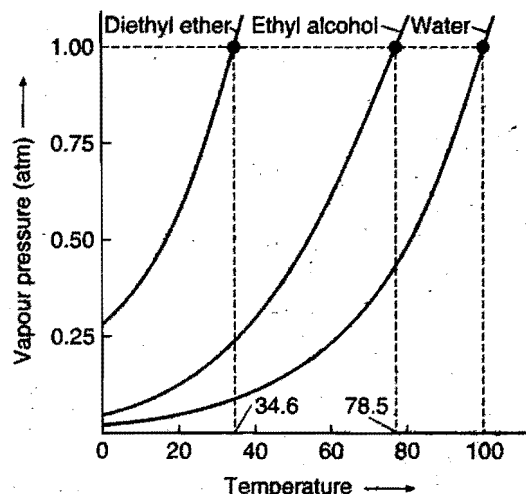


Fig. 4.16 Vapour pressure curves for diethyl ether, ethyl alcohol and water

(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 its 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 form. At the freezing point the temperature of the solid-liquid system remains constant until all the liquid is frozen. 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 sideways. 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} or Newton metre $^{-1}$ (N m^{-1}). It is a scalar quantity. Surface

tension is, thus, defined as the force acting on unit length of a line imagined to be drawn tangentially anywhere on the free surface of a liquid at rest. It acts at right angles on both sides of the line and along the tangent to the liquid surface. Surface tension depends on the area, not on the length, like elastic properties.

As the intermolecular forces of attraction decrease 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.

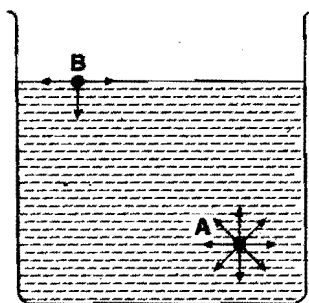


Fig. 4.17 (a) Molecules at the surface are under unequal tension

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 drowning. 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) **Cleaning action of soap and detergents:** Soap and detergent solutions due to their lower surface tensions penetrate into the fibre and surround the greasy substances and wash them away.

(d) **Capillary 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 force of adhesion between the molecules of water and 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 of resulting water column is just balanced by the force of surface tension.

The rise of 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.

Note: At the critical temperature, surface tension of liquid becomes zero (where the meniscus between the liquid and the vapour disappears). Surface tension is scalar quantity.

In general, the liquids which wet the material show capillary rise. Those liquids which do not wet the material of a capillary always show depression, e.g., glycerine, honey, mercury, etc.

When a liquid rises in a column, its upper surface becomes concave and when the liquid goes down in a capillary, its upper surface becomes convex.

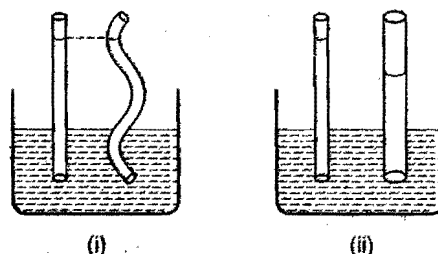


Fig. 4.17 (b) Effect of shape and radius on capillary rise

(i) Height of liquid in the column of capillary is independent of shape of capillary if its radius is same.

(ii) Thinner is the capillary, greater is the height of liquid in the column.

(e) **Surface energy:** The work in erg required to be done to increase or extend surface area by 1 sq. cm is called surface energy. The units of surface energy are, therefore, erg per sq. cm (or joule per sq. metre, i.e., J m^{-2} in SI system). Surface tension of liquid is numerically equal to the surface energy.

Surface energy,

$\gamma = \text{Work done to increase the surface area by one unit}$

$$= \frac{\text{Work}}{\text{Change in area}}$$

$$= \frac{\text{force} \times \text{displacement in the direction of force}}{\text{area}}$$

$$= \frac{\text{Force}}{\text{Length}}$$

The unit of surface tension is therefore dyne cm^{-1} (force per unit length).

Measurement of surface tension: The surface tension of a liquid is measured by the drop count method using a stalagmometer.

Let 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 be 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.

Surface tension of the liquid can also be measured by capillary rise method.

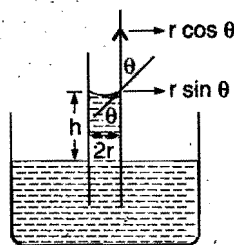


Fig. 4.18 Capillary rise

When liquid rises in a capillary, upward force due to surface tension is balanced by gravitational force.

$$\therefore 2\pi r \gamma \cos \theta = mg$$

where, m = mass of liquid in column

r = radius of capillary

h = capillary rise

g = gravitational force

$$\begin{aligned} \text{Mass of liquid in column (m)} &= V \times \rho \\ &= \pi r^2 h \times \rho \end{aligned}$$

$$\therefore 2\pi r \gamma \cos \theta = \pi r^2 h \rho g$$

$$\gamma = \frac{r h \rho g}{2 \cos \theta} \quad (\rho = \text{density of liquid})$$

If angle of contact between glass and liquid is zero, i.e., $\cos \theta = 1$, then

$$\gamma = \frac{r h \rho g}{2}$$

Effect of temperature on surface tension : Surface tension decreases with rise in temperature because the intermolecular force also decreases with rise in temperature. The decrease in surface tension with rise in temperature continues till critical temperature at which the surface tension of liquid becomes zero, i.e., meniscus between liquid and vapour disappears.

According to Eotvos equation,

$$\gamma = \left(\frac{M}{\rho} \right)^{2/3} = K (t_c - t)$$

$\therefore$ As t increases, γ decreases linearly, when $t = t_c$, $\gamma = 0$, here t_c is the critical temperature.

(xii) Viscosity

All 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 two layers. This internal friction or resistance is called viscosity.

Imagine a liquid to be made up of a large number of thin cylindrical coaxial layers.

It has been found that force of friction ' f ' between two cylindrical layers each having area ' A ' sq. cm separated by a distance ' x ' cm and having a velocity difference ' v ' cm/sec is given by:

$$\begin{aligned} f &\propto A \frac{v}{x} \\ f &= \eta A \frac{v}{x} \end{aligned}$$

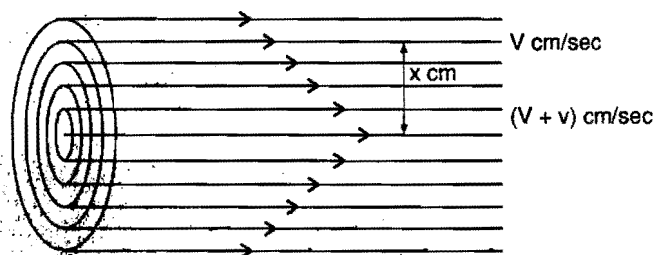


Fig. 4.19

Here, η is a constant known as coefficient of viscosity. If $x = 1$ cm, $A = 1$ cm² and $v = 1$ cm/sec., then $f = \eta$.

Thus, coefficient of viscosity can be defined as the force per unit area needed to maintain unit difference of velocity between two consecutive 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 as poise, centipoise (10⁻² poise) and millipoise (10⁻³ poise), after the name of Poiseuille who derived the formula and gave the method for its determination. 1 poise is equal to a force of 1 dyne per unit area which maintains a velocity difference of 1 cm per second between two parallel consecutive layers of the liquid 1 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 is 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. This property is used to select the lubricant for a machine and engine. The variation of viscosity with temperature can be expressed by the following relationship:

$$\eta = Ae^{-E_a/RT} \quad \dots(i)$$

where, A = Pre-exponential factor (constant)

E_a = Activation energy

Taking logarithm of equation (i) we get :

$$\log_{10} \eta = \log_{10} A - \frac{E_a}{2.303R} \times \frac{1}{T} \quad \dots(ii)$$

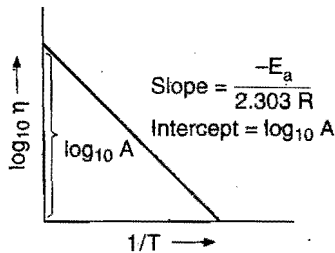


Fig. 4.20

This equation represents straight line with formula $y = mx + C$
Equation (ii) may also be given as

$$\log_{10} \frac{\eta_2}{\eta_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

where η_2 is the coefficient of viscosity at temperature T_2 and η_1 is the coefficient of viscosity at temperature T_1 .

(e) **Pressure:** The increase of pressure increases the intermolecular forces. Thus, the viscosity of a given liquid increases with increase of pressure.

(f) **Density :** Viscosity of a liquid increases with increase in density while that of gas decreases.

Measurement of viscosity: Viscosity is generally determined by Ostwald's method. It involves the comparison of time of flow of equal volumes of two liquids through the same capillary using an apparatus called **viscometer**.

$$\frac{\eta}{\eta_w} = \frac{d \times t}{d_w \times t_w}$$

where, η_w, η = coefficients of viscosity of water and liquid respectively; d = density of liquid; d_w = density of water; t = time of flow of liquid; t_w = time of flow of water.

Note: Viscosity of gases increases with increase in temperature.

Comparison between viscous force and solid friction

Points of differences :

Viscous force	Solid friction
1. It is directly proportional to the area of layers in contact.	It is independent of the area of the surfaces in contact.
2. It is directly proportional to the relative velocity between the two liquid layers.	It is independent of the relative velocity between two solid surfaces.

Point of similarities:

- (i) Both viscous force and solid friction come into action where ever there is relative motion.
- (ii) Both these forces oppose the motion.
- (iii) Both are due to molecular attraction.

SECTION 3 : SOLID STATE

4.12 THE SOLID STATE

In solid state, the particles (molecules, ions or atoms) are closely packed. These are held together by strong intermolecular attractive forces (cohesive forces) and cannot move at random. These are held at fixed positions and surrounded by other particles. There is only one form of molecular motion in solids, namely vibrational motion by virtue of which the particles move about fixed positions and cannot easily leave the solid surface. The following general characteristics are exhibited by solids:

(i) **Definite shape and volume:** Unlike gases and liquids, solids have definite shape and rigidity. This is due to the fact that constituent particles do not possess enough energy to move about to take-up different positions. Solids are characterised by their definite volume which does not depend on the size and shape of

the container. This is due to close packing of molecules and strong short range intermolecular forces between them.

(ii) **High density and low compressibility:** Solids have generally high density and low compressibility due to close packing of molecules which eliminates free space between molecules.

(iii) **Very slow diffusion:** The diffusion of solid is negligible or rather very slow as the particles have permanent positions from which they do not move easily.

(iv) **Vapour pressure:** The vapour pressure of solids is generally much less than the vapour pressure of liquids at a definite temperature. Some particles near the surface may have high energies (kinetic) as to move away and enter the vapour state.

(v) **Melting point:** The temperature at which the solid and the liquid forms of a substance exist at equilibrium or both the forms have same vapour pressure, is called the **melting point**. On supplying heat energy, the particles acquire sufficient energy and move away from their fixed positions in space. This results in the formation of liquid state. The solids have definite melting points depending on the strength of binding energy. However, in some solids (amorphous solids)* the melting point is not sharp.

4.13 FORMS OF SOLIDS

Solids are divided into two classes on the basis of haphazard and regular arrangement of the building constituents.

(i) **Amorphous solids:** The term 'amorphous' has been derived from a Greek word '*Omorphe*' meaning shapeless. In amorphous solids the arrangement of building constituents is not regular but haphazard. Although these solids possess some of the mechanical properties such as rigidity, incompressibility, refractive index, etc., but do not have characteristic shapes or geometrical forms. Amorphous solids in many respects resemble liquids which flow very slowly at room temperature and regarded as supercooled liquids in which the cohesive forces holding the molecules together are so great that the material is rigid but there is no regularity of the structure. Glass, rubber, plastics, etc., are some of the examples of amorphous solids.

Amorphous solids do not have sharp melting points. For example, when glass is heated, it softens and then starts flowing without undergoing any abrupt change from solid to liquid state.

Thus, amorphous substances are not true solids but can be regarded as intermediate between liquids and solids.

(ii) **Crystalline solids:** In crystalline solids, the building constituents arrange themselves in regular manner throughout the entire three-dimensional network. The ordered arrangement of building constituents (molecules, atoms or ions) extends over a large distance. Thus, crystalline solids have long range order. A crystalline solid consists of a large number of units, called crystals. A crystal is defined as a solid figure which has a definite geometrical shape, with flat faces and sharp edges.

A crystalline substance has a sharp melting point, i.e., it changes abruptly into liquid state. Strictly speaking 'a solid state refers to crystalline state' or 'only a crystalline substance can be considered to be a true solid'.

4.14 ISOTROPY AND ANISOTROPY

The substances which show same properties in all directions are said to be isotropic and the substances exhibiting directional differences in properties are termed **anisotropic**.

Amorphous solids like liquids and gases are said to be isotropic as arrangement of building constituents is random and disordered. Hence, all directions are equal and therefore, properties are same in all the directions.

Crystalline solids are anisotropic. Magnitude of some of the physical properties of crystalline solids such as refractive index, coefficient of thermal expansion, electrical and thermal conductivities, etc., is different in different directions, within the crystal. For example, in the crystal of silver iodide (AgI), the coefficient of thermal expansion is positive in one direction and negative in the other direction.

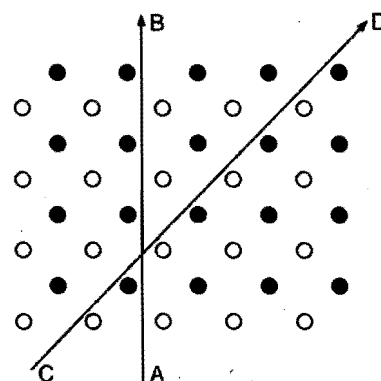


Fig. 4.21 Anisotropic behaviour of crystals

The phenomenon of anisotropy provides a strong evidence for the presence of ordered molecular arrangement in crystals. This can be explained with the help of Fig. 4.21 in which a simple two dimensional arrangement of two different kinds of atoms has been depicted. When a physical property is measured along the slanting line CD, it will be different from that measured in the direction of vertical line AB, as line CD contains alternate types of atoms while line AB contains one type of atoms only.

4.15 DIFFERENCES BETWEEN CRYSTALLINE AND AMORPHOUS SOLIDS

Crystalline solids	Amorphous solids
1. They have definite and regular geometry due to definite and orderly arrangement of atoms, ions or molecules in three dimensional space.	They do not have any pattern of arrangement of atoms, ions or molecules and, thus, do not have any definite geometrical shape.
2. They have sharp melting points and change abruptly into liquids.	Amorphous solids do not have sharp melting points and do not change abruptly into liquids.
3. Crystalline solids are anisotropic. Some of their physical properties are different in different directions.	Amorphous solids are isotropic. Their physical properties are same in all directions.
4. These are considered as true solids.	These are considered pseudo-solids or supercooled liquids.
5. Crystalline solids are rigid and their shape is not distorted by mild distorting forces.	Amorphous solids are not very rigid. These can be distorted by bending or compressing forces.

* Melting point of a solid depends on the structure of the solid. It is used for the identification of solids whether it is crystalline or amorphous.

Crystalline solids	Amorphous solids
6. Crystals are bound by plane faces. The angle between any two faces is called interfacial angle. For a given crystalline solid, it is a definite angle and remains always constant no matter how the faces develop. When a crystalline solid is hammered, it breaks up into smaller crystals of the same geometrical shape.	Amorphous solids do not have well defined planes. When an amorphous solid is broken, the surfaces of the broken pieces are generally not flat and intersect at random angles.
7. An important property of crystals is their symmetry. There are: (i) plane of symmetry, (ii) axis of symmetry and (iii) centre of symmetry.	Amorphous solids do not have any symmetry.

4.16 TYPES OF SYMMETRY IN CRYSTALS

(i) **Centre of symmetry:** It is such an imaginary point within the crystal that any line drawn through it intersects the surface of the crystal at equal distances in both directions. A crystal always possesses only one centre of symmetry [Fig. 4.22 (f)].

(ii) **Plane of symmetry:** It is an imaginary plane which passes through the centre of a crystal and divides it into two equal portions such that one part is exactly the mirror image of the other.

A cubical crystal like NaCl possesses, in all, nine planes of symmetry; three rectangular planes of symmetry and six diagonal planes of symmetry. One plane of symmetry of each of the above is shown in Fig. 4.22 (a) and (b).

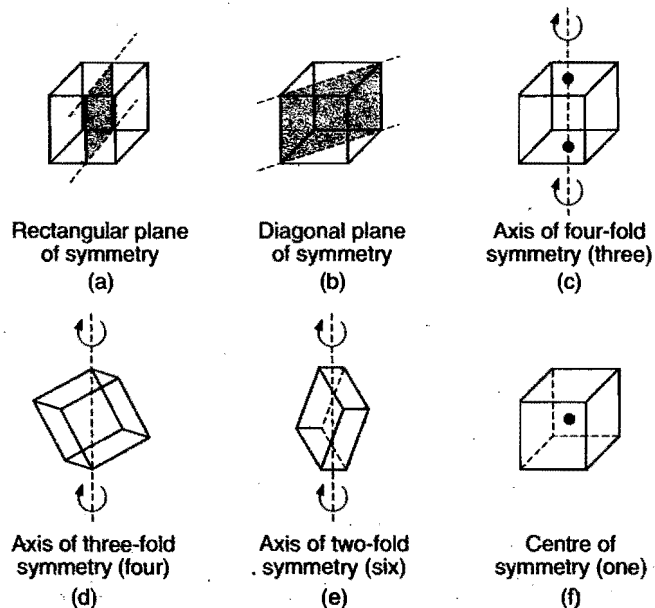


Fig. 4.22 Various elements of symmetry in a cubic crystal

(iii) **Axis of symmetry:** It is an imaginary straight line about which, if the crystal is rotated, it will present the same appearance more than once during the complete revolution. The

axes of symmetry are called diad, triad, tetrad and hexad, respectively, if the original appearance is repeated twice (after an angle of 180°), thrice (after an angle of 120°), four times (after an angle of 90°) and six times (after an angle of 60°) in one rotation. These axes of symmetry are also called two-fold, three-fold, four-fold and six-fold, respectively.

In general, if the same appearance of a crystal is repeated on rotating through an angle of $\frac{360^\circ}{n}$, around an imaginary axis, the axis is called an n -fold axis.

In all, there are 13 axes of symmetry possessed by a cubical crystal like NaCl as shown in Fig. 4.22 (c), (d) and (e).

(iv) **Elements of symmetry:** The total number of planes, axes and centre of symmetry possessed by a crystal are termed as elements of symmetry. A cubic crystal possesses a total of 23 elements of symmetry.

$$\text{Planes of symmetry} = (3 + 6) = 9 \quad [\text{Fig. 4.22 (a) and (b)}]$$

$$\text{Axes of symmetry} = (3 + 4 + 6) = 13 \quad [\text{Fig. 4.22 (c), (d) and (e)}]$$

$$\text{Centre of symmetry} = 1 \quad [\text{Fig. 4.22 (f)}]$$

$$\text{Total number of symmetry elements} = 23$$

4.17 SPACE LATTICE AND UNIT CELL

All crystals are polyhedra consisting of regularly repeating arrays of atoms, molecules or ions which are the structural units. A crystal is a homogeneous portion of a solid substance made of regular pattern of structural units bonded by plane surfaces making definite angles with each other. The geometrical form consisting only of a regular array of points in space is called a **lattice** or **space lattice** or it can be defined as an array of points showing how molecules, atoms or ions are arranged in different sites, in three-dimensional space. Fig. 4.23 shows a space lattice. A space lattice can be subdivided into a number of small cells known as unit cells. It can be defined as the smallest repeating unit in space lattice which, when repeated over and over again, results in a crystal of the given substance or it is the smallest block or geometrical figure from which entire crystal can be built up by its translational repetition in three-dimensions. A unit cell of a crystal possesses all the structural properties of the given crystal. For example, if a crystal is a cube, the unit cell must also have its atoms, molecules or ions arranged so as to give a cube.

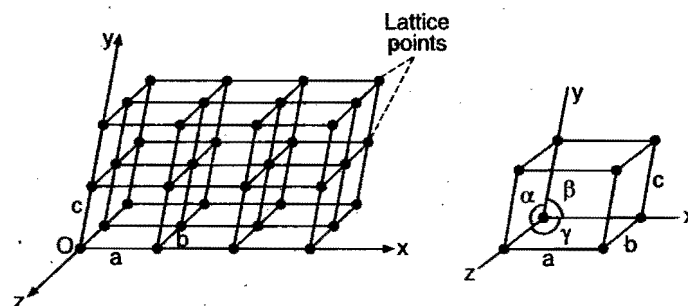


Fig. 4.23 Space lattice and unit cell

System	Edges	Angles	Maximum symmetry elements	Examples
1. Cubic $a = b = c, \alpha = \beta = \gamma = 90^\circ$	All the three equal	All right angles	Nine planes, thirteen axes	NaCl, KCl, ZnS, diamond, alums
2. Orthorhombic $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	All unequal	All right angles	Three planes, three axes	KNO_3 , BaSO_4 , K_2SO_4 , rhombic sulphur.
3. Tetragonal $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	Two equal	All right angles	Five planes, five axes	TiO_2 , PbWO_4 , SnO_2 , NH_4Br
4. Monoclinic $a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	All unequal	Two right angles	One plane, one axis	Monoclinic sulphur, KClO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
5. Triclinic $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	All unequal	None right angles	No planes, no axis	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_3BO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$
6. Hexagonal $a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	Two equal	Angle between equal edges = 120°	Seven planes, seven axes	ZnO, CdS, HgS, SiC, AgI
7. Rhombohedral $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	All three equal	All equal but none 90°	Seven planes, seven axes	NaNO_3 , ICl, quartz (CaCO_3)

Each unit cell has three vectors a, b and c as shown in Fig. 4.23. The distances a, b and c are the lengths of the edges of the unit cell and angles α, β and γ are the angles between three imaginary axes OX, OY and OZ , respectively.

For example: For a crystal system, $a = b = c$ and $\alpha = \beta = \gamma \neq 90^\circ$:

- (a) tetragonal (b) hexagonal
(c) rhombohedral (d) monoclinic

[Ans. (c)]

[Hint: From the table $a = b = c$ for rhombohedral and cubic system both but $\alpha = \beta = \gamma \neq 90^\circ$ for rhombohedral only.]

4.18 CRYSTAL SYSTEMS

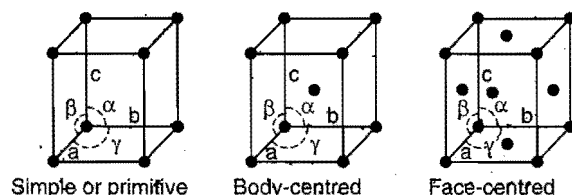
On the basis of geometrical considerations, theoretically there can be 32 different combinations of elements of symmetry of a crystal. These are called 32 systems. Some of the systems have been grouped together. In all, seven types of **basic** or **primitive unit cells** have been recognised among crystals. These are cubic, orthorhombic, tetragonal, monoclinic, triclinic, hexagonal and rhombohedral. These are shown in Fig. 4.24 and their characteristics are summarised in the following table.

All crystals do not have simple lattices. Some are more complex. Bravais pointed out that there can be 14 different ways in which similar points can be arranged in a three-dimensional space. Thus, the total number of space lattices belonging to all the seven crystal systems are 14.

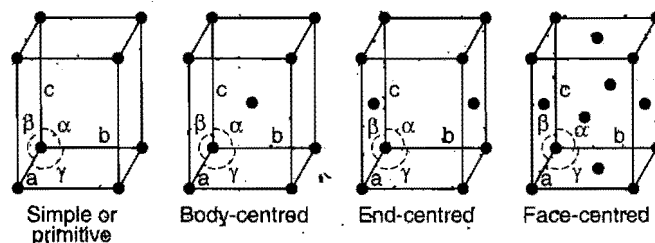
The crystals belonging to cubic system have three kinds of Bravais lattices. These are:

(i) **Simple cubic lattice:** There are points only at the corners of each unit.

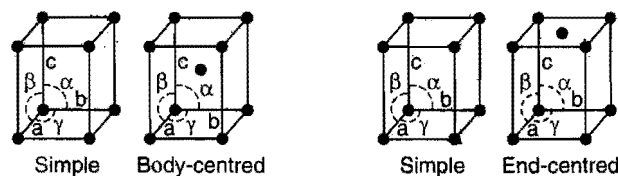
(ii) **Face-centred cubic lattice:** There are points at the corners as well as at the centre of each of the six faces of the cube.



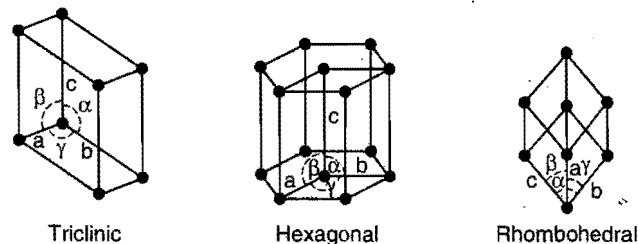
(a) Cubic space lattices



(b) Orthorhombic space lattices



(c) Tetragonal and monoclinic space lattices



(d) Triclinic, hexagonal and rhombohedral space lattices

Fig. 4.24 Bravais lattices

(iii) **Body-centred cubic lattice:** There are points at the corners as well as in the body-centre of each cube.

The number of Bravais space lattices in a given system is listed in the following table and shown in Fig. 4.24.

Crystal system	No. of space lattices	Lattice type
1. Cubic	3	Simple, face-centred and body-centred.
2. Orthorhombic	4	Rectangular and body-centred rectangular prism; rhombic and body-centred rhombic prism.
3. Tetragonal	2	Simple and body-centred tetragonal prism.
4. Monoclinic	2	Monoclinic parallelepiped, monoclinic face-centred parallelepiped.
5. Triclinic	1	Triclinic parallelepiped.
6. Hexagonal	1	Hexagonal prism.
7. Rhombohedral	1	Rhombohedron.

In various unit cells, there are three kinds of lattice points: points located at the corners, points in the face-centres and points that lie entirely within the unit cell. In a crystal, atoms located at the corner and face-centre of a unit cell are shared by other cells and only a portion of such an atom actually lies within a given unit cell.

(i) A point that lies at the corner of a unit cell is shared among eight unit cells and, therefore, only one-eighth of each such point lies within the given unit cell.

(ii) A point along an edge is shared by four unit cells and only one-fourth of it lies within any one cell.

(iii) A face-centred point is shared by two unit cells and only one half of it is present in a given unit cell.

(iv) A body-centred point lies entirely within the unit cell and contributes one complete point to the cell.

Type of lattice point	Contribution to one unit cell
Corner	1/8
Edge	1/4
Face-centre	1/2
Body-centre	1

Total number of constituent units per unit cell

$$= \frac{1}{8} \times \text{occupied corners} + \frac{1}{4} \times \text{occupied edge-centres} + \frac{1}{2} \times \text{occupied face-centres} + \text{occupied body-centre.}$$

Determination of Number of Constituent units per unit cell:

Let edge length of cube = a cm

Density of substance = d g cm⁻³

Volume of unit cell = a^3 cm³

Mass of unit cell = volume $\times$ density = $(a^3 \times d)$ g

$$\text{Number of mol per unit cell} = \frac{a^3 \times d}{M};$$

where, M = molar mass

Number of molecules per unit cell = Number of mole $\times$ Avogadro's number

$$Z = \frac{a^3 \times d}{M} \times N = \frac{a^3 \times d \times N}{M}$$

Calculation of number of constituent units in hexagonal unit cell

(i) Constituent units at each corner of unit cell is common among six unit cells hence contribute 1/6th to each unit cell.

(ii) Constituent unit at edge is common to three unit cells hence contribute 1/3rd to each unit cell.

(iii) Constituent units present at the body centre is considered in single unit cell.

(iv) Constituent unit at face centre is common between two unit cells hence contribute 1/2 to each unit cell.

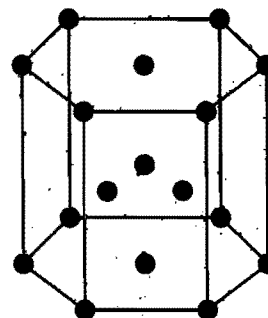


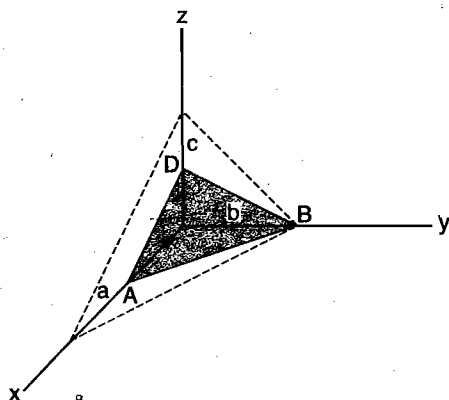
Fig. 4.25 Hexagonal unit cell

In the hexagonal unit cell (Fig 4.25), 12 corners, 2 face centres and 3 constituent units within the unit cells are occupied, hence effective number of constituent units present in the unit cell may be calculated as

$$\begin{aligned} z &= \frac{1}{6} \times \text{occupied corners} + \frac{1}{2} \times \text{occupied face centres} + \text{Central constituent units} \\ &= \frac{1}{6} \times 12 + \frac{1}{2} \times 2 + 3 \\ &= 6 \end{aligned}$$

4.19 DESIGNATION OF PLANES IN CRYSTALS—MILLER INDICES

Planes in crystals are described by a set of integers (h, k and l) known as Miller indices. Miller indices of a plane are the reciprocals of the fractional intercepts of that plane on the various crystallographic axes. For calculating Miller indices, a reference plane, known as parametral plane, is selected having intercepts a, b and c along x, y and z -axes, respectively (Fig. 4.26). Then, the intercepts of the unknown plane are given with respect to a, b and c of the parametral plane.

Fig. 4.26 Parametral (intercepts a, b, c along x, y and z -axes)

Thus, the Miller indices are:

$$h = \frac{a}{\text{intercept of the plane along } x\text{-axis}}$$

$$k = \frac{b}{\text{intercept of the plane along } y\text{-axis}}$$

$$l = \frac{c}{\text{intercept of the plane along } z\text{-axis}}$$

Consider the shaded plane ABD in Fig. 4.26. The intercepts of the shaded plane along X, Y and Z -axes are $a/2, b$ and $c/2$, respectively. Thus,

$$h = \frac{a}{a/2} = 2;$$

$$k = \frac{b}{b} = 1;$$

$$l = \frac{c}{c/2} = 2$$

The plane is, therefore, designed as (212) plane.

Note: (i) If a plane is parallel to an axis, its intercept with that axis is taken as infinite and the Miller indices will be zero.

(ii) While defining Miller indices for orthogonal crystal, X, Y and Z -axes are considered crystallographic axes.

Some of the important planes of cubic crystals are shown in Fig. 4.27.

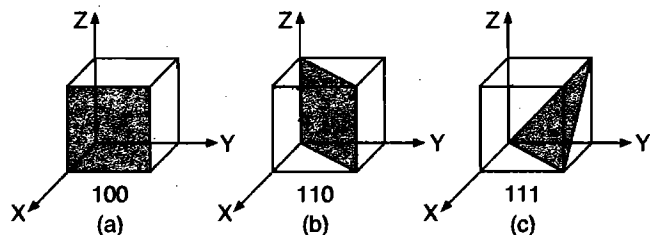


Fig. 4.27 Miller indices of planes in cubic lattice

In (a) intercepts are	1	∞	∞
So, Miller indices are	1	0	0
The plane is designated (100)			
In (b) intercepts are	1	1	∞
So, Miller indices are	1	1	0
The plane is designated (110)			
In (c) intercepts are	1	1	1
So, Miller indices are	1	1	1
The plane is designated (111)			

The distances between the parallel planes in crystals are designated as d_{hkl} . For different cubic lattices these interplanar spacings are given by the general formula,

$$d_{(hkl)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where, a is the length of the cube side while h, k and l are the Miller indices of the plane.

The spacings of the three planes (100), (110) and (111) of simple cubic lattice can be calculated.

$$d_{(100)} = \frac{a}{\sqrt{1^2 + 0 + 0}} = a$$

$$d_{(110)} = \frac{a}{\sqrt{1^2 + 1^2 + 0}} = \frac{a}{\sqrt{2}}$$

$$d_{(111)} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

The ratio is,

$$d_{(100)} : d_{(110)} : d_{(111)} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.577$$

Similarly, $d_{(hkl)}$ ratios for face-centred cubic and body-centred cubic can be calculated. For face-centred cubic,

$$d_{(100)} : d_{(110)} : d_{(111)} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1 : 0.707 : 1.154$$

For body-centred cubic,

$$\begin{aligned} d_{(100)} : d_{(110)} : d_{(111)} &= \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} \\ &= 1 : \sqrt{2} : \frac{1}{\sqrt{3}} \\ &= 1 : 1.414 : 0.577 \end{aligned}$$

4.20 CRYSTALLOGRAPHY AND X-RAY DIFFRACTION

Crystallography is the branch of science which deals with the geometry, properties and structure of crystals and crystalline substances. Geometric crystallography is concerned with the external spatial arrangement of crystal planes and geometric shapes of crystals.

Atoms, molecules or ions are too small to be seen with naked eye. The arrangement of particles in crystalline solids is determined indirectly by X-ray diffraction. In 1912, **Von Laue** showed that any crystal could serve as a three-dimensional grating to the incident electromagnetic radiation with wavelength approximately equal to the internuclear separations ($\approx 10^{-8}$ cm) of atoms in the crystal. Such radiation is in the X-ray region of the electromagnetic spectrum.

The apparatus used is shown in Fig. 4.28. A monochromatic X-ray beam is directed towards the surface of a slowly rotated crystal so as to vary the angle of incidence θ . At various angles, strong beams of deflected X-rays strike the photographic plate. The photographic plate after developing shows a central spot due to primary beam and a set of symmetrically disposed spots due to deflected X-rays. Different kinds of crystals produce different arrangements of spots.

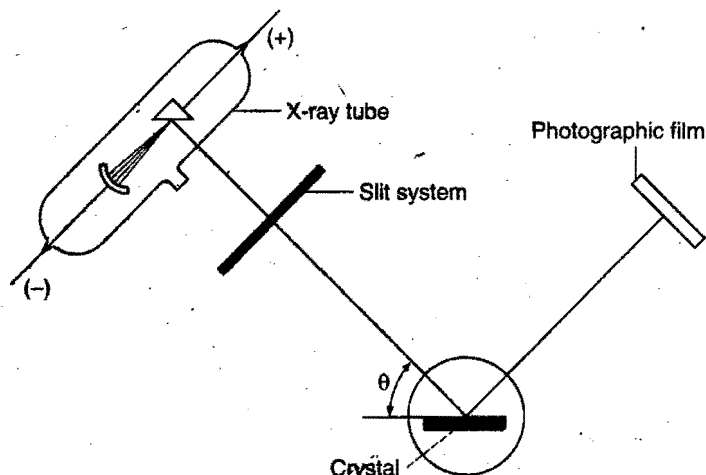


Fig. 4.28 X-ray diffraction of crystals

In 1913, **Bragg** found that Laue photographs are more easily interpreted by treating the crystals as a reflection grating rather than a diffraction grating. Fig. 4.29 illustrates the way by which the crystal spacings can be determined by use of X-rays of a single wavelength, λ . The rays strike the parallel planes of the crystal at angle θ . Some of the rays are reflected from the upper plane, some from the second and some from the lower planes. A strong reflected beam will result only if all the reflected rays are in phase. The waves reflected by different layer planes will be in

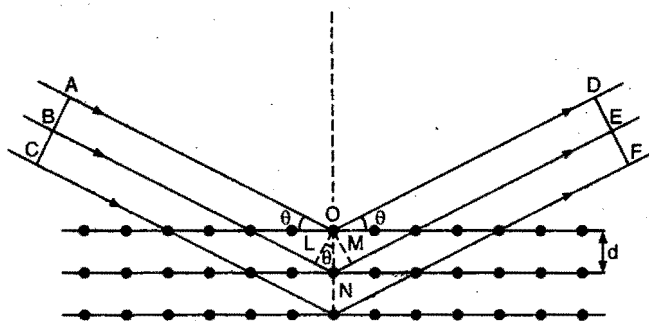


Fig. 4.29 X-ray reflection from crystals

phase with one another only if the difference in the path length of the waves reflected from the successive planes is equal to an integral number of wavelengths. OL and OM are the perpendiculars drawn to the incident and reflected beams. The difference in path lengths of waves deflected from the first two planes is given by:

$$LN + NM = n\lambda \quad (n = 1, 2, 3, \dots)$$

Since, the triangles OLN and OMN are congruent, hence $LN = NM$.

So, Path difference = $2LN$

as $LN = d \sin \theta$ where, d is the distance between two planes.

So, Path difference = $2d \sin \theta$

When two reflected waves reinforce each other (maximum reflection), the path difference should be $= n\lambda$ (where, $n = 1, 2, 3, \dots$).

So, for maximum reflection,

$$n\lambda = 2d \sin \theta$$

This relation is called Bragg's equation. Distance between two successive planes d can be calculated from this equation. With X-rays of definite wavelength, reflections at various angles will be observed for a given set of planes separated by a distance d . These reflections correspond to $n = 1, 2, 3$ and so on and are spoken of as first order, second order, third order and so on. With each successive order, the angle θ increases and the intensity of the reflected beam weakens.

The values of θ for the first order reflection from the three faces of sodium chloride crystal were found to be 5.9° , 8.4° and 5.2° respectively. As n and a are same in each case, the distance d between successive planes in three faces will be in the ratio of

$$\begin{aligned} \frac{1}{\sin 5.9^\circ} : \frac{1}{\sin 8.4^\circ} : \frac{1}{\sin 5.2^\circ} &= 9.61 : 6.84 : 11.04 \\ &= 1 : 0.70 : 1.14 \\ &= 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} \end{aligned}$$

This ratio corresponds to spacings along the three planes of a face-centred cubic structure. Thus, the NaCl crystal has face-centred cubic structure.

Example 63. X-rays of wavelength $1.54 \text{ \AA}$ strike a crystal and are observed to be deflected at an angle of 22.5° . Assuming that $n = 1$, calculate the spacing between the planes of atoms that are responsible for this reflection.

Solution: Applying Bragg's equation,

$$n\lambda = 2d \sin \theta$$

Given, $n = 1$, $\lambda = 1.54 \text{ \AA}$, $\theta = 22.5^\circ$.

Using relation $n\lambda = 2d \sin \theta$,

$$d = \frac{1.54}{2 \sin 22.5^\circ} = \frac{1.54}{2 \times 0.383} = 2.01 \text{ \AA}$$

Example 64. The first order reflection of a beam of X-rays of wavelength $1.54 \text{ \AA}$ from the (100) face of a crystal of the simple

cubic type occurs at an angle of 11.29° . Calculate the length of the unit cell.

Solution: Applying Bragg's equation,

$$2d \sin \theta = n\lambda$$

Given, $\theta = 11.29^\circ$, $n = 1$, $\lambda = 1.54 \text{ \AA} = 1.54 \times 10^{-8} \text{ cm}$

$$d = \frac{1.54 \times 10^{-8}}{2 \times \sin 11.29^\circ} = \frac{1.54 \times 10^{-8}}{2 \times 0.1957} = 3.93 \times 10^{-8} \text{ cm}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = a$$

$a = 3.93 \times 10^{-8} \text{ cm} = \text{length of the unit cell}$

Example 65. When an electron in an excited state of Mo atom falls from L to K-shell, an X-ray is emitted. These X-rays are diffracted at angle of 7.75° by planes with a separation of $2.64 \text{ \AA}$. What is the difference in energy between K-shell and L-shell in Mo, assuming a first order diffraction ($\sin 7.75^\circ = 0.1349$)?

Solution: According to Bragg's equation:

$$n\lambda = 2d \sin \theta$$

$$1 \times \lambda = 2 \times 2.64 \sin 7.75^\circ = 2 \times 2.64 \times 0.1349$$

$$\lambda = 0.712 \text{ \AA}$$

Energy difference between K and L-shell of Mo

$$= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{0.712 \times 10^{-10}} = 2.791 \times 10^{-15} \text{ J}$$

4.21 ANALYSIS OF CUBIC SYSTEMS

The following characteristics are reflected by cubic systems when analysed mathematically:

(i) Atomic Radius

It is defined as half the distance between nearest neighbouring atoms in a crystal. It is expressed in terms of length of the edge 'a' of the unit cell of the crystal.

(a) Simple cubic unit cell : In a simple cubic unit cell, atoms at the corners touch each other along the edge.

Distance between the nearest neighbours,

$$d = AB = a = 2r$$

(where r = radius of the atom)

or Atomic radius,

$$r = \frac{a}{2} = 0.5a$$

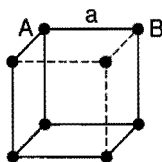


Fig. 4.30
Simple cubic unit cell

(b) Body-centred cubic unit cell : The distance between the two nearest neighbours is represented by length AE or ED , i.e., half of the body diagonal, AD .

$$d = AE = ED = \frac{AD}{2}$$

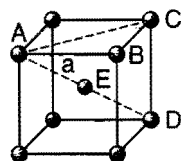


Fig. 4.31
Body-centred cubic unit cell

$$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$$

or

$$AC = \sqrt{2}a$$

Now, in $\triangle ADC$,

$$AD^2 = AC^2 + CD^2 \\ = (\sqrt{2}a)^2 + a^2 = 3a^2$$

or

$$AD = \sqrt{3}a$$

$\therefore$

$$d = \frac{\sqrt{3}}{2}a$$

$$d = 2r = \frac{\sqrt{3}}{2}a$$

or Atomic radius, $r = \frac{\sqrt{3}}{4}a$

(c) Face-centred cubic unit cell

The distance between the two nearest neighbours is represented by length AB or BC , i.e., half of the face diagonal, AC .

$$d = AB = BC = \frac{AC}{2}$$

In $\triangle ACD$, $AC^2 = CD^2 + AD^2$

$$= a^2 + a^2 = 2a^2$$

$$AC = \sqrt{2}a$$

or $d = \frac{AC}{2} = \frac{\sqrt{2}}{2}a = \frac{1}{\sqrt{2}}a$

$$d = 2r = \frac{1}{\sqrt{2}}a$$

or Atomic radius, $r = \frac{1}{2\sqrt{2}}a$

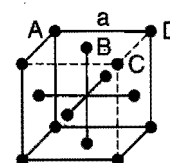


Fig. 4.32
Face-centred cubic unit cell

(ii) No. of Atoms Per Unit Cell

Different types of cubic unit cells are given in following figure:

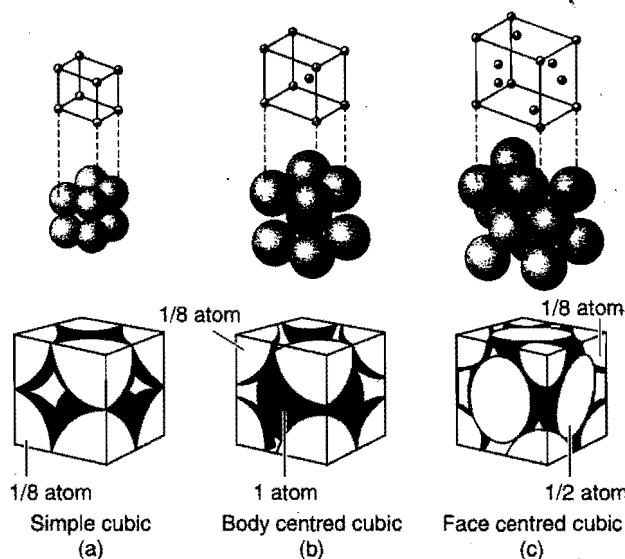


Fig. 4.33 (a) Simple or primitive cubic lattice;
(b) Body-centred cubic lattice; (c) Face-centred cubic lattice

(a) **Simple cubic structure:** Since, each corner atom is shared by eight surrounding cubes, therefore, it contributes for $\frac{1}{8}$ of an atom.

Thus, for simple cube $= 8 \times \frac{1}{8} = 1$ atom per unit cell

(b) **Face-centred cubic structure:** Since, the structure possesses 8 corner atoms and six at the centre of each face, the contribution will be

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} \quad (\text{Face atom is shared by two cubes})$$

$$= 1 + 3 = 4 \text{ atoms per unit cell}$$

(c) **Body-centred cubic structure:** Since, the structure possesses 8 corner atoms and one body-centre, the contribution will be $= 8 \times \frac{1}{8} + 1 = 2$ atoms per unit cell.

(iii) Coordination Number

It is defined as the number of nearest neighbours that an atom has in a unit cell. It depends upon structure.

(a) **Simple cubic structure:** Coordination number = 6

(b) **Face-centred cubic structure:** Coordination number = 12

(c) **Body-centred cubic structure:** Coordination number = 8

(iv) Density of Lattice Matter

Knowing the unit cell dimensions, the theoretical density of a crystal can be calculated as:

$$\text{Density of the unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of the unit cell}}$$

$$\text{Mass of the unit cell} = \text{number of atoms in the unit cell} \times \text{mass of each atom}$$

$$\text{Mass of each atom} = \frac{\text{Atomic mass}}{\text{Avogadro's number}} = \frac{M}{N_0}$$

$$\text{So, density of a unit cell} = \frac{Z \times M}{N_0 \times V} = \frac{n \times M}{N_0 \times a^3} \quad (\text{For a cube})$$

where, Z is the number of atoms in a unit cell and V is the volume of unit cell.

For a cube $V = a^3$ where, a is the edge length of the cubic unit cell.

(v) Packing Fraction or Density of Packing

It is defined as the ratio of volumes occupied by atoms in unit cell to the total volume of the unit cell.

$$\text{Packing fraction} = \frac{\text{Volume occupied by atoms in unit cell}}{\text{Total volume of the unit cell}} = \frac{v}{V}$$

(a) **Simple cubic structure:** Let a be the cube edge and r the atomic radius.

$$V = \text{volume of the unit cell} = a^3$$

Since, one atom is present in a unit cell, its

$$\text{Volume, } v = \frac{4}{3} \pi r^3 \quad (r = a/2)$$

$$= \frac{4}{3} \pi \left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6}$$

$$\text{Packing fraction} = \frac{v}{V} = \frac{\pi a^3/6}{a^3} = \frac{\pi}{6} = 0.52$$

i.e., 52% of the unit cell is occupied by atoms and 48% is empty.

(b) **Face-centred cubic structure:** Since, four atoms are present in a unit cell, their volume is

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

$$\text{Putting the value of } r = \frac{a}{2\sqrt{2}},$$

$$v = \frac{16}{3} \pi \left(\frac{a}{2\sqrt{2}}\right)^3 = \frac{\pi}{3\sqrt{2}} a^3$$

$$\text{Volume of unit cell, } V = a^3$$

$$\text{Packing fraction} = \frac{\pi a^3}{3\sqrt{2} a^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

i.e., 74% of unit cell is occupied by atoms and 26% is empty.

(c) **Body-centred cubic structure:** Since, two atoms are present in a unit cell, their volume is

$$v = 2 \times \left(\frac{4}{3} \pi r^3\right)$$

$$\text{Putting the value of } r = \frac{\sqrt{3}}{4} a, \quad v = 2 \times \frac{4}{3} \pi \times \left(\frac{\sqrt{3}}{4} a\right)^3$$

$$= \frac{\sqrt{3} \pi a^3}{8}$$

$$\text{Volume of unit cell, } V = a^3$$

$$\text{Packing fraction} = \frac{\sqrt{3} \pi a^3}{8 a^3} = \frac{\sqrt{3}}{8} \pi = 0.68$$

i.e., 68% of the unit cell is occupied by atoms and 32% is empty.

Characteristics of cubic unit cells are summarised in following tables :

	Simple	Body-centered	Face-centered
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2} a^3$	$\frac{1}{4} a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	a	$3^{1/2} a/2$ $= 0.866a$	$a/2^{1/2}$ $= 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2} a$	a	a
Packing fraction	$\frac{1}{6} \pi$ $= 0.524$	$\frac{1}{6} \pi \sqrt{3}$ $= 0.680$	$\frac{1}{6} \pi \sqrt{2}$ $= 0.740$

Hexagonal Unit Cell

Let us consider hexagonal unit cell of height 'h'; its constituent units are spherical having radius 'r'.

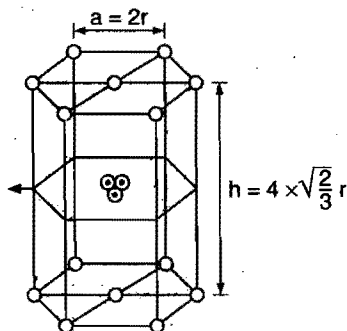


Fig. 4.34 Hexagonal unit cell

Number of constituent units in the hexagonal unit cell = 6

Thus, occupied volume in the unit cell = $6 \times \frac{4}{3} \pi r^3$

Volume of unit cell = Area of base $\times$ height

= $6 \times$ Area of equilateral triangle $\times$ height

$$= 6 \times \frac{\sqrt{3}}{4} a^2 \times 4r \sqrt{\frac{2}{3}}$$

$$= 6 \times \frac{\sqrt{3}}{4} (2r)^2 \times 4r \sqrt{\frac{2}{3}}$$

(Height of the unit cell can be calculated geometrically)

$$\begin{aligned} \text{Percentage occupied space} &= \frac{\text{occupied volume}}{\text{volume of unit cell}} \times 100 \\ &= \frac{6 \times \frac{4}{3} \pi r^3}{6 \times \frac{\sqrt{3}}{4} (2r)^2 \times 4r \sqrt{\frac{2}{3}}} \times 100 = 74.06\% \end{aligned}$$

SOME SOLVED EXAMPLES

Example 66. A compound formed by elements A and B crystallises in cubic structure where A atoms are at the corners of a cube and B atoms are at the face-centre. What is the formula of the compound?

Solution: An atom at the corner of the cube contributes $\frac{1}{8}$ to the unit cell. Hence, number of atoms of A in the unit cell = $8 \times \frac{1}{8} = 1$.

An atom at the face of the cube contributes $\frac{1}{2}$ to the unit cell. Hence, number of atoms of B in the unit cell = $6 \times \frac{1}{2} = 3$.

Thus, the formula is AB_3 .

Example 67. At room temperature, sodium crystallises in body-centred cubic lattice with $a = 4.24 \text{ \AA}$. Calculate the theoretical density of sodium (At. mass of Na = 23.0).

Solution: A body-centred cubic unit cell contains 8 atoms at the 8 corners and 1 in the centre.

Hence,

$$\text{Total number of atoms in a unit cell} = 8 \times \frac{1}{8} + 1 = 2$$

$$\text{Volume of unit cell} = a^3 = (4.24 \times 10^{-8})^3 \text{ cm}^3$$

$$\begin{aligned} \text{So, Density} &= \frac{Z \times M}{N_0 \times V} = \frac{2 \times 23}{(6.023 \times 10^{23})(4.24 \times 10^{-8})^3} \\ &= 1.002 \text{ g cm}^{-3} \end{aligned}$$

Example 68. The density of KCl is 1.9893 g cm^{-3} and the length of a side of unit cell is $6.29082 \text{ \AA}$ as determined by X-ray diffraction. Calculate the value of Avogadro's number.

Solution: KCl has face-centred cubic structure, i.e.,

$$Z = 4$$

$$\text{Avogadro's number} = \frac{Z \times M}{d \times V}$$

Given that, $d = 1.9893$; $M = 74.5$; $V = (6.29082 \times 10^{-8})^3 \text{ cm}^3$

$$\begin{aligned} \text{Avogadro's number} &= \frac{4 \times 74.5}{1.9893 \times (6.29082 \times 10^{-8})^3} \\ &= 6.017 \times 10^{23} \end{aligned}$$

Example 69. Silver crystallises in a face-centred cubic unit cell. The density of Ag is 10.5 g cm^{-3} . Calculate the edge length of the unit cell.

Solution: For face-centred cubic unit, $Z = 4$.

$$\begin{aligned} \text{We know that, } V &= \frac{Z \times M}{N_0 \times d} \\ &= \frac{4 \times 108}{(6.023 \times 10^{23}) \times 10.5} = 6.83 \times 10^{-23} \\ &= 68.3 \times 10^{-24} \end{aligned}$$

Let a be the edge length of the unit cell.

$$\text{So, } V = a^3$$

or

$$\begin{aligned} a^3 &= 68.3 \times 10^{-24} \\ a &= (68.3 \times 10^{-24})^{1/3} \text{ cm} \\ &= 4.09 \times 10^{-8} \text{ cm} \\ &= 409 \text{ pm} \end{aligned}$$

Example 70. An element occurs in bcc structure with a cell edge of 288 pm . The density of metal is 7.2 g cm^{-3} . How many atoms does 208 g of the element contain?

$$\begin{aligned} \text{Solution: Volume of the unit cell} &= (288 \times 10^{-10})^3 \\ &= 23.9 \times 10^{-24} \text{ cm}^3 \end{aligned}$$

$$\text{Volume of 208 g of the element} = \frac{208}{7.2} = 28.88 \text{ cm}^3$$

$$\begin{aligned} \text{Number of unit cells in } 28.88 \text{ cm}^3 &= \frac{28.88}{23.9 \times 10^{-24}} \\ &= 12.08 \times 10^{23} \text{ unit cells} \end{aligned}$$

Each bcc structure contains 2 atoms.

So, Total atoms in 12.08×10^{23} unit cells
 $= 2 \times 12.08 \times 10^{23}$
 $= 24.16 \times 10^{23}$

Example 71. Lithium forms body-centred cubic crystals. Calculate the atomic radius of lithium if the length of the side of a unit cell of lithium is 351 pm.

Solution: In body-centred cubic crystals,

$$r = \frac{\sqrt{3}}{4} a$$

$$= \frac{\sqrt{3}}{4} \times 351 \text{ pm} = 151.98 \text{ pm}$$

Example 72. Ammonium chloride crystallises in a body-centred cubic lattice with a unit distance of 387 pm. Calculate (a) the distance between oppositely charged ions in the lattice and (b) the radius of the NH_4^+ ion if the radius of Cl^- ion is 181 pm.

Solution: (a) In a body-centred cubic lattice, oppositely charged ions touch each other along the cross-diagonal of the cube.

So, $2r_c + 2r_a = \sqrt{3}a$

or $r_c + r_a = \frac{\sqrt{3}}{2} a$

$$= \frac{\sqrt{3}}{2} \times 387 = 335.15 \text{ pm}$$

(b) Given that, $r_a = 181 \text{ pm}$

$$r_c = 335.15 - 181.0 = 154.15 \text{ pm}$$

Example 73. The unit cell cube length for LiCl (NaCl structure) is 5.14 Å. Assuming anion-anion contact, calculate the ionic radius for chloride ion.

Solution: In a face-centred cubic lattice, anions touch each other along the face diagonal of the cube.

$$4r_{\text{Cl}^-} = \sqrt{2}a$$

$$r_{\text{Cl}^-} = \frac{\sqrt{2}}{4} a$$

$$= \frac{\sqrt{2}}{4} \times 5.14 = 1.82 \text{ Å}$$

Alternative: Distance between Li^+ and Cl^- ion

$$= \frac{5.14}{2} = 2.57 \text{ Å}$$

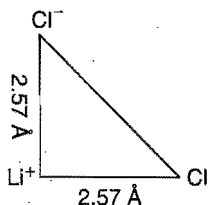
Thus, distance between two chloride ions

$$= \sqrt{(2.57)^2 + (2.57)^2}$$

$$= 3.63 \text{ Å}$$

Hence,

$$\text{radius of } \text{Cl}^- = \frac{3.63}{2} = 1.82 \text{ Å}$$



Example 74. The density of crystalline sodium chloride is 2.165 g cm^{-3} . What is the edge length of the unit cell. What would be the dimensions of cube containing one mole of NaCl?

Solution: We know that,

$$\rho = \frac{N}{a^3} \left(\frac{M}{N_A} \right)$$

where;

$$\rho = \text{density} = 2.165 \text{ g cm}^{-3}$$

$$M = \text{molar mass} = 58.5$$

$$N_A = \text{Avogadro's number} = 6.023 \times 10^{23}$$

$$N = \text{number of formula unit per unit cell} = 4 \text{ (for fcc)}$$

$$a^3 = \frac{N}{\rho} \left(\frac{M}{N_A} \right) = \frac{4}{2.165} \left[\frac{58.5}{6.023 \times 10^{23}} \right]$$

$$= 1.794 \times 10^{-22}$$

$$a = 5.64 \times 10^{-8} \text{ cm}$$

$$\text{Molar volume} = \frac{\text{Molar mass}}{\text{Density}} = \frac{58.8}{2.165}$$

$$\text{Edge length (a)} = \left[\frac{58.8}{2.165} \right]^{1/3} = 3 \text{ cm}$$

Example 75. The density of potassium bromide crystal is 2.75 g cm^{-3} and the length of an edge of a unit cell is 654 pm. The unit cell of KBr is one of three types of cubic unit cells. How many formula units of KBr are there in a unit cell? Does the unit cell have a NaCl or CsCl structure?

Solution: We know that,

$$\rho = \frac{N}{a^3} \left(\frac{M}{N_A} \right)$$

$$N = \frac{\rho \times a^3 \times N_A}{M}$$

$$= \frac{2.75 \times (654 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{119} = 3.89 \approx 4$$

Number of mass points per unit cell = 4

It is NaCl type crystal, i.e., fcc structure.

Example 76. A unit cell of sodium chloride has four formula units. The edge length of unit cell is 0.564 nm. What is the density of sodium chloride? (IIT May 1997)

Solution: $\rho = \frac{ZM}{a^3 N} = \frac{4 \times 58.5}{(5.64 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$

$$= 2.16 \text{ g cm}^{-3}$$

Example 77. Chromium metal crystallises with a body-centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g cm^{-3} ? (IIT July 1997)

Solution: In body-centred cubic unit cell,

$$a\sqrt{3} = 4r$$

where, a = edge length, r = radius of atom

$$r = \frac{a\sqrt{3}}{4} = \frac{\sqrt{3} \times 4.29}{4} = 1.8574 \text{ \AA}$$

Example 78. When heated above 916°C , iron changes its crystal structure from body-centred cubic to cubic closed packed structure. Assuming that the metallic radius of the atom does not change, calculate the ratio of density of the bcc crystal to that of the ccp crystal.

Solution: In body-centred packing, the efficiency of packing is 67.92%. In the cubic closed packing, the packing efficiency is 74.02%.

Let d_1 be the density when packing efficiency is 74.02% and d_2 is the density when packing efficiency is 67.92%.

$$\frac{d_2}{d_1} = \frac{67.92}{74.02} = 0.918$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

30. An element 'A' has face-centred cubic structure with edge length equal to 361 pm. The apparent radius of atom 'A' is:

- (a) 127.6 pm (b) 180.5 pm
(c) 160.5 pm (d) 64 pm

[Ans. (a)]

[Hint: For face-centred unit cell,

$$a\sqrt{2} = 4r$$

$$\frac{361 \times 1.414}{4} = r$$

$$\therefore r = 127.6 \text{ pm}]$$

31. The packing fraction of the element that crystallises in simple cubic arrangement is:

- (a) $\frac{\pi}{4}$ (b) $\frac{\pi}{6}$ (c) $\frac{\pi}{3}$ (d) $\frac{\pi}{2}$

[Ans. (b)]

[Hint: In simple unit cell $a = 2r$

$$Z = 1$$

$$\therefore \text{Packing fraction} = \frac{\text{Occupied volume}}{\text{Total volume}} = \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

32. How many unit cells are present in 39 g of potassium that crystallises in body-centred cubic structure?

- (a) N_A (b) $\frac{N_A}{4}$ (c) $0.5 N_A$ (d) $0.75 N_A$

[Ans. (c)]

$$\begin{aligned} \text{[Hint: Number of atoms} &= \frac{\text{Mass}}{\text{Atomic mass}} \times N_A \\ &= \frac{39}{39} \times N_A = N_A \end{aligned}$$

In bcc unit cell, $Z = 2$

$$\therefore \text{Number of unit cells} = \frac{N_A}{2} = 0.5 N_A]$$

33. Sodium metal exists in bcc unit cell. The distance between nearest sodium atoms is 0.368 nm. The edge length of the unit cell is:

- (a) 0.368 nm (b) 0.184 nm
(c) 0.575 nm (d) 0.424 nm

[Ans. (d)]

[Hint: In bcc unit cell, $a\sqrt{3} = 4r$

$$a = \frac{4r}{\sqrt{3}} = \frac{2}{\sqrt{3}} \times 2r$$

$$= \frac{2}{\sqrt{3}} \times 0.368 = 0.425 \text{ nm}]$$

34. If the distance between Na^+ and Cl^- ions in NaCl crystal is 265 pm, then edge length of the unit cell will be?

- (a) 265 pm (b) 530 pm (c) 795 pm (d) 132.5 pm

[Ans. (b)]

[Hint: In NaCl:

Edge length = $2 \times$ distance between Na^+ and Cl^- ions

$$= 2 \times 265 = 530 \text{ pm}]$$

35. The interionic distance for caesium chloride crystal will be:

[PMT (MP) 2007]

- (a) a (b) $\frac{a}{2}$ (c) $\frac{a\sqrt{3}}{2}$ (d) $\frac{2a}{\sqrt{3}}$

[Ans. (c)]

4.22 PACKING OF IDENTICAL SOLID SPHERES

The constituent particles in the formation of crystals are either atoms, ions or molecules. These particles may be of various shapes and thus, the mode of packing of these particles will change according to their shapes. The simplest way will be to consider these particles as spheres of equal size. The packing of spheres is done in such a way as to use the available space in the most economical manner.

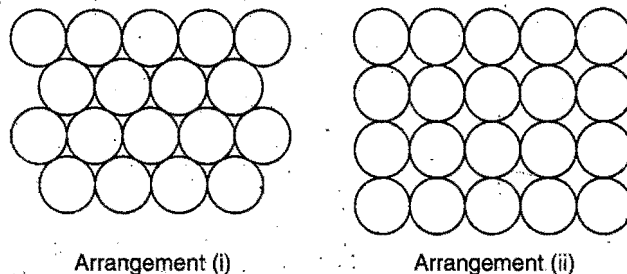


Fig. 4.35 Two common ways of packing spheres of equal size

There are two common ways in which spheres of equal size can be packed. This has been shown in Fig. 4.35. The arrangement (i) is more economical in comparison to arrangement (ii) as 60.4% volume is occupied in arrangement (i) and 52.4% volume in arrangement (ii). Arrangement (i) represents a close packing of spheres.

In arrangement (i), the spheres are packed in such a manner that their centres are at the corners of an equilateral triangle. Each sphere is surrounded by six other similar spheres as shown in Fig. 4.36. This arrangement can be extended in three dimensions by adjusting spheres on the top of hollows or voids of the two-dimensional layer which is called the first layer or 'A' layer. There are two types of hollows in the first layer which have been marked by dots (•) and cross (×). All the hollows are equivalent. The spheres of the second layer may be put either on hollows marked by dots or by crosses. Half of the hollows remain unoccupied in the second layer (Fig. 4.37). The second layer is marked as 'B' layer. The spheres have been placed on the hollows marked by dots.

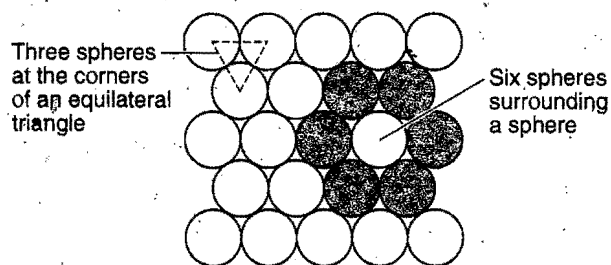


Fig. 4.36 Close packing of spheres

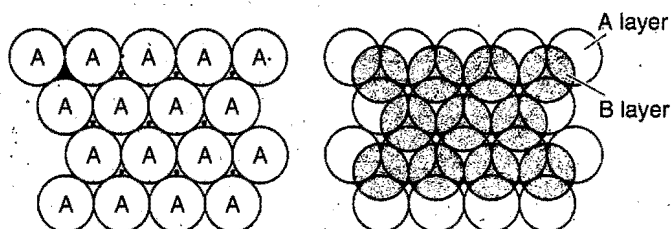


Fig. 4.37 Building of second layer (B, shown shaded) covering hollows marked by dots (•). The hollows marked by a cross (×) unoccupied

To build up the third layer of spheres, there are two alternative ways. In the first way the spheres are placed on the hollows of second layer. It is observed that each sphere of third layer lies exactly above the spheres of first layer. When this arrangement is continued indefinitely, the system obtained is found to possess hexagonal symmetry and is called hexagonal close packing of

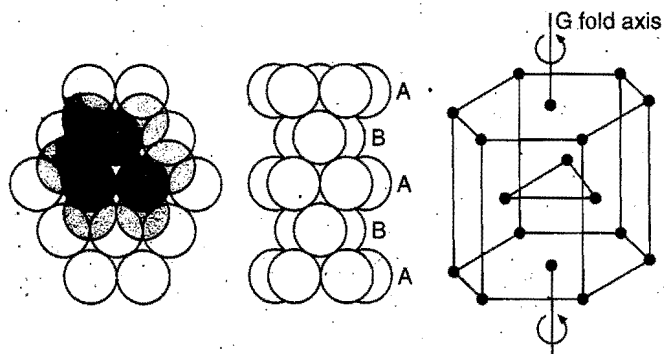


Fig. 4.38 ABABAB... or hexagonal close packing (hcp) of spheres

spheres and is abbreviated as hcp or ABABAB... This is shown in Fig. 4.38. In the second way, spheres are placed on the unoccupied hollows of the first layer, marked by 'crosses'. It is observed that spheres of the third layer do not come over those of first layer. This arrangement of close packing is referred to as ABC. However, it is noted that spheres in the fourth layer will correspond with those in the first layer. When such an arrangement is continued indefinitely, the system is found to possess cubic symmetry and called cubic close packing of spheres and is abbreviated as ccp or ABCABC... This is shown in Fig. 4.39. The system ABCABC... shows that there is a sphere at the centre of each face of the unit cube and thus, this system is also referred to as face-centred cubic or fcc.

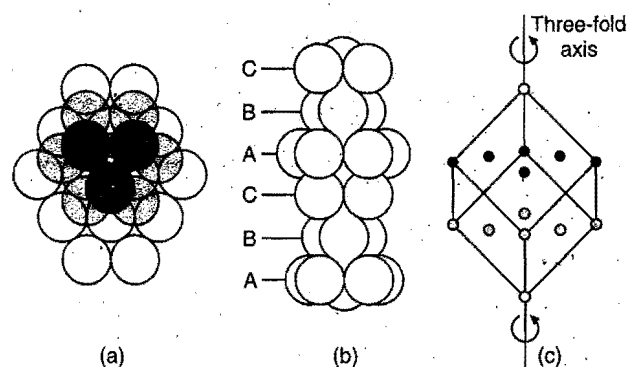


Fig. 4.39 ABCABC... or cubic close packing (ccp) of spheres

It is noted that in both the above systems hcp or ccp, each sphere is surrounded by twelve other spheres shown in Fig. 4.40. There is a third arrangement of packing of spheres which is known as **body-centred cubic arrangement (bcc)**. This arrangement is obtained when the spheres in the first layer are slightly opened up, i.e., none of the spheres touches each other. In the second layer, the spheres are placed at the top of hollows in the first layer. In the third layer, spheres are placed exactly above the first layer. Each sphere in this system of packing is in contact with eight spheres, four in the lower layer and four in the upper layer. This arrangement has been shown in Fig. 4.41.

Most of the metals belonging to s-block and d-block elements possess any one of the following close packing arrangements:

- (i) Cubic closed packed, (ii) Hexagonal closed packed and
- (iii) Body-centred cubic packed.

Examples:

Metals	Structure
Mg, Zn, Mo, V, Cd	hcp
Cu, Ag, Au, Ni, Pt	ccp or fcc
Li, Na, K, Rb, Cs, Ba	bcc

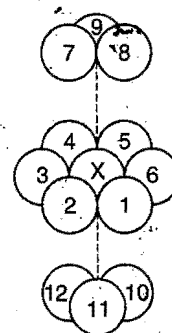


Fig. 4.40 Coordination number in hcp and ccp structure

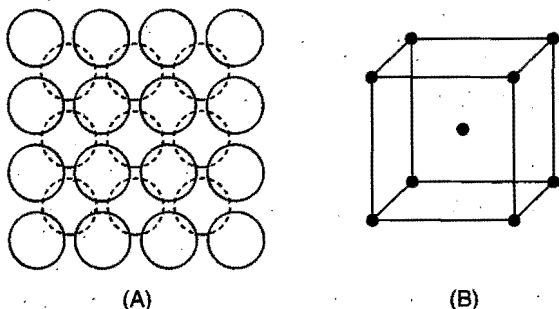


Fig. 4.41 (A) Body-centred cubic packing of spheres
(B) Body-centred cubic arrangement

Interstitial sites in close packed lattices: In a close packing of spheres, there is always some empty space left. The empty space is called hole or void or interstitial site. Common interstitial sites in closely packed spheres are tetrahedral and octahedral.

Tetrahedral site: When one sphere is placed upon the three other spheres which are touching each other, tetrahedral structure results. The four spheres leave a small space in between which is called a tetrahedral site. The site is much smaller than that of the spheres. However, when the spheres are bigger in size, the tetrahedral site becomes larger. In hcp and ccp, each sphere is in contact with three spheres above and three spheres below. Thus, there are two tetrahedral sites associated with each sphere.

Octahedral site: This site is formed at the centre of six spheres, the centres of which lie at the apices of a regular octahedron. Each octahedral site is created by superimposing two equilateral triangles with apices in opposite direction, drawn by joining centres of three spheres in one plane and three spheres in other plane. There is an octahedral site for each sphere. Thus, octahedral sites are half of tetrahedral sites. Tetrahedral and octahedral voids are represented in Fig. 4.42 and 4.43.



Fig. 4.42 Tetrahedral voids

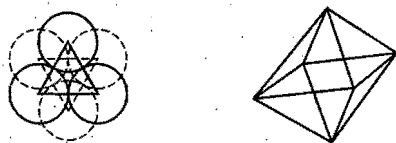


Fig. 4.43 Octahedral voids

Location of Octahedral and Tetrahedral Voids in Cubic Close Packing

Octahedral voids: In the Fig. 4.44 a unit cell of ccp or fcc lattice is drawn. Corners and face-centres are the packing sites. In the face-centred cubic unit cell; octahedral voids are located at the body-centre and all the edge centres of cube.

$$\text{Number of constituent units at packing sites} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\text{Number of octahedral voids (one at body-centre and twelve at edge-centres)} = 1 + \frac{1}{4} \times 12 = 4$$

$\therefore$ Number of octahedral voids is equal to the number of constituent units at packing sites. Each octahedral void is surrounded by six constituent units.

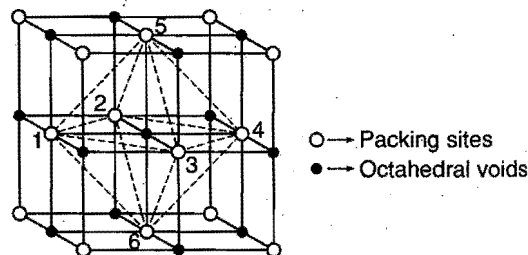


Fig. 4.44

Tetrahedral voids: In cubic close packing, there are eight tetrahedral voids in each unit cell. Tetrahedral voids are located on body diagonals. Two tetrahedral voids are located on each body diagonal; these are represented in the Fig. 4.45.

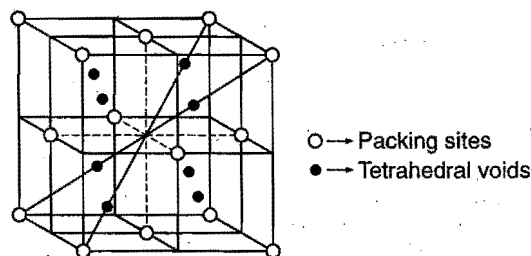


Fig. 4.45

$$\text{Number of constituent units at packing sites (corners and face-centres)} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\text{Number of tetrahedral voids} = 8$$

Thus, number of tetrahedral voids is twice the number of constituent units present at packing sites.

In a multilayered closest-packed structure, there is a tetrahedral void above and below each atom, hence there are twice as many tetrahedral voids as those of closest-packed constituent units.

Tetrahedral and octahedral voids can be located as

- _____ Second closest packed layer
- _____ Tetrahedral voids
- _____ Octahedral voids
- _____ Tetrahedral voids
- _____ First closest packed layer

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

36. In a compound, atoms of element Y form ccp lattice and those of element X occupy $\frac{2}{3}$ rd tetrahedral voids. The formula of the compound will be : (AIEEE 2008)

- (a) X_3Y_4 (b) X_4Y_3 (c) X_2Y_3 (d) X_2Y

[Ans. (b)]

[Hint : Let number of atoms of Y used in packing = n

Number of tetrahedral voids = $2n$

Number of atoms of $X = \frac{2}{3} \times 2n = \frac{4}{3}n$

$$Y : X = n : \frac{4}{3}n = 3 : 4$$

Formula of compound = X_4Y_3

37. A solid compound contains X, Y and Z atoms in a cubic lattice with X atoms occupying the corners, Y atoms in the body centred positions and Z atoms at the centre of the faces of the unit cell. What is the empirical formula of the compound?

(a) XY_2Z_3 (b) XYZ_3 (c) $X_2Y_2Z_3$ (d) X_8YZ_6
(e) XYZ

[Ans. (b)]

[Hint : Number of atoms of X in a unit cell = $\frac{1}{8} \times 8 = 1$

Number of atoms of Y in a unit cell = 1

Number of atoms of Z in a unit cell = $\frac{1}{2} \times 6 = 3$

Empirical formula of the compound = XYZ_3

38. In a crystalline solid, atoms of X form fcc packing and the atoms of Y occupy all octahedral voids. If all the atoms along one body diagonal are removed then the simplest formula of the crystalline solid will be :

(a) XY (b) X_4Y_3 (c) X_5Y_4 (d) X_4Y_5

[Ans. (c)]

[Hint : Number of atoms of X in fcc packing (at corners and face centres of cubic unit cell) = $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

Number of atoms of Y at octahedral voids = 4

Along one body diagonal there are two X atoms and one Y atom.

Number of effective atoms of X after removal

$$= 4 - 2 \times \frac{1}{8} = \frac{15}{4}$$

Number of effective atoms of Y after removal = $4 - 1 = 3$

$$X : Y = \frac{15}{4} : 3$$

$$= 5 : 4$$

$\therefore$ Simplest formula = X_5Y_4

4.23 TYPES OF CRYSTALS

Crystals are classified into four main types depending upon the nature of forces that hold the constituent particles together in the crystal lattice.

1. Ionic crystals: The forces operating in ionic crystals are electrostatic. The lattice points in such crystals are occupied by positively and negatively charged ions. Each ion is surrounded by the largest possible number of oppositely charged ions. This number of oppositely charged ions surrounding each ion is termed its **coordination number**. The coordination numbers of positive or negative ions may be same or different. For example, in sodium chloride, each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. Thus, both the

ions have coordination number six. In CsCl , each Cs^+ ion is surrounded by eight Cl^- ions and *vice-versa*. Thus, both the ions have coordination number eight. In the case of CaF_2 , the coordination number of Ca^{2+} is eight while that of F^- ion, is four.

The coordination numbers commonly encountered in ionic crystals are 8 (body-centred cubic arrangement), 6 (octahedral arrangement) and 4 (tetrahedral arrangement).

It is impossible for both anions and cations to have closed packed structures but if one of the ions is much bigger than the other, it is common for the bigger ions alone to approach a closed packed structure and smaller ions to fit into holes in this structure.

In ionic crystals, the coordination numbers as well as the geometrical shapes of the crystals depend mainly on the relative sizes of the ions. The ratio of the radii of the positive and negative ions is called radius ratio.

$$\text{Radius ratio} = \frac{\text{Radius of positive ion (cation)}}{\text{Radius of negative ion (anion)}} = \frac{r_{c^+}}{r_{a^-}}$$

Common coordination numbers are 3, 4, 6 and 8.

The following table shows the radius ratio values, permitted coordination numbers and the shapes of ionic crystals:

Radius ratio (r_{c^+} / r_{a^-})	Permitted coordination number	Arrangement of anions round the cations	Example
0.155–0.225	3	Plane Triangular	B_2O_3
0.225–0.414	4	Tetrahedral	ZnS
0.414–0.732	6	Octahedral	NaCl
0.732–1.000	8	Cubic (body-centred)	CsCl

Types of Structure of Ionic Solids

Crystal structure of ionic solids are described into following types:

Crystal structure (Type)	Example
1. Rock salt	NaCl , LiCl , KBr , RbI , AgCl , AgBr , FeO , CaO
2. Cesium chloride	CsCl , CaS , CsCN
3. Fluorite	CaF_2 , UO_2 , BaCl_2 , HgF_2
4. Antifluorite	K_2O , K_2S , Li_2O , Na_2O , Na_2S
5. Nickel Arsenite	NiAs , NiS , FeS , CoS
6. Rutile	TiO_2 , MnO_2 , SnO_2
7. Perovskite	CaTiO_3 , BaTiO_3 , SrTiO_3
8. Zinc blende (sphalerite)	ZnS , CuCl , CdS , HgS
9. Wurtzite	ZnS , ZnO , BeO , MnS , AgI

Packing of ions in ionic crystal (Formation of NaCl crystal): The formation of NaCl crystal can be explained in the following manner. The two ions form one ion-pair of opposite charges by the electrostatic force of attraction. Each of the ions

has a strong residual field around it and will naturally attract another ion-pair much in the same way as two magnets attract each other, *i.e.*, a cluster is formed. Two clusters combine together to give a unit cell. Finally, large number of unit cells unite together to form three-dimensional cubic crystal.

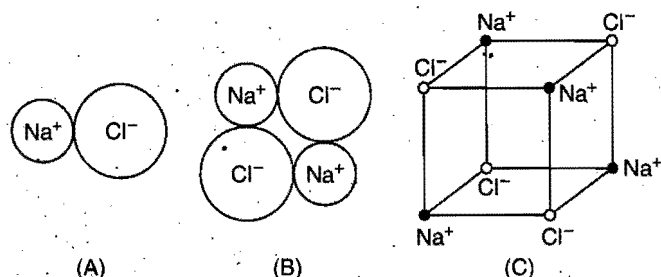


Fig. 4.46 Filling up of ion pairs in stages: (A) shows an ion-pair, (B) two ion-pairs and (C) four ion-pairs of sodium chloride

An examination of NaCl crystal (Fig. 4.47) makes the following points clear:

(i) Each Na^+ ion is surrounded by six Cl^- ions at the corners of a regular octahedron and similarly each Cl^- ion is surrounded by six Na^+ ions. It is, therefore, termed as 6 : 6 arrangement. The radius ratio $[r_{\text{Na}^+} / r_{\text{Cl}^-} = 0.95/1.81 = 0.524]$ suggests that coordination number of each ion is six.

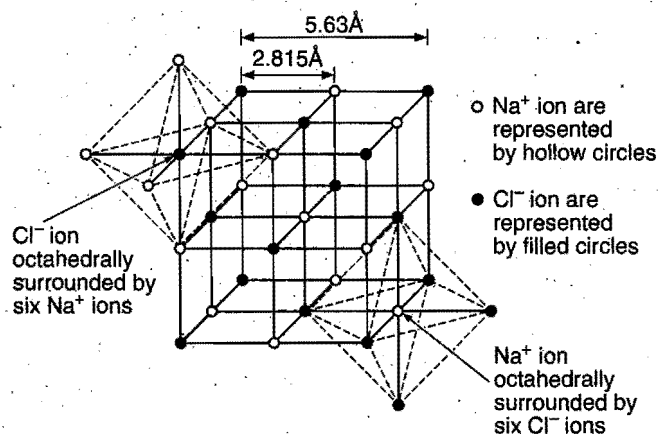


Fig. 4.47 Unit cell representation on NaCl structure

(ii) In the octahedral structure, Cl^- ions may be regarded as having a cubic closed packed (ccp) arrangement in which all octahedral holes are filled by Na^+ ions.

(iii) This type of structure is possessed by most of the alkali metal halides (KCl, NaI, RbF, RbI), alkaline earth metal oxides and AgF, AgCl, AgBr, NH_4Cl , NH_4Br , etc.

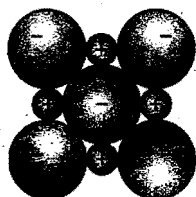


Fig. 4.48

Here, $4r_- = \sqrt{2}a$ and $(2r_- + 2r_+) = a$

Packing fraction (ϕ):

$$\phi = 4 \times \frac{4}{3} \pi \frac{(r_+^3 + r_-^3)}{a^3} = \frac{\pi}{3\sqrt{2}} \left[\left(\frac{r_+}{r_-} \right)^3 + 1 \right]$$

The unit cell of sodium chloride has four sodium ions and four chloride ions.

(a) Number of sodium ions = 12 (at the edge-centres) $\times \frac{1}{4}$ + 1 (at body-centre) = 4

(b) Number of chloride ions = 8 (at the corners) $\times \frac{1}{8}$ + 6 (at face-centres) $\times \frac{1}{2}$ = 4

Structure of Some Other Ionic Compounds

In CsCl crystal, the coordination number of each ion is 8 as the radius ratio $\left(\frac{r_{\text{Cs}^+}}{r_{\text{Cl}^-}} \right)$ is 0.933. It is termed as 8 : 8 arrangement.

The arrangement of the ions in this crystal is body-centred cubic type, *i.e.*, the unit cell has one ion at the centre and oppositely charged ions at the corners of the cube. This has been shown in Fig. 4.49. This type of structure is possessed by CsBr, CsI, TlCl, TlBr, etc.

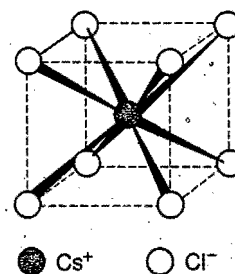


Fig. 4.49 Structure of CsCl

Here, Cs^+ ion is present at the body centre and chloride ions at eight corners. In their limiting case:

$$2r_- = a \text{ and } (2r_- + 2r_+) = \sqrt{3}a$$

a = edge length of unit cell

Packing fraction (ϕ):

$$\phi = \frac{4}{3} \pi \frac{(r_+^3 + r_-^3)}{a^3} = \frac{4\pi}{3 \times 8} \left[\left(\frac{r_+}{r_-} \right)^3 + 1 \right]$$

ZnS crystal has two types of structures:

- Zinc blende structure and
- Wurtzite structure.

(i) **Zinc blende structure:** It has cubic close-packed (ccp) structure. The S^{2-} ions are present at the corners of the cube and at the centre of each face. Zinc ions occupy half of the tetrahedral sites. Each zinc ion is surrounded by four sulphide ions which are disposed towards the corners of a regular tetrahedron. Similarly,

each S^{2-} ion is surrounded by four Zn^{2+} ions. This structure is similar to diamond.

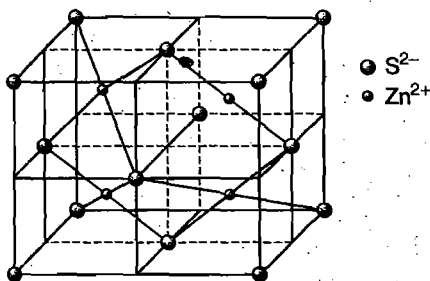


Fig. 4.50 Zinc blende

$$4r_- = \sqrt{2}a$$

Packing fraction (ϕ) :

$$= 4 \times \frac{4}{3} \pi \frac{(r_+^3 + r_-^3)}{a^3} = \frac{\pi}{3\sqrt{2}} \left[\left(\frac{r_+}{r_-} \right)^3 + 1 \right]$$

(ii) Wurtzite structure: It has hexagonal close-packed (hcp) structure. S^{2-} ions adopt hcp arrangement and Zn^{2+} ions occupy half of the tetrahedral sites.

The above structures are termed 4 : 4 arrangement possessed by ZnO, AgI, SiC, etc.

CaF_2 crystal: The Ca^{2+} ions are arranged in ccp arrangement, i.e., Ca^{2+} ions are present at all corners and at the centre of each face of the cube. The fluoride ions occupy all the tetrahedral sites. This is 8 : 4 arrangement, i.e., each Ca^{2+} ion is surrounded by 8 F^- ions and each F^- ion by four Ca^{2+} ions.

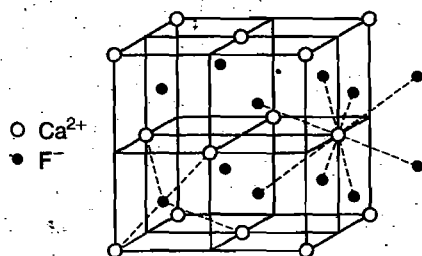


Fig. 4.51 Fluorite structure—Structure of calcium fluoride

Structure of Sodium Oxide (Na_2O)—Antifluorite Structure

Sodium oxide has antifluorite structure. The structure is similar to the structure of calcium fluoride with the difference that the anions occupy the positions of cations and vice-versa.

(i) It has cubic close packing arrangement of O^{2-} ions, i.e., these ions are present at the corners and at the centres of all the six faces of the unit. Sodium ions on the other hand, are present at the sites of all the tetrahedral voids.

(ii) Each Na^+ ion is surrounded by four O^{2-} ions and each O^{2-} ion is surrounded by eight Na^+ ions. Thus, Na_2O has 4 : 8 coordination structure.

Other examples with antifluorite structures are :

Cl_2O , Na_2S , K_2O , Li_2S , K_2S , etc.

Structures of Oxides of Iron

Iron is known to form three major oxides, which are FeO, Fe_2O_3 , Fe_3O_4 . These oxides are interconvertible due to oxidation and reduction. Non-metal excess non-stoichiometry is also known in these oxides. Crystal structures of these oxides are very interesting.

1. Structure of FeO : This oxide has a structure like rock salt (NaCl). Oxide ions (O^{2-}) form a face-centred cubic close packing and Fe^{2+} ions occupy all octahedral voids. It is a perfect rock salt type structure with formula FeO. This oxide is known to form non-metal excess non-stoichiometric compound with the composition $Fe_{0.95}O$ (Wüstite). In the non-stoichiometric compound some of the Fe^{2+} ions present in octahedral voids are replaced by Fe^{3+} ions. Three Fe^{2+} ions will be replaced by two Fe^{3+} ions to maintain electrical neutrality.

[Normal Spinel Structure : Spinel is the common name of the mineral, $MgAl_2O_4$. The crystal structure of this mineral is also called spinel structure. In this type of structure, both tetrahedral and octahedral voids are simultaneously occupied. General formula of the compound having spinel structure is AB_2O_4 where 'A' stands for a divalent cation and 'B' stands for a trivalent cation. It has a cubic close packed arrangement of oxide ions. Half of the octahedral voids are occupied by trivalent cations and one-eighth of the tetrahedral voids are occupied by divalent cations.

Ferrites are the spinel type compounds having the general formula AFe_2O_4 where A stands for divalent cation such as Zn^{2+} . Ferrites are used for making powerful, permanent and non-rusting magnets. Ferrites are used in telephones and memory units of computers.]

2. Structure of Fe_3O_4 : Magnetite, Fe_3O_4 , is considered as a mixed oxide. It contains mixture of FeO and Fe_2O_3 . It has an **inverse spinel structure**. Oxide ions (O^{2-}) form face-centred cubic arrangement. Divalent ions (Fe^{2+}) are present in octahedral voids and trivalent ions (Fe^{3+}) are equally distributed among tetrahedral and octahedral voids.

Number of O^{2-} ions in the unit cell = 4

Thus, Number of tetrahedral voids = 8

and Number of octahedral voids = 4

Number of Fe^{2+} ions present in octahedral void = 1

Number of Fe^{3+} ions present in tetrahedral void = 1

Number of Fe^{3+} ions present in octahedral void = 1

Thus, half of the octahedral voids are occupied by Fe^{2+} and Fe^{3+} ions and one-eighth of the tetrahedral voids are occupied by Fe^{3+} ions.

3. **Structure of Fe_2O_3** : If all the Fe^{2+} ions are replaced by Fe^{3+} ions, then as every three Fe^{2+} ions can be replaced by two Fe^{3+} ions to maintain electrical neutrality, the ratio between Fe and O will now be 2 : 3, i.e., we get Fe_2O_3 .

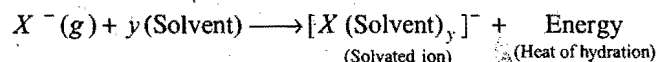
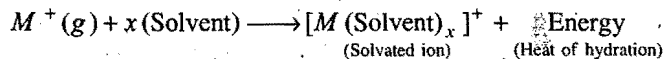
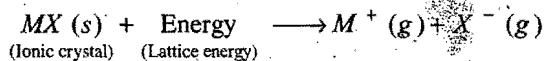
Properties of Ionic Crystals

(i) **Physical state**: Ionic crystals are crystalline solids at room temperature. They are never liquids or gases under ordinary temperature and pressure as the ions do not have freedom of movement.

Since, high energy is required to separate cations and anions from one another from their allotted positions on account of very strong electrostatic forces of attraction, the **ionic crystals are quite hard, have low volatility and have high melting and boiling points.**

(ii) **Electrical conductivity**: Ionic crystals are insulators, i.e., do not conduct electricity in solid state. The reason is that ions are held firmly in fixed positions in the crystal lattice and cannot move when electric field is applied. **However, when melted they become good conductors of electricity, i.e., ions are free to move in liquid medium.**

(iii) **Solubility**: Ionic crystals are soluble in polar solvents or solvents having high values of dielectric constant. They are insoluble in non-polar solvents. When they dissolve in non-polar medium colloidal solutions are formed, e.g., NaCl in kerosine oil. The dissolution of an ionic crystal in a polar solvent depends on the relative magnitudes of lattice and hydration energies.



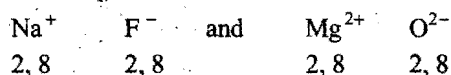
The ionic compound will be soluble if total hydration energy is higher than lattice energy.

Ionic crystals are good conductors in molten state or when dissolved in water.

(iv) **Brittleness**: Ionic solids are highly brittle in nature. When external force is applied, these are easily broken into pieces. Ionic solids are composed of parallel layers which contain cations and anions. When external force is applied, one layer slides a bit over the other and like ions come in front of each other. Due to repulsion between two layers the ionic solid breaks down.

Ionic crystals have high density due to close packing.

(v) **Isomorphism**: Ionic crystals possess same crystalline structure, i.e., show isomorphism if the ions (cations and anions) have same electronic configuration. NaF and MgO are isomorphous compounds.



2. **Covalent crystals**: In covalent crystals, the lattice points are occupied by neutral atoms either of same element or of

different elements. These atoms are held together by covalent bonds. Covalent crystals are of two types:

(i) The covalent bonds extend in three-dimensions forming a giant interlocking structure. Examples are diamond, silicon carbide (SiC), aluminium nitride, etc.

In **diamond**, each carbon atom is sp^3 -hybridized and thus, covalently bonded to four other carbon atoms present at the four corners of a regular tetrahedron. This leads to a rigid three-dimensional network. The entire crystal is regarded as one large carbon molecule and is called a **macromolecule**. The structure of diamond explains the properties such as high density, non-conducting nature, extreme hardness and high melting and boiling point of the diamond.

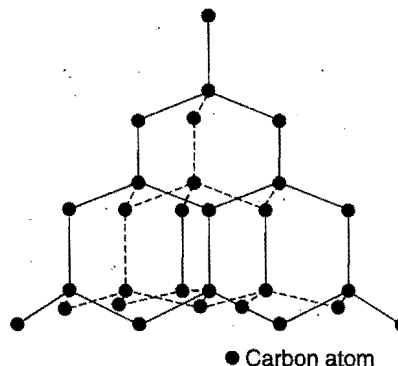


Fig. 4.52 Structure of diamond

(ii) The covalent bonds extend in two-dimensions forming a giant layer. These layers are then held together by van der Waals' forces. Examples are graphite, boron nitride (BN), cadmium iodide, etc.

In **graphite**, each carbon is sp^2 -hybridized and is thus bonded to three carbon atoms in the same plane. The C—C distance is 1.42 Å which is intermediate between single bond distance (1.54 Å) and double bond distance (1.33 Å). The unit cell consists of a hexagon of six carbon atoms. The unit cells are interlocked giving a layer or sheet structure. The distance between two adjacent layers is 3.35 Å. The structure explains the properties of graphite such as being soft, good conductor of electricity, flaky and slippery.

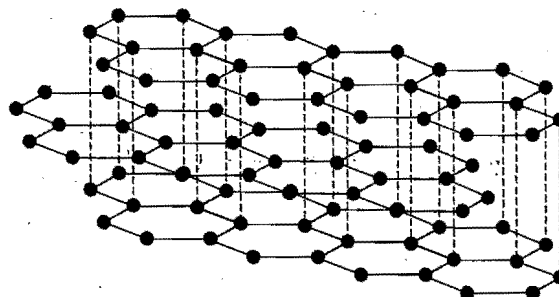


Fig. 4.53 Structure of graphite

In general, the packing of atoms in covalent crystals is loose in comparison to ionic and metallic crystals. Thus, covalent crystals have open structure.

3. Metallic crystals: The metallic crystals have positive metal ions as lattice points surrounded by a sea of mobile electrons. Each electron belongs to a number of positive ions and each positive ion belongs to a number of electrons. The force that binds a metal ion to a number of electrons within its sphere of influence is known as **metallic bond**. Metallic crystals mostly belong to cubic face-centred (fcc), cubic body-centred (bcc) and hexagonal close-packed (hcp) systems. Metallic crystals exhibit the following properties:

(i) **Good conductors:** On account of the presence of mobile electrons, metals are good conductors of electricity. The electrical conductivity decreases with increase of temperature. This is due to the fact that positive ions also begin to oscillate with the increase of temperature. The oscillation of positive ions hinders the movement of mobile electrons. Metals are also good conductors of heat.

(ii) **Lustre:** When freshly cut or scratched, most of the metals have a shining surface. When light falls on freshly cut surface, the electrons get excited. The excited electrons give off energy in the form of light when they return to their original position and hence the metal looks bright. The metallic properties are explained on the basis that the metallic bond is non-directional and non-rigid. The result is that M^{n+} ions can be easily moved from one lattice site to another. The nearest neighbours can be thus changed easily and new metal bonds can be formed readily. This explains why metals are malleable and ductile.

(iii) **Physical characteristics:** Most of the metals are quite hard and tough. They are malleable and ductile. They have high tensile strength. Except alkali metals, they have high melting and boiling points. They also possess elasticity.

4. Molecular crystals: In molecular crystals, the lattice points are occupied by molecules which do not carry any charge. The forces responsible for binding these molecules are dipole-dipole attractions and van der Waals' forces. Dipole-dipole forces are present in solids when polar molecules occupy the lattice points as in the case of water. van der Waals' forces are more general and occur in all kinds of molecular crystals. The binding energy in molecular crystals is, therefore, weak. Molecular crystals show the following general properties:

- They are generally soft and easily compressible.
- They have low melting or boiling points.
- They are bad conductors of electricity as the electrons are localised in the bonds.
- They have low density.

The following table provides a comparative summary of the properties of various types of crystals:

Property	Ionic crystals	Covalent crystals	Metallic crystals	Molecular crystals
1. Constituent particles occupying lattice points	Positive and negative ions	Neutral atoms	Positive ion in sea of electrons	Molecules polar or non-polar
2. Binding force	Electrostatic attraction	Shared pairs of electrons	Electrostatic attractions between positive ions and electrons	Weak polar forces or van der Waals' forces
3. Hardness	Hard and brittle	Very hard	Hard or soft	Very soft
4. Melting and boiling points	High	Very high	High or low	Low
5. Electrical conductivity	Bad conductors; Good conductors in fused state or in solution	Bad conductors with few exceptions	Good conductors	Bad conductors
6. Examples	NaCl, KNO ₃ , CaF ₂	Diamond, graphite, carborundum	Cu, Na, Fe metals	Ice, solid CO ₂

4.24 IMPERFECTION IN SOLIDS

An ideal crystal is one which has the same unit cell containing the same lattice points across the whole crystal. Any departure from perfectly ordered arrangement of constituent particles in the crystals is called imperfection or defect.

Perfect of ideal crystals can exist only at absolute zero or zero Kelvin. At absolute zero the crystalline substances have zero entropy, i.e., have no randomness. Above absolute zero, entropy or randomness increases, i.e., some deviations from perfectly ordered arrangement takes places.

The imperfection may be **intrinsic** or **extrinsic**. Crystalline defects can profoundly alter the properties of a solid material. Imperfections or defects not only alter the properties but also give rise to new characteristics. Extrinsic defects due to presence of certain impurities give rise to interesting changes in the properties. For example, gem stones are crystals containing impurities that give them beautiful colours. The presence of Fe^{3+} ions makes sapphire blue and Cr^{3+} ions presence makes ruby red. (Gems are actually crystals of Al_2O_3 which is colourless).

There are mainly two types of imperfections.

- Electronic imperfections
- Atomic imperfections.

1. Electronic Imperfections

This type of imperfection arises due to irregular arrangement of electrons in the crystal structure. At 0 K (absolute zero), the electrons in both ionic and covalent solids are present in fully occupied lowest energy orbitals or states and these electrons do not move under the influence of applied electric field. However, when temperature is raised above 0 K, some electrons may occupy higher energy states. For example, in crystals of pure silicon or germanium, some electrons are released from the covalent bonds above 0 K. These free or mobile electrons become responsible for electrical conductance. The bonds from which the electrons have been removed on heating become electron deficient and these are referred to as **holes**. Like free electrons, holes also conduct electric current. Holes in an electric field move in a direction opposite to that in which electrons move. Both electrons and holes present in the solids give rise to electronic imperfection. Electrons and holes are denoted by the symbols ' e^- ' and ' h^+ ' and their concentrations are represented by ' n ' and ' p '. In pure covalent solids like silicon and germanium, the number of free electrons and holes will be equal. Electrons and holes can be obtained preferentially according to the requirement by adding appropriate impurities.

Silicon and germanium are the elements of group 14th; thus, they have maximum covalency of four. A number of solids can be obtained by the combination of the elements of groups 13 and 15 or groups 12 and 16 to get average valency of four as in silicon and germanium. Examples are : InSb, AlP, GaAs. In these materials, In, Al and Ga belong to group 13 and Sb, P and As belong to group 15 of the extended form of the periodic table. Other examples are : ZnS, CdS, CdSe, HgTe. In these materials, Zn, Cd and Hg belong to group 12 and S, Se and Te belong to group 16 of the periodic table. These combinations are not purely covalent but possess an ionic character due to difference in the electronegativities of the two elements. These combinations show interesting electrical, magnetic and optical properties which have been utilised in the electronic industries for photovoltaic cells, light emitting diodes, thermocouples and semiconductors, etc.

2. Atomic Imperfections or Point Defects

When the deviations exist in the regular or periodic arrangement of the constituent particles (atoms or ions) in the crystal, these defects are termed **atomic imperfections or point defects**.

These defects are caused by the following points.

(i) When some of the constituent particles are missing from their normal positions, these unoccupied positions are termed **holes or vacancies**.

(ii) When some of the constituent particles are missing from their positions and these particles have shifted either to interstitial vacant sites or to positions which are meant for other particles.

Types of point defects : Point defects are classified into the following three types:

- (A) Defects in stoichiometric crystals,
- (B) Defects in non-stoichiometric crystals,
- (C) Impurity defects

(A) Defects in stoichiometric crystals

The crystals in which cations and anions are exactly in the same ratio as indicated by their molecular formulae are termed **stoichiometric crystals**. Point defects do not alter the stoichiometry of the solid; these defects are called as **intrinsic or thermodynamic defect**. Two types of point defects are observed in these crystals :

- (i) Schottky defect, (ii) Frenkel defect.

(i) **Schottky defect** : This defect was first observed by the German scientist Schottky in 1930. In this defect equal number of cations and anions (from AB type crystal) are missing from their normal lattice sites, i.e., equal number of cationic and anionic **vacancies** or **holes** will be developed. The crystal maintains electrical neutrality.

This defect is usually observed in strongly ionic compounds which have high coordination number and the sizes of two ions (cations and anions) are almost same.

Examples : NaCl, KCl, KBr, CsCl, AgBr etc.

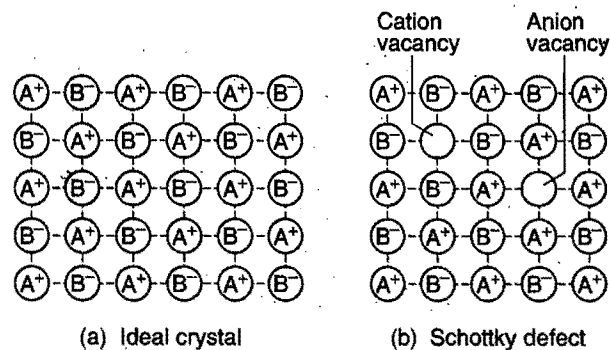


Fig. 4.54

In 1 cm^3 of NaCl there are 10^{22} ions and 10^6 Schottky pairs, thus there is one Schottky defect per 10^{16} ions.

Consequences of Schottky defect

- (a) Due to Schottky defect, the density of crystalline solid decreases.
- (b) Lattice energy and thereby stability of the crystalline solid decreases.
- (c) Entropy increases.

(ii) **Frenkel defect** : This defect was discovered and studied by a Russian scientist, Frenkel, in 1926. This defect is caused if some of the ions (usually the cations) of the lattice occupy interstitial sites leaving a corresponding number of normal lattice sites vacant. This defect creates **vacancy defect** at original site and **interstitial defect** at new site. Frenkel defect is also called **dislocation defect**.

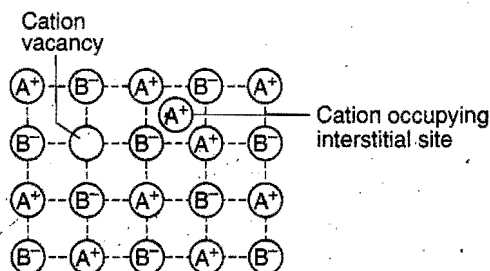


Fig. 4.55 Frenkel defect in the crystal

Main conditions for Frenkel defect are:

- Coordination number should be low.
- Size of anion should be bigger than cation.

Examples : This defect is not found in alkali metal halides because cations and anions have almost equal sizes and cations cannot be accommodated in interstitial sites. This defect is mainly found in transition metal halides like AgCl, AgBr, AgI, ZnS, etc. Silver ion (Ag^+) being smaller in size can be accommodated in interstitial site. AgBr shows both Frenkel and Schottky defect.

Consequences of Frenkel defect

- (a) There is no change in the density of the solid.
- (b) There is increase in the dielectric constant as the like charge ions come closer.
- (c) The solids having Frenkel defect show conductivity and diffusion in solid state due to presence of vacant lattice sites.
- (d) Lattice energy and thereby stability of crystalline solids decreases.
- (e) This defect influences the chemical properties of ionic compound.
- (f) Entropy of the solid increases.

Thermodynamic facts about point defects in stoichiometric solids : Frenkel and Schottky defects are also called as intrinsic or thermodynamic defects.

Number of point defects increases with temperature. The number of defects formed per unit volume (cm^3) n is given by,

$$n = Ne^{-W/2RT}$$

where, N = number of sites per unit volume (cm^3) which could be left vacant

W = Work necessary to create a defect

T = Absolute temperature

Electrical conductance of crystals increases due to point defects. When potential difference is applied to the solid then ions may move from the lattice sites to occupy the holes or vacancies. Such movement is responsible for electrical conductance.

Difference between Schottky and Frenkel defect

Schottky defect	Frenkel defect
1. Equal number of cationic and anionic vacancies are present in this defect.	Some ions are displaced from normal lattice sites to the interstitial sites.

2. Density is lowered in this defect.	Density is unaffected in it.
3. Dielectric constant remains same.	Dielectric constant increases.
4. It is shown by those ionic compounds which have high coordination number, sizes of cations and anions are almost equal.	It is shown by those ionic compounds which have low coordination number and size of cations is smaller than size of anions.

(B) Defects in non-stoichiometric solids

The compounds in which the number of positive and negative ions are not exactly in the ratio as indicated by their chemical formulae are called non-stoichiometric compounds. Non-stoichiometric solids are also known as **Berthollide compounds**.

Examples :

- (i) Ferrous oxide FeO exists in non-stoichiometric form as $\text{Fe}_{0.95}\text{O}$ called *wüstite*.
- (ii) Vanadium oxide has non-stoichiometric formula VO_x , where x lies between 0.6 and 1.3.
- (iii) ZnO exists as a non-stoichiometric compound having excess zinc.
- (iv) Stoichiometric compounds like NaCl, KCl, etc., can be non-stoichiometric under suitable conditions.

The defects which bring change in overall chemical composition are termed as **non-stoichiometric defects**. In such crystals, there is excess of either positive particles (cations) or negative particles (anions). However, the crystal as a whole is neutral in nature. If positive particles are in excess, the charge is balanced by the presence of extra electrons. In case the negative particles are in excess, the charge is balanced by acquiring higher oxidation state by metal atoms.

Non-stoichiometric defects are of two types:

1. Metal excess defect, 2. Non-metal excess defect

1. Metal excess defect : In this defect, metal ions or cations are in excess. This defect may develop on account of the following two ways :

(a) **Anion vacancies :** A negative ion may be missing from its lattice site leaving behind a vacancy or hole. This vacancy or hole is occupied by an extra electron to maintain electrical neutrality. This defect is somewhat similar to Schottky defect but differs in having only one hole and not a pair as in the latter case.

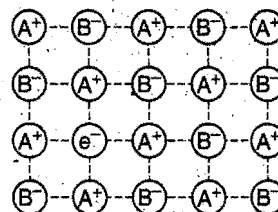


Fig. 4.56 Metal excess defect due to anion vacancy

Anion vacancies in alkali metal halides are produced by heating the metal halides in the atmosphere of alkali metal

vapours. Metal atoms get adsorbed on the surface of the metal halides. Halide ions move towards the surface and combine with metal ions formed by the adsorbed atoms on account of their ionisation. The electrons released in the process diffuse into the crystal and occupy anion vacancies. The electrons trapped in anion vacancies are referred to as **F-centres**. 'F' stands for **Farben**, a German word, meaning colour. Greater is the number F-centres, more is the intensity of colour. For example, non-stoichiometric sodium chloride with excess sodium is yellow, non-stoichiometric; potassium chloride with excess of potassium is violet and non-stoichiometric; lithium chloride with excess of lithium is pink.

(b) **Excess cations occupying interstitial positions** : Metal excess defect may also be developed by the presence of extra cation in the interstitial site. Electrical neutrality is achieved by an electron presence in another interstitial site. This defect is similar to Frenkel defect. For example, when ZnO is heated, it loses oxygen and turns yellow.

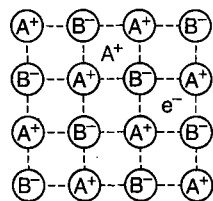
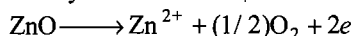


Fig. 4.57 Metal excess defect due to the presence of extra cation in the interstitial position

The Zn^{2+} ions thus formed occupy interstitial sites and the electrons occupy the neighbouring interstitial sites. The crystals having metal excess defects contain few free electrons and, thus, such solids act as semi-conductors.

2. Non-metal excess or metal deficiency defect : These contain lesser number of positive particles than negative particles. These defects arise due to cation vacancies or anions occupying interstitial sites. the extra negative charge is balanced by oxidation of some of the nearby metal ions. Thus, this defect occurs when metal shows variable valency, i.e., especially in the case of transition metals. Examples are : FeO, FeS, NiO, etc. Crystals with metal deficient defects are semiconductors of *p*-type.

(C) Impurity defects in ionic crystalline solids

A defect in an ionic solid can be introduced by adding foreign ions. If the impurity ions have a different oxidation state than that

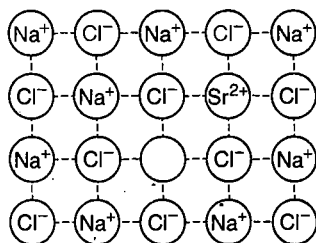


Fig. 4.58 Impurity defect

of the host ions, vacancies are created. For example, if molten NaCl containing a little SrCl_2 or CaCl_2 as impurity is allowed to cool, some lattice sites will be occupied either by Ca^{2+} ions or Sr^{2+} ions in place of Na^+ ions. For every Ca^{2+} ion or Sr^{2+} ion, two Na^+ ions are removed in the crystal lattice in order to maintain electrical neutrality. Thus, one of these lattice sites is occupied by Ca^{2+} or Sr^{2+} ion and the other site remains vacant.

Cationic vacancies developed due to introduction of impurity cause higher electrical conductivity of ionic solids. Addition of about 0.1% SrCl_2 to NaCl increases the electrical conductivity by 10000 times. Solid solution of CdCl_2 and AgCl is another example of this type of impurity defect.

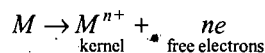
Electric Properties of Solids

On the basis of electrical conductivity, solids are divided into three categories:

(i) Metals (ii) Insulators (iii) Semiconductors

Metals have conductivity $10^8 \text{ ohm}^{-1} \text{ cm}^{-1}$ and insulators have $10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$.

Metals: Metals have free electrons and fixed **kernels** at their lattice sites:



Free electrons make the metal good conductor of electricity and heat. Conductivity of metals is nearly independent of impurity of metals. Resistance ratio may be taken to check the impurity level of metals, i.e., $\rho_{300\text{K}} / \rho_{4.2\text{K}}$. Conductivity of metals depends on number of valence electrons, i.e., number of free electrons produced by the metal.

Nature of Metallic Bond

A metal is regarded as group of positively charged metal ions packed as closely as possible in a regular geometrical fashion and immersed in a sea or pool of mobile electrons. The attraction force that binds the metal ions and mobile electrons is called metallic bonding.

1. Conductivity: When potential difference is applied electrons (mobile) conduct electric current. It has been observed that the conductivity of most of the metals decreases with increase in temperature. At high temperature, positive metal ions start vibration and create resistance to the flow of electrons; thus resistance of metal increases.

Good thermal conductivity of metals can also be explained on the basis of mobile electrons.

2. Opacity and lustre: Mobile electrons absorb quantum energy of visible light and become excited; when excited electrons return to normal state, visible light is evolved. Since, the light is fully absorbed by metal hence it is opaque.

3. Elasticity: On applying mechanical stress, temporary deformation of the metal crystal takes place and the kernels with their electron cloud return to their original position as soon as mechanical stress is removed.

4. Microproperties of metals: Some other properties of metals are summarised ahead:

- (a) Metals possess high tensile stress.
- (b) Metals are usually hard and solid.
- (c) Some metals like alkali and alkaline earth metals show photoelectric effect, *i.e.*, ejection of electron from metal surface when exposed to light of appropriate energy.
- (d) Metals have low ionization energy.
- (e) Strength of metallic bond depends on the following factors:

Strength increases with:

- (i) increase in number of valence electrons,
- (ii) increase in charge on the nucleus,
- (iii) decrease in size of positive metal ion.

Valence band: Group of electrons containing valence electrons.

Conduction band: The free electrons for conduction constitute conduction band.

Band structure of metals may be given as shown in Fig. 4.59.

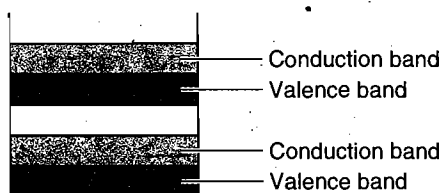


Fig. 4.59

There is no energy gap between valence and conduction band, *i.e.*, width of forbidden zone is zero. Thus, as soon as potential difference is applied electrons jump to conduction band from valence band and conduct electric current. All valence electrons are free to conduct electric current. **When temperature is raised conductance of metals decreases because at high temperature kernels vibrate and create obstruction in the flow of electron.**

Semiconductors: Conductivity of semiconductors is intermediate between metals and insulators. These are of two types:

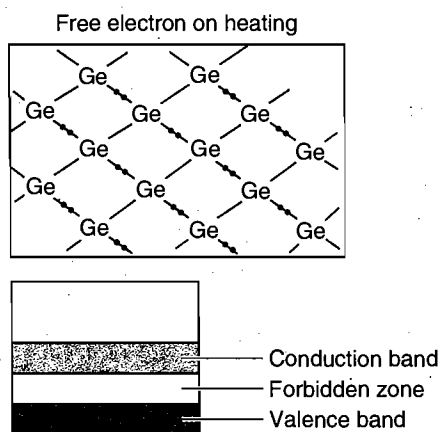


Fig. 4.60

(i) Intrinsic semiconductors: These are insulators at room temperature and become semiconductors when temperature is raised.

On heating, some covalent bonds are broken to give free electrons. These free electrons make it semiconductor.

Width of forbidden zone in semiconductors is very low; thus on heating, electrons are easily tossed to conduction band from valence band and conduct electric current.

(ii) Extrinsic semiconductors or Impurity semiconductors: These are formed by doping impurity of lower or higher group.

***n*-type Semiconductor**

Doping of higher group impurity forms *n*-type semiconductor, *e.g.*, when 'As' is doped to 'Ge', an extra valence electron of arsenic makes the mixture *n*-type semiconductor. Current carriers are negatively charged, hence called *n*-type.

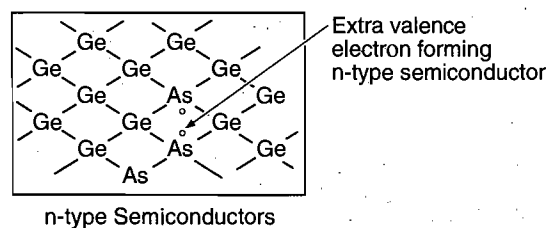


Fig. 4.61 *n*-type Semiconductor

Impurity doping creates donor level just below the conduction band.

On applying potential difference, electrons jump from donor level to the conduction band and conduct electric current.

***p*-type Semiconductor**

Impurity of lower group creates acceptor level just above the valence band. When electrons jump from valence band to acceptor level, a *p*-hole (positively charged hole) is created in valence band. On applying potential difference, these *p*-holes conduct electric current.

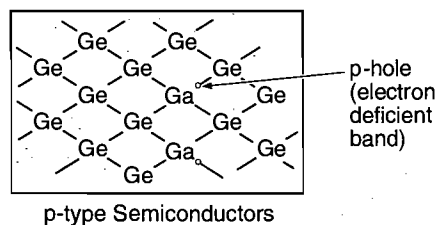


Fig. 4.62 *p*-type Semiconductor

Insulators: Such substances do not conduct electric current; their conductivity is very low. Width of forbidden zone between valence and conduction band is very big; hence electrons are not tossed from valence band to conduction band. On heating they decompose but do not give free conducting electrons.

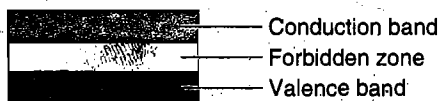


Fig. 4.63

Examples: Classification of transition metal oxides

Metallic	Semiconductors	Insulators
VO	FeO, V ₂ O ₅	MnO
TiO	Fe ₂ O ₃ , Mn ₂ O ₃ Co ₃ O ₄ , Mn ₃ O ₄	
CrO ₂	CuO Cu ₂ O	

TiO and NbO become superconductors at low temperature, about 2 K.

4.25 MAGNETIC PROPERTIES

(i) Paramagnetic Solids

The presence of one or more unpaired electrons in an atom, molecule or ion gives rise to paramagnetism. Such materials are weakly attracted in the field. When they are placed in a magnetic field they become parallel to the field. Domain significance of unpaired electrons are given below:

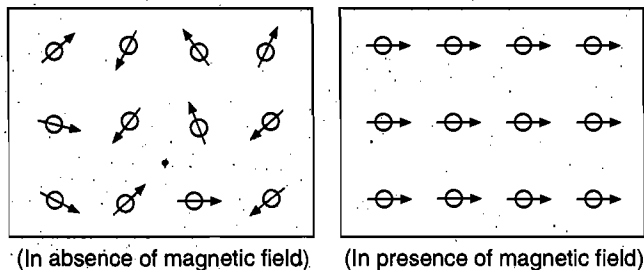


Fig. 4.64

Resultant magnetic field for n -unpaired electrons may be calculated as:

$$\mu_M = \sqrt{n(n+2)}$$

The magnetic field produced by unpaired electrons is due to—
(a) their spin and (b) their orbital motion.

Magnetic moment is measured in Bohr Magnetron (BM)

$$BM = \frac{eh}{4\pi mc}$$

$\mu_S = 1.73$ BM (one unpaired electron)

$\mu_S = 2.83$ BM (two unpaired electrons)

$\mu_S = 3.87$ BM (three unpaired electrons)

$\mu_S = 4.90$ BM (four unpaired electrons)

5.92, 6.93, 7.94 values for five, six and seven unpaired electrons respectively.

(ii) Diamagnetic Solids

The solids, which are weakly repelled by external magnetic field, are called diamagnetic solids and the property thus exhibited is called diamagnetism.

In diamagnetic solids, all electrons have paired spins, i.e., only fully filled orbitals are present. Examples are : NaCl, TiO₂, ZrO₂, KCl etc. Some diamagnetic solids like TiO₂ show para magnetism due to presence of slight non-stoichiometry.

(iii) Ferromagnetic Solids

The solids which are strongly attracted by external magnetic field and do not lose their magnetism when the external field is removed, are called ferromagnetic solids. The property thus, exhibited is termed ferromagnetism.

Ferromagnetic substances can be permanently magnetised. Only three elements, iron (Fe), cobalt (Co) and nickel (Ni) show ferromagnetism at room temperature. Some other examples are : EuO, CrO₂, etc. CrO₂ is the oxide used to make magnetic tapes for use in cassette recorders.

Ferromagnetism arises due to spontaneous alignment of magnetic moments due to unpaired electrons in the same direction as shown below (Fig. 4.65).

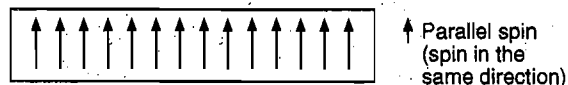


Fig. 4.65 Ferromagnetism

Mechanism of magnetisation of ferromagnetic substances:
Unpaired electron in one atom interacts strongly with unpaired electron of neighbourhood atom, thus they align themselves spontaneously in a common direction in a small volume of solid called domains. Magnetic moments of all atoms in a domain are parallel to each other hence the domain possesses a net magnetic dipole moment. In absence of external magnetic field, the direction of magnetic moments in different domains are randomly oriented in different direction. When external magnetic field is applied then the domains in which the magnetic moments are parallel to external field, expand at the expense of remaining domains and ultimately all the magnetic moments align themselves in the direction of external magnetic field.

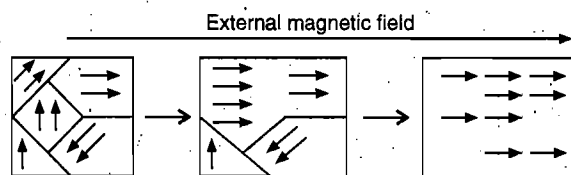


Fig. 4.66 Magnetisation of ferromagnetic substance

(iv) Antiferromagnetic Solids

The solids which are expected to show paramagnetism or ferromagnetism on the basis of unpaired electrons but actually

have zero net magnetic moment are called antiferromagnetic solids.

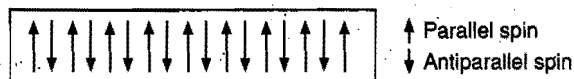


Fig. 4.67 Antiferromagnetism

Magnetic moments are aligned in a compensatory way so as to give zero net magnetic moment. Antiferromagnetism is due to the presence of equal number of magnetic moments in opposite directions as shown above (Fig. 4.67). The important examples are : MnO , MnO_2 , Mn_2O_3 , NiO , CoO , etc.

(v) Ferrimagnetic Solids

The solids which are expected to show large magnetism due to the presence of unpaired electrons but in fact have small net magnetic moment are called ferrimagnetic solids.

Ferrimagnetism arises due to alignment of magnetic moments in parallel and antiparallel directions in unequal numbers resulting in some net magnetic moment. This alignment has been shown ahead (Fig. 4.68).

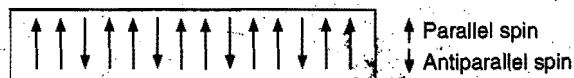


Fig. 4.68 Ferrimagnetism

Examples are : Fe_3O_4 and ferrites of the formula $M^{2+}\text{Fe}_2\text{O}_4$ where $M = \text{Zn}$, Cu , Mg , etc.

Influence of temperature on magnetic character of solids : All magnetically ordered solids (ferromagnetic, antiferromagnetic and ferrimagnetic) change into paramagnetic state on increasing temperature. This is due to randomisation of their spins. The following examples explain this point :

(i) Ferrimagnetic solid, Fe_3O_4 , becomes paramagnetic when heated to 850 K.

(ii) Antiferromagnetic solid, V_2O_3 , becomes paramagnetic when heated to 750 K.

It should be noted that each ferromagnetic solid has a characteristic temperature above which it becomes paramagnetic. The characteristic temperature is called **Curie point** for **Curie temperature**.

Table 4.1 Magnetic Properties of Solid at a Glance

Properties	Information	Magnetic alignment	Example	Application
1. Diamagnetic	Repelled weakly in magnetic field. Such solids have only paired electrons.	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	Benzene, NaCl , TiO_2 , V_2O_5 , etc.	Insulators
2. Paramagnetic	Have unpaired electrons; weakly attracted in magnetic field. They cannot be permanently magnetised.	$\uparrow \downarrow \uparrow \downarrow$	O_2 , VO , CuO , TiO	Electronic devices
3. Ferromagnetic	Also, have unpaired electrons. Strongly attracted in magnetic field. Such solids can be permanently magnetised. On heating to a temperature called Curie Point , these solids change to paramagnetic solid.	$\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$	Fe , Ni , Co , CrO_2	CrO_2 is used in audio, video tapes.
4. Antiferromagnetic	In these solids, unpaired electrons align themselves in such a way that resultant magnetic moment is zero.	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	Cr_2O_3 , CoO , Co_3O_4 , Fe_2O_3 , MnO , MnO_2	Used in the instruments of magnetic susceptibility measurement
5. Ferrimagnetic	Unpaired electrons align themselves in such a way that there is a net magnetic moment.	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$ OR $\uparrow \uparrow \downarrow \downarrow \uparrow \uparrow \downarrow \downarrow$ and so on	Fe_3O_4 , ferrites	—

Table 4.2 Dielectric Properties of Solid at a Glance

Properties	Information	Dipolar property	Example	Application
1. Piezoelectricity	When a crystal of dielectrics is subjected to mechanical stress, then small magnitude current is produced. It is called direct Piezoelectric effect.	Development of charge in some part of crystal.	Quartz and Rochelle salt	Used in mechanical electric transducer, e.g., in record player, transmission of direct signals, sounding of sea depths.
2. Anti piezoelectricity	In some solids, electric field develops mechanical effect.	Crystal suffers elastic deformation in an electric field	—	
3. Ferroelectricity	Piezoelectric crystals having permanent dipoles are said to possess ferroelectricity.	↑↑↑↑↑↑	Ba TiO ₃ , KH ₂ PO ₄ Rochelle salt	Electromagnetic appliances.
4. Anti ferroelectricity	Piezoelectric crystals with zero dipole are said to possess anti ferroelectricity.	↑↓↑↓↑↓	PbZrO ₃ Lead zirconate	
5. Pyroelectricity	Some polar crystals produce electric impulse on heating.	—	Crystals of tartaric acid	Used in fire alarms, and thermostat

Superconductors

Copper and most other metals are good conductors of electricity. But even the best conductors present some resistance to the flow of electricity and a part of electrical energy is converted into heat energy. Thus, generators, turbines, motors of all kinds, transmission lines and other electrical equipment always operate at less than 100% efficiency.

A superconductor is a material that loses all electrical resistance below a characteristic temperature called the superconducting transition temperature, i.e., a superconductor presents no resistance to the flow of electricity.

Electrons move freely through a superconductor without any resistance or friction.

This phenomenon was discovered, in 1911, by the Dutch scientist **Heike Kamerlingh Onnes**, who found that mercury abruptly loses its electrical resistance when it is cooled with liquid helium to 4.2 K. Below its critical temperature (T_c), a superconductor becomes a perfect conductor and an electric current, once started, flows indefinitely without loss of energy. Most metals become superconductors at very low temperatures (generally around 2–5 K), but this temperature is far too cold for any commercial applications.

Since, 1911, scientists have been searching for materials that superconduct or at higher temperatures and more than 6000 superconductors are now known. Niobium alloys are particularly good superconductors and in 1973, a niobium alloy, Nb₃Ge, was found to show superconductivity at 23.2K. The situation changed dramatically in 1986 when **Müller** and **Bednorz** reported a T_c of 35K for the non-stoichiometric barium lanthanum copper oxide, Ba_xLa_{2-x}CuO₄, where x has a value of about 0.1. Soon

thereafter even higher values of T_c for other copper containing oxides : 90 K for YBa₂Cu₃O₇, 125K for Tl₂Ca₂Ba₂Cu₃O₁₀ and 133 K for HgCa₂Ba₂Cu₃O_{8+x}. [YBa₂Cu₃O₇ is also called 1-2-3 compound, i.e., 1 yttrium, 2 bariums and 3 coppers].

Room temperature ' T_c ' superconductors are yet to be discovered. The great advantage of these materials that offer no electrical resistance is the elimination of heating effects as electricity passes through. The energy saving and efficiencies that would be realised are substantial. Superconducting coils of wire could store electricity (in principle) forever, since no energy is lost. Thus, the energy can be tapped as needed. One of the most dramatic properties of a superconductor is its ability to levitate a magnet. When a superconductor is cooled below its T_c and a magnet is lowered towards it, the superconductor and magnet repel each other and the magnet hovers above the superconductor as though suspended in midair. The potential application of this effect will be in the high speed magnetically levitated trains. Some applications of superconductors already exist. For example, powerful superconducting magnets are essential components in the magnetic resonance imaging (MRI) instruments used in medical diagnosis. Superconductors are also used to make the magnets that bend the path of the charged particles in high energy particle accelerators. All the present applications, however, use conventional superconductors ($T_c \leq 20$ K). Of course, the search goes on for materials with higher values of T_c . For applications such as long distance electric power transmission, the goal is a material that superconducts at room temperature.

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. There is a collection of crystalline substances in a hexagonal closed packing. If the density of matter is 2.6 g/cm^3 , what would be the average density of matter in collection? What fraction of space is actually unoccupied?

Solution: In hexagonal closed packing, the packing efficiency is 74.05%.

$$\begin{aligned} \therefore \text{Density of matter} &= \text{Packing fraction} \times \text{Total density} \\ &= \frac{74.05}{100} \times 2.6 = 1.93 \text{ g cm}^{-3} \end{aligned}$$

$$\% \text{ empty space} = 100 - 74.05 = 25.95\%$$

Example 2. The unit cell length of NaCl is observed to be 0.5627 nm by X-ray diffraction studies; the measured density of NaCl is 2.164 g cm^{-3} . Correlate the difference of observed and calculated density and calculate % of missing Na^+ and Cl^- ions.

Solution: We know that,

$$Z = \frac{a^3 \times d \times N}{M}$$

where, Z = number of constituent units per unit cell
= 4 in fcc

$$a = \text{edge length} = 0.5627 \times 10^{-7} \text{ cm}$$

d = density

N = Avogadro's number

M = molar mass

$$\frac{(0.5627 \times 10^{-7})^3 \times d \times 6.023 \times 10^{23}}{58.5} = 4$$

$$d = 2.1805 \text{ g/cm}^3$$

Observed density = 2.164 g/cm^3 which is less than calculated density because some places are missing.

Actual constituent units per unit cell can be calculated as:

$$Z = \frac{(0.5627 \times 10^{-7})^3 \times 2.164 \times 6.023 \times 10^{23}}{58.5} = 3.969$$

$$\text{Missing units} = 4 - 3.969 = 0.031$$

$$\% \text{ missing} = \frac{0.031}{4} \times 100 = 0.775\%$$

Example 3. In a cubic lattice, the closed packed structure of mixed oxides of the lattice is made up of oxide ions; one eighth of the tetrahedral voids are occupied by divalent ions (A^{2+}) while one half of the octahedral voids are occupied by trivalent ions (B^{3+}). What is the formula of the oxides?

Solution: Let there be 80 O^{2-} in the crystal.

$$\therefore \text{Octahedral voids} = 80$$

$$\text{Tetrahedral voids} = 160$$

$$A^{2+} \text{ ions} = \frac{1}{8} \times 160 = 20$$

$$B^{3+} \text{ ions} = \frac{1}{2} \times 80 = 40$$

$$A^{2+} : B^{3+} : O^{2-} = 20 : 40 : 80$$

$$= 1 : 2 : 4$$

$\therefore$ Formula is AB_2O_4 .

Example 4. At 1425°C , Fe crystallises in a body-centred cubic lattice whose edge length is $2.93 \text{ \AA}$. Assuming the atoms to be packed spheres, calculate:

- the radius of the spheres,
- the distance between centres of neighbouring spheres,
- the number of atoms of Fe per unit lattice and
- the total volume occupied by an atom of Fe.

Solution: (a) $a\sqrt{3} = 4r$ where, a = edge length

$$r = \frac{a\sqrt{3}}{4} = \frac{2.93 \times \sqrt{3}}{4} = 1.268 \text{ \AA}$$

- (b) Distance between the centres of neighbouring spheres

$$= 2r = 2 \times 1.268 = 2.537 \text{ \AA}$$

- (c) No. of atoms per unit cell = $8 \times \frac{1}{8} + 1 = 2$.

- (d) Volume occupied by an atom of iron = $\frac{4}{3} \pi r^3$.

Example 5. In face-centred cubic (fcc) crystal lattice, edge length of the unit cell is 400 pm . Find the diameter of the greatest sphere which can be fitted into the interstitial void without distortion of lattice. (IIT 2005)

Solution: In fcc unit cell, we can use

$$a\sqrt{2} = 4r$$

$$r = \frac{a\sqrt{2}}{4} = \frac{400 \times \sqrt{2}}{4} = 141.4 \text{ pm}$$

For octahedral void,

$$2(r + R) = a$$

$$2R = a - 2r$$

$$2R = a - 2r = 400 - 2 \times 141.4 = 117.16 \text{ pm}$$

Diameter of greatest sphere = 117.16 pm .

Example 6. The distance between planes of ions parallel to the face of the unit cell of sodium chloride is 282 pm . The smallest angle of reflection observed in the X-ray diffraction pattern is 5.97° . Calculate the wavelength of the incident radiation.

Solution: Using Bragg's equation,

$$n\lambda = 2d \sin \theta$$

$$1 \times \lambda = 2 \times 282 \times 10^{-12} \sin 5.97$$

$$\lambda = 5.86 \times 10^{-11} \text{ m} = 58.6 \text{ pm}$$

Example 7. CsCl has cubic structure of ions in which Cs^+ ion is present in the body-centre of the cube. If density is 3.99 g cm^{-3} :

- (a) Calculate the length of the edge of a unit cell.
 (b) What is the distance between Cs^+ and Cl^- ions?
 (c) What is the radius of Cs^+ ion if the radius of Cl^- ion is 180 pm?

Solution: We know that,

$$(a) \quad Z = \frac{a^3 \times \rho \times N}{M}$$

$$Z = 1, 1\text{Cs}^+ + 1\text{Cl}^- = 1\text{CsCl}$$

$$M = 168.5$$

$$1 = \frac{a^3 \times 3.99 \times 6.023 \times 10^{23}}{168.5}$$

$$a = 4.123 \times 10^{-8} \text{ cm} = 412 \text{ pm}$$

- (b) Distance between Cs^+ and Cl^- ions

$$= \frac{a\sqrt{3}}{2} = \frac{412 \times \sqrt{3}}{2} = 356.8 \text{ pm}$$

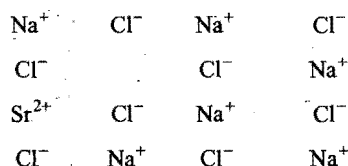
- (c) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = 356.8$

$$r_{\text{Cs}^+} + 180 = 356.8$$

$$r_{\text{Cs}^+} = 176.8 \text{ pm}$$

Example 8. If NaCl is doped with 10^{-3} mol per cent of SrCl_2 , what is the concentration of cation vacancy?

Solution:



Number of cationic vacancies per mol

$$= \frac{10^{-3} \times 6.023 \times 10^{23}}{100} = 6.023 \times 10^{18} \text{ vacancies per mol}$$

Example 9. A metal crystallises into two cubic phases, face-centred cubic (fcc) and body-centred cubic (bcc) whose unit lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of fcc and bcc. (IIT 1999)

Solution: Density of fcc = $\frac{Z_1 \times \text{At. mass}}{\text{Av. no.} \times V_1}$

and density in bcc = $\frac{Z_2 \times \text{At. mass}}{\text{Av. no.} \times V_2}$

$$\frac{d_{\text{fcc}}}{d_{\text{bcc}}} = \frac{Z_1}{Z_2} \times \frac{V_2}{V_1}$$

For fcc $Z_1 = 4; V_1 = a^3 = (3.5 \times 10^{-8})^3$

For bcc $Z_2 = 2; V_2 = a^3 = (3.0 \times 10^{-8})^3$

$$\frac{d_{\text{fcc}}}{d_{\text{bcc}}} = \frac{4 \times (3.0 \times 10^{-8})^3}{2 \times (3.5 \times 10^{-8})^3} = 1.259$$

Example 10. A solid AB has the NaCl structure. If radius of the cation A^+ is 120 pm, calculate the maximum value of the radius of the anion B^- .

Solution: Since, NaCl has octahedral structure,

$$\text{The limiting ratio } \frac{r_A^+}{r_B^-} = 0.414$$

or

$$r_B^- = \frac{r_A^+}{0.414} = \frac{120}{0.414} = 290 \text{ pm}$$

Example 11. You are given marbles of diameter 10 mm. They are to be placed such that their centres are lying in a square bond by four lines each of length 40 mm. What will be the arrangement of marbles in a plane, so that, maximum number of marbles can be placed inside the area. Sketch the diagram and derive expression for the number of marbles per unit area. (IIT 2003)

Solution: In order to accommodate maximum number of spheres, there should be hcp (hexagonal closed packing).

$$\text{Area of square having spherical marbles} = 16 \text{ cm}^2$$

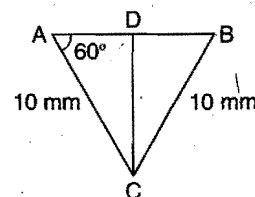
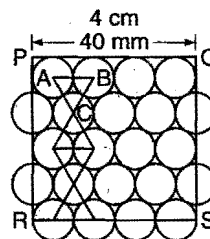
$$\text{Maximum number of spheres} = 14 (\text{full}) + 8 (\text{half})$$

$$\text{Number of spheres} = 18$$

$$\text{Per unit area (per cm}^2\text{)} = \frac{18}{16} = 1.125$$

$$\text{Length } PQ \text{ of square} = 4 \text{ cm}$$

$$\text{Length } PR = 5 + 4 \times 5\sqrt{3} = 40 \text{ mm} = 4 \text{ cm}$$



$$CD = 10 \sin 60^\circ = \frac{10\sqrt{3}}{2} = 5\sqrt{3}$$

Example 12. Calculate the density of diamond from the fact that it has face-centred cubic structure with two atoms per lattice point and a unit cell of edge length 3.569 Å.

Solution: $Z = 8, M = 12$

$$Z = \frac{l^3 \times \rho \times N}{M}$$

$$\text{Density } \rho = \frac{ZM}{l^3 N} = \frac{8 \times 12}{(3.569 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 3.506 \text{ g cm}^{-3}$$

Example 13. An element crystallises into a structure which may be described by a cubic unit cell having one atom at each corner of the cube and two atoms on one of its diagonals. If the volume of this unit cell is $24 \times 10^{-24} \text{ cm}^3$ and density of element is 7.2 g/cm^3 . Calculate the number of atoms present in 200 g of the element.

Solution: Number of atoms in a unit cell (Z) = $1 + 2 = 3$

$$Z = \frac{l^3 \times \rho \times N_A}{M}$$

$$M = \frac{l^3 \times \rho \times N_A}{Z}$$

$$= \frac{24 \times 10^{-24} \times 7.2 \times 6.023 \times 10^{23}}{3} = 34.69$$

$$\text{Number of atoms} = \frac{\text{Mass}}{\text{Molar mass}} \times 6.023 \times 10^{23}$$

$$= \frac{200}{34.69} \times 6.023 \times 10^{23} = 3.47 \times 10^{24}$$

Example 14. Analysis shows that nickel oxide has formula $\text{Ni}_{0.98}\text{O}_1$. What fraction of nickel exist as Ni^{2+} and Ni^{3+} ions?

Solution: Let number of Ni^{3+} ions = x

$$\therefore \text{Number of } \text{Ni}^{2+} \text{ ions} = (0.98 - x)$$

Since, molecule is neutral, its total charge is zero.

$$(+3 \times x) + (0.98 - x) \times 2 - 2 = 0$$

$$x = 0.04, \text{ i.e., } \text{Ni}^{3+} = 0.04; \text{Ni}^{2+} = 0.94$$

Example 15. Calcium crystallises in face-centred cubic unit cell with $a = 0.556 \text{ nm}$. Calculate density if

(i) it contained 0.1% Frenkel defect.

(ii) it contained 0.1% Schottky defect.

Solution: (i) Frenkel defect does not alter the density of solid.

$$d = \frac{MZ}{l^3 N_A} = \frac{40 \times 4}{(0.556 \times 10^{-7})^3 \times 6.023 \times 10^{23}}$$

$$= 1.5455 \text{ g/cm}^3$$

(ii) Schottky defect lowers the density of solid

$$Z = 4 - \frac{4 \times 0.1}{100} = 3.996$$

$$d = \frac{40 \times 3.996}{(0.556 \times 10^{-7})^3 \times 6.023 \times 10^{23}}$$

$$= 1.5440 \text{ g/cm}^3$$

Example 16. Density of lithium atom is 0.53 g/cm^3 . The edge length of Li is $3.5 \text{ \AA}$. Find out the number of lithium atoms in a unit cell. Atomic mass of lithium is 6.94.

[CBSE-PMT (Mains) 2005]

Solution:

$$Z = \frac{a^3 \times \rho \times N_A}{M}$$

$$= \frac{(3.5 \times 10^{-8})^3 \times 0.53 \times 6.023 \times 10^{23}}{6.94}$$

$$= 2$$

Example 17. Cu metal crystallises in face centred cubic lattice with cell edge, $a = 361.6 \text{ pm}$. What is the density of Cu crystal? (Atomic mass of copper = 63.5 amu , $N_A = 6.023 \times 10^{23}$)

[CBSE-PMT (Mains) 2008]

Solution: We know

$$Z = \frac{a^3 \times d \times N_A}{M}$$

$$\therefore d = \frac{ZM}{a^3 N_A} \quad \dots(i)$$

$$Z = 4 \text{ for fcc unit cell ; } M = 63.5 \text{ g mol}^{-1}$$

$$a = 361.6 \times 10^{-10} \text{ cm ; } N_A = 6.023 \times 10^{23}$$

Putting these values in (i), we get

$$d = \frac{4 \times 63.5}{(361.6 \times 10^{-10})^3 \times 6.023 \times 10^{23}} = 8.94 \text{ g cm}^{-3}$$

Example 18. An LPG cylinder weighs 14.8 kg when empty. When full, it weighs 29 kg and shows a pressure of 2.5 atm . In the course of use at 27°C , the weight of the full cylinder reduced to 23.2 kg . Find out the volume of n -butane in cubic metres used up at 27°C and 1 atm .

[Molecular mass of n butane = 58] [CBSE-PMT (Mains) 2008]

Solution: Mass of n -butane used = $29 - 23.2 = 5.8 \text{ kg}$

$$\text{Number of moles of butane used} = \frac{5800}{58} = 100$$

$$V = \frac{nRT}{P} = \frac{100 \times 0.0821 \times 300}{1}$$

$$= 2463 \text{ litre}$$

$$= 2.463 \text{ m}^3$$

Example 19. r_{Na^+} and r_{Cl^-} represents radius of Na^+ and Cl^- ions respectively. If ' n ' is the number of NaCl units per unit cell then give the equation you will use to obtain molar volume.

[CBSE-PMT (Mains) 2009]

Solution: Edge length of unit cell ' a ' = $2(r_{\text{Na}^+} + r_{\text{Cl}^-})$

$$\text{Volume of unit cell} = a^3 = 8(r_{\text{Na}^+} + r_{\text{Cl}^-})^3$$

Volume occupied by one mole of NaCl

$$= \frac{8(r_{\text{Na}^+} + r_{\text{Cl}^-})^3}{n} \times N_A$$

$$\text{where } N_A = 6.023 \times 10^{23}$$

Example 20. Two gases A and B of mass 70.6 g and 167.5 g (M_w of A = 32 and M_w of B = 20) are mixed. Then total pressure of mixture is 25 bar . Calculate partial pressure of A and B.

[CBSE-PMT (Mains) 2009]

Solution: Number of moles A, $n_A = \frac{70.6}{32} = 2.2$

$$\text{Number of moles of } B, n_B = \frac{167.5}{20} = 8.375$$

$$\text{Partial pressure of gas } A, p_A = \frac{n_A}{n_A + n_B} \times p$$

$$= \frac{2.2}{2.2 + 8.375} \times 25 = 5.20 \text{ bar}$$

$$p_B = 25 - 5.20 = 19.8 \text{ bar}$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. **Matter:** Matter is anything which has mass and occupies space. Matter exists in three states, viz., solid, liquid and gas. Any substance can exist in either of the three states depending on temperature and pressure. Liquid and solid states are condensed states as they have much higher densities. Both liquids and gases are termed as fluids as they have flowing ability.

2. **Gaseous state:** It is the simplest state and shows greatest uniformity in behaviour. The gases show almost the same behaviour irrespective of chemical nature, colour or odour. The molecules in a gas possess random motion in all directions. A gas has neither a definite shape nor a definite volume. Gases are characterised by low density, high degree of compressibility and expandability. Gases exert uniform pressure on the walls of the container. They diffuse rapidly and intermix to form homogeneous mixtures. All gases obey certain laws called gas laws.

3. **Gas laws:** Gas laws are based on experiments.

(i) **Boyle's law:** It states that the volume of the given amount of a gas is inversely proportional to its pressure at a constant temperature.

$$V \propto \frac{1}{P} \text{ or } PV = \text{constant} \text{ or } P_1V_1 = P_2V_2 = P_3V_3 = \dots$$

or

$$\frac{P_1}{d_1} = \frac{P_2}{d_2} \quad (\text{at constant temperature})$$

where, d_1 and d_2 are the densities of a gas at pressures P_1 and P_2 . The curves between P and V at constant temperature are hyperbolas and called isotherms.

(ii) **Charles' law:** At constant pressure, the volume of a given amount of a gas is directly proportional to its absolute temperature.

$$V \propto T \text{ or } \frac{V}{T} = \text{constant} \text{ or } \frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = \dots$$

Absolute temperature scale or Kelvin scale starts with -273°C as zero.

$$\text{Absolute temperature (in K)} = 273 + t^\circ\text{C}$$

The absolute zero is that temperature where no gas can exist. The plots of volume against temperature (at constant pressure) are termed as isobars.

(iii) **Pressure law or Gay-Lussac law:** At constant volume, the pressure of a given amount of a gas varies directly as its absolute temperature.

$$P \propto T \text{ or } \frac{P}{T} = \text{constant} \text{ or } \frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{P_3}{T_3} = \dots$$

$$(iv) \text{ Gas equation: } \frac{PV}{T} = \text{constant}$$

$$\text{For one mole of an ideal gas, } PV = RT$$

$$\text{For } n \text{ moles of an ideal gas, } PV = nRT$$

For w g of the gas (mol. mass M),

$$PV = \frac{w}{M} RT$$

or

$$P = \frac{w}{V} \frac{RT}{M} = d \times \frac{RT}{M} \quad (d = \text{density})$$

R is a universal gas constant. It is expressed in the units of work per degree kelvin per mol. Value of R in different units is

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

$$= 82.1 \text{ mL-atm K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

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

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

(v) **Avogadro's law:** Equal volumes of all gases contain equal number of molecules under similar conditions of temperature and pressure. Volume occupied by one mole of any gas at NTP (0°C and 1 atm) is termed **molar volume**. It is 22.4 litre or 22400 mL.

[Note : At 25°C and 1 bar, one mole of a gas has a volume of 25 litre.]

(vi) **Dalton's law of partial pressures:** The total pressure exerted by a mixture of gases which do not react chemically is equal to the sum of their individual pressures (partial pressures) under similar conditions of temperature.

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

$$\text{Partial pressure of a gas} = \text{Molar fraction}$$

$$\times \text{Total pressure of the gas}$$

(vii) **Graham's law of diffusion:** The property of gases to mix with each other to form homogeneous mixture irrespective of gravity is called diffusion. Effusion is a special case of diffusion in which gas passes through a small aperture.

Under similar conditions of temperature and pressure, the relative rates of diffusion of gases are inversely proportional to the square root of their densities or vapour densities or molecular masses. This is Graham's law of diffusion.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{VD_2}{VD_1}} = \sqrt{\frac{M_2}{M_1}}$$

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

4. **Kinetic theory of gases:** The theory with the help of which behaviour of gases can be interpreted mathematically is termed kinetic theory of gases. The main postulates of the theory are:

(a) All gases consist of very large number of small spherical elastic particles called molecules. These are in constant rapid motion in all directions.

(b) There is a lot of empty space between the molecules. The actual volume of gas molecules is negligible in comparison to total volume of the gas.

(c) The pressure exerted by the gas molecules is due to its recorded by molecules against the walls of containing vessel. The collisions between gas molecules are perfectly elastic, i.e., there is no loss of energy during collisions.

(d) There is no effective force of attraction or repulsion between gas molecules. There is no effect of gravity on the motion of gas molecules.

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

On the basis of above postulates, the following equation, known as kinetic gas equation, has been derived.

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

where, P = pressure; V = volume; m = mass of gas molecules; n = number of gas molecules and c = root mean square speed of the gas molecules.

$$\text{Also } PV = RT = \frac{1}{3} mnc^2 = \frac{2}{3} \cdot \frac{1}{2} mnc^2 = \frac{2}{3} \text{ KE}$$

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

$$\begin{aligned} \text{KE of single molecule} &= \frac{3}{2} \frac{RT}{N} \\ &= \frac{3}{2} kT \end{aligned}$$

where, k = Boltzmann constant.

5. **Molecular speeds:** There are three kinds of speed.

(a) **Root mean square speed:** It is the square root of the mean of the squares of the speeds of all the molecules present in a gas.

$$\begin{aligned} \text{rms} = c &= \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n}} \\ &= \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}} \end{aligned}$$

(b) **Average speed:** It is the arithmetic mean of speeds of the molecules present in the gas.

$$\begin{aligned} \text{Average speed} &= \frac{c_1 + c_2 + c_3 + \dots + c_n}{n} = \sqrt{\frac{8RT}{\pi M}} \\ &= 0.9213 \times \text{rms} \end{aligned}$$

(c) **Most probable speed:** It is the speed possessed by majority of the gas molecules. It is equal to

$$\sqrt{\frac{2RT}{M}} \quad \text{or } (0.8164 \times \text{rms})$$

Most probable speed : Average speed : rms speed

$$:: 1 : 1.128 : 1.224$$

6. **van der Waals' equation:** It is an improved form of ideal gas equation. It has been derived after applying two corrections due to two wrong assumptions in kinetic theory of gases. Two corrections are:

(i) volume correction, $V_i = (V - b)$ and

(ii) pressure correction, $P_i = P_{\text{obs}} + \frac{a}{V^2}$.

The equation is $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ for one mole

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

a and b are constants. Units of a are $\text{atm lit}^2 \text{mol}^{-2}$ or $\text{Pa m}^6 \text{mol}^{-2}$ and units of b are litre or dm^3 or m^3 . This equation is applicable to real gases.

Real gases: These do not obey various gas laws strictly under all conditions of temperature and pressure. Deviations are large under high pressure and low temperature.

Ideal gases: These obey laws strictly under all conditions. Actually no gas is ideal.

(a) At very low pressure or at very high temperature, V is large, so $\frac{a}{V^2}$ and b can be neglected. The equation becomes $PV = RT$, i.e., the gas behaves like ideal gas.

(b) At moderate pressure, V is not so large and $\frac{a}{V^2}$ cannot be neglected. However, b can be neglected, so that we have

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

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

(c) At high pressure, V is so small that b cannot be neglected but a/V^2 can be neglected. Hence, the equation becomes

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

$$PV = RT + Pb$$

(d) In case of H_2 and He , the intermolecular forces of attraction are negligible, i.e., a is very small, so that $\frac{a}{V^2}$ can be neglected. The equation becomes

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

$$PV = RT + Pb$$

7. Compressibility factor: The extent of deviation of a real gas from ideal behaviour is expressed in terms of compressibility factor, Z .

$$Z = \frac{PV}{nRT}; Z \text{ is unitless quantity.}$$

(i) For ideal gas $Z = 1$.

(ii) For real gas $Z \neq 1$.

When $Z < 1$, there is negative deviation from ideal behaviour and the gas is more compressible than ideal gas.

When $Z > 1$, there is positive deviation from ideal behaviour and the gas is less compressible than ideal gas.

8. Critical phenomenon: (i) **Critical temperature** is that temperature above which the gas cannot be liquefied with the help of pressure (ii) **Critical pressure** is the minimum pressure required to liquefy the gas at critical temperature (iii) **Critical volume** is the volume occupied by one mole of the gas at its critical temperature and critical pressure.

$$V_c = 3b; P_c = \frac{a}{27b^2}; T_c = \frac{8a}{27bR}$$

Boyle's temperature: It is the temperature above which the gas behaves like an ideal gas. In terms of van der Waals' constants,

$$\text{Boyle's temperature } (T_B) = \frac{a}{Rb}$$

$$T_B > T_c$$

Inversion temperature: It is the temperature to which the gas should be cooled so that expansion is accompanied by further cooling.

9. Molar heat capacity: It is the quantity of heat required to raise the temperature of one mole of a substance through 1°C .

Molar heat capacity = Specific heat capacity $\times$ Molar mass

(i) **Molar heat capacity at constant pressure (C_P):** It is the quantity of heat required to raise the temperature of 1 mole of gas through 1°C under constant pressure. It is equal to $\frac{5}{2}R$.

(ii) **Molar heat capacity at constant volume (C_V):** It is the quantity of heat required to raise the temperature of 1 mole of gas through 1°C under constant volume. It is equal to $\frac{3}{2}R$.

$$C_P - C_V = R$$

For monoatomic gases, $\frac{C_P}{C_V} = \gamma = 1.66$

For diatomic gases, $\frac{C_P}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$

and for triatomic gases, $\frac{C_P}{C_V} = \frac{8R}{6R} = \frac{4}{3} = 1.33$

$$(C_P)_{\text{mixture}} = \frac{n_1 \times (C_P)_1 + n_2 \times (C_P)_2}{n_1 + n_2}$$

10. (i) Volume coefficient, $\alpha_V = \frac{V_t - V_0}{V_0 \times t}$

$$\alpha_V = \frac{1}{273} \quad (\text{for all gases})$$

At constant pressure, increase in volume of a gas per degree rise of temperature per cc of gas at 0°C is called coefficient of volume expansion. Similarly, the pressure coefficient α_P is defined as,

$$\alpha_P = \frac{P_t - P_0}{P_0 \times t} = \frac{1}{273} \quad (\text{for all gases})$$

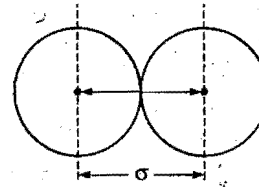
(ii) CO , N_2 , C_2H_4 and B_2H_6 have same molar mass (28) and show same rate of diffusion under identical conditions.

(iii) **Atmolysis** is the process to separate two gases on the basis of difference in their densities and rate of diffusion.

(iv) Average molecular mass of air is 29. If a gas has molecular mass less than air, it is lighter than air and if it has molecular mass greater than air, it is heavier than air, e.g., Cl_2 (71), CO_2 (44) and SO_2 (64) are heavier than air, while H_2 (2), He (4), NH_3 (17) and H_2O (18) are lighter than air.

11. Transport phenomena of gases:

(i) **Collision diameter (σ)** = Distance of closest approach when two molecules are under collision.



(ii) **Collision number:** It is the number of collisions of a molecule with other molecules in one second.

$$N_c = \frac{\sqrt{2} \pi v_{av} \sigma^2 N}{V}$$

where, v_{av} = Average velocity of molecules

N = Number of molecules

V = Volume of molecules

(iii) **Collision frequency (Z):** It is the number of molecular collisions taking place per second per unit volume of the gas.

$$Z = \frac{1}{\sqrt{2}} \pi v_{av} \sigma^2 \left(\frac{N}{V} \right)^2$$

(iv) **Mean free path λ :** It is the average distance travelled between two successive collisions.

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 \left(\frac{N}{V} \right)}$$

$\lambda \propto T$ (at constant pressure)

$\lambda \propto \frac{1}{P}$ (at constant temperature)

$\lambda \propto \frac{1}{\sigma}$ (at constant temperature and pressure)

12. Liquid state: Liquid state is condensed gas or molten solid. Liquids have definite volume but no definite shape.

Liquids diffuse slowly and are almost incompressible. Some important properties of liquids are:

(i) **Evaporation:** It is the spontaneous change in which a liquid changes into vapours at the surface of liquid. It increases with increase of surface area, increase in temperature and decrease in intermolecular forces. It causes cooling.

(ii) **Vapour pressure:** It is the pressure exerted by the vapours of a liquid in equilibrium with the liquid at a given temperature. It increases with increase of temperature. Liquids with low intermolecular forces have high vapour pressure.

(iii) **Boiling point:** It is the temperature at which the vapour pressure of a liquid becomes equal to atmospheric pressure. Temperature of the liquid remains constant after it starts boiling as the energy supplied increases the potential energy but its kinetic energy remains constant. Boiling point changes with the pressure of surroundings.

$$\log \left(\frac{P_2}{P_1} \right) = \frac{\Delta H_v}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where, ΔH_v = latent heat of vaporisation; P_2 and P_1 are vapour pressures at T_2 and T_1 .

(iv) **Surface tension:** It is the force in dyne acting on the surface at right angles to any line of unit length. It decreases generally with increase in temperature. It is expressed in J m^{-2} or N m^{-1} or dyne cm^{-1} .

(a) Surface tension is molecular phenomenon of liquid involving the force of cohesion among the liquid molecules.

(b) Maximum potential energy of liquid molecules is on the surface.

(c) Surface tension is numerically equal to the surface energy. The work required to increase or extend the surface area by 1 sq. cm is called surface energy.

(d) Surface tension is a scalar quantity.

(e) Sparingly soluble solutes like soap and detergent decrease the surface tension of the liquid. However, fairly soluble solutes like sugar and salt increase the surface tension of the liquid.

(f) Liquid drops are spherical because liquid surface has a tendency to acquire minimum surface area.

(g) Greater is the intermolecular force, more is the surface tension.

e.g.,

Soap in water < Water < Mercury

$\text{H}_2\text{O} > \text{C}_2\text{H}_5\text{OH} > \text{CH}_3\text{OCH}_3$

CH_2OH

	CH_2OH	
CHOH		$\text{CH}_3\text{CH}_2\text{OH}$
	CH_2OH	Ethanol
CH_2OH	Glycerol	
	Glycerol	

(v) **Viscosity:** It is the resistance in a liquid to flow. The force in newton per square metre required to maintain a difference of velocity of one metre per second between two parallel layers of a liquid at a distance of one metre from each other is called coefficient of viscosity. It is expressed in $\text{g m}^{-1} \text{s}^{-1}$.

Or

The force per unit area required to maintain unit difference of velocity between two consecutive parallel layers of the liquid which are one centimetre apart. It is expressed in $\text{dyne cm}^{-2} \text{s}^{-1}$ or poise.

The reciprocal of coefficient of viscosity is called **fluidity**. Liquids with low viscosity are termed mobile while others with high viscosity are called viscous. Viscosity is high in liquids with high intermolecular forces, high molecular masses and having branching in the chain of the molecule. Viscosity decreases with increase in temperature.

(vi) **Reynold's number:** The nature of flow of a liquid through a tube depends on the value of Reynold's number N_R .

$$N_R = \frac{2r\bar{v}\rho}{\eta}$$

where, r = Radius of the tube

$\bar{v}$ = Average velocity of the fluid

ρ = Density of liquid

η = Coefficient of viscosity

Case I: When $N_R > 4000$, the flow is called turbulent flow.

Case II: When $N_R < 2100$, the flow is called laminar flow.

13. **The solid state:** The particles are closely packed and are held together by strong intermolecular forces. The particles cannot move at random. They have only vibrational motion. Solids have definite shape and definite volume. They possess high density and low compressibility. Solids are divided into two classes: (i) amorphous solids and (ii) crystalline solids. In amorphous solids, the arrangement of building constituents is not regular but haphazard. Their melting points are not sharp. These are isotropic in nature.

In crystalline solids, building constituents arrange themselves in regular manner throughout the entire three-dimensional network. Crystalline solids consist of large number of units called crystals. A crystal is defined as a solid figure which has definite geometrical shape with flat faces and sharp edges. It has a sharp melting point and anisotropic in nature.

14. **Types of symmetry in crystals:** The total number of planes, axes and centres of symmetry possessed by a crystal are termed as elements of symmetry.

(i) **Centre of symmetry:** It is an imaginary point within the crystal such that any line drawn through it intersects the surface of the crystal at equal distances in both directions. A crystal always possess only one centre of symmetry.

(ii) **Plane of symmetry:** It is an imaginary plane which passes through the centre of a crystal and divides it into two equal portions such that one part is exactly the mirror image of the other.

(iii) **Axis of symmetry:** It is an imaginary straight line about which, if the crystal is rotated, it will present the same appearance more than once during the complete revolution.

A cubic crystal possesses a total of 23 elements of symmetry.

15. **Space lattice and unit cell:** The geometrical form consisting of a regular array of points in space is called a space

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

The smallest repeating unit in a space lattice which when repeated over and over again results in a crystal of the given substance is termed unit cell. A unit cell possesses all the structural properties of the given crystal. The edges of the unit cell are designated as a , b and c , and the angles between three imaginary axes as α , β and γ respectively.

16. Crystal systems: Seven types of basic or primitive unit cells have been recognised among crystals. These are:

1. Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$ NaCl, KCl, ZnS
2. Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ KNO_3 , BaSO_4
3. Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ NH_4Br , SnO_2
4. Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$ Monoclinic sulphur, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
5. Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_3BO_3
6. Hexagonal $a \neq b \neq c$ $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$ ZnO, AgI, SiC
7. Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$ NaNO_3 , CaCO_3

All crystals do not have simple lattices. There can be 14 different ways in which similar points can be arranged in a three dimensional space. The crystals belonging to a cubic system have three kinds of lattices:

(i) **Simple cubic lattice:** There are points only at the corners of each unit.

(ii) **Face-centred cubic lattice:** There are points at the corners as well as at the centre of each of the six faces of the cube.

(iii) **Body-centred cubic lattice:** There are points at the corners as well as in the centre of each cube.

Type of lattice point	Contribution to one unit cell
Corner	$\frac{1}{8}$
Edge	$\frac{1}{4}$
Face-centre	$\frac{1}{2}$
Body-centre	1

- Halides of alkali metals except those of Cs, ammonium halides, oxides and sulphides of alkaline earth metals except BeS and halides of silver except AgI have rock salt (NaCl type) structure.
- CsCl, CsBr, CsI, TiCl, TiBr, TiI have CsCl type structure.
- CuCl, CuBr, CuI, AgI, BeS have zinc blende structure (ZnS type).
- SrCl_2 , SrF_2 , BaCl_2 , BaF_2 , CdF_2 , HgF_2 have fluorite (CaF_2) structure.
- Na_2O , K_2O , Na_2S , K_2S have antifluorite (Li_2O type) structure.

17. Bragg's law: When X-rays are incident on a crystal face, they penetrate into the crystal and strike the atoms in different planes. From each of these planes, X-rays are deflected.

Bragg presented a relationship between the wavelength of the X-rays and the distance between the planes.

$$n\lambda = 2d \sin \theta$$

Where, n is an integer such as, 1, 2, 3, ..., λ is the wavelength, d is the distance between repeating planes of particles and θ the angle of deflection or glancing angle.

18. Characteristics of cubic systems:

(i) **Number of atoms per unit cell:** (a) Simple cubic structure—one atom per unit cell, (b) Face-centred cubic structure—4 atoms per unit cell and (c) Body-centred cubic structure—2 atoms per unit cell.

(ii) **Density of lattice matter** = $\frac{n \times M}{N_0 \times a^3}$

where, n is the number of atoms in unit cell, M is the atomic mass or molecular mass, N_0 is Avogadro's number and a = edge length of the cubic unit cell.

(iii) Atomic radius:

(a) Simple cubic cell—Radius of atom = $\frac{a}{2}$

(b) Face-centred cubic cell—Radius of atom = $\frac{a}{2\sqrt{2}}$

(c) Body-centred cubic cell—Radius of atom = $\frac{\sqrt{3}}{4} a$

19. Close packing of constituents: It refers to the arrangement in which constituents occupy maximum available space. The two common types of close packing are:

(a) **AB AB ... arrangement.** This gives hexagonal close packing.

(b) **ABC ABC ... arrangement.** This gives cubical close packing.

In the packing of constituents, some interstitial sites are left. These sites are termed voids. The interstitial site between four spheres is tetrahedral and between six spheres is octahedral.

The space occupied by hard spheres in hcp; ccp (fcc) is 74%; in bcc it is 68%; in simple cubic it is 52% and in diamond it is 34%; thus, only fcc and hcp are close packed structures.

(i) hcp is present in Be, Mg, Ca, Cr, Mo, V and Zn.

(ii) ccp is present in Fe, Cu, Ag, Au, Pt, Al and Ni.

(iii) bcc is present in alkali metals.

(iv) All noble gases have ccp structure except helium which has hcp structure.

If 'n' spheres are present in packing, then the numbers of tetrahedral and octahedral voids are $2n$ and n respectively.

20. The coordination number: The nearest neighbours with which a given sphere is in contact is called coordination number. It depends upon structure.

(a) Simple cubic structure: coordination number = 6

(b) Face-centred cubic structure: coordination number = 12

(c) Body-centred cubic structure: coordination number = 8

For ionic solids, the ratio of the radius of cation to that of anion is called radius ratio. The radius ratio for a given coordination number is fixed.

For radius ratio (0.155–0.225) coordination number = 3

For radius ratio (0.225–0.414) coordination number = 4

For radius ratio (0.414–0.732) coordination number = 6

For radius ratio (0.732–1.0) coordination number = 8

21. Types of crystals: Depending upon the nature of forces that hold the constituent particles together in the crystal lattice, crystals are classified into four types:

(i) **Ionic crystals:** The forces are electrostatic. The lattice points are occupied by positively and negatively charged ions. These crystals are quite hard, have low volatility and have high melting and boiling points. These are insulators but become good conductors in molten state. These are soluble in polar solvents and highly brittle in nature. NaCl, KCl, BaCl₂, etc., belong to this class.

(ii) **Covalent crystals:** The constituent particles are the atoms of same or different elements which are held by strong covalent bonds. These solids are very hard and have very high melting points. Diamond and carborundum belong to this class.

(iii) **Metallic crystals:** The metallic crystals have positive metal ions as lattice points surrounded by a sea of mobile electrons. Each electron belongs to a number of positive ions and each positive ion belongs to a number of electrons. The force that binds a metal ion to a number of electrons is known as metallic bond. Metallic crystals mostly belong to fcc, bcc and hcp systems. These are good conductors, possess lustre and are hard, tough, malleable and ductile in nature.

(iv) **Molecular crystals:** The constituent units of molecular crystals are molecules. The forces holding the molecules are weak van der Waals' forces. Molecular solids are soft and vaporise easily. These are bad conductors of electricity and possess low density. Examples are ice, solid, CO₂, etc.

22. Defects in crystals: An ideal crystal is the one which has the same unit cell containing the same lattice points

throughout the whole of the crystal. At absolute zero, the crystals are ideal but with rise in temperature, there is a chance of distortion. The defect may be at a point along a line or over a surface.

(i) **Schottky defect:** This defect is caused if some of the lattice points are unoccupied. The points which are unoccupied are called vacancies or holes. The number of missing positive and negative ions is the same and, thus, the crystal is neutral. Such defect is common in ionic compounds with high coordination number where the cations and anions are of similar size, e.g., NaCl, KCl, KBr, etc.

(ii) **Frenkel defect:** This defect is caused when some of the ions of the lattice occupy interstitial sites leaving lattice sites vacant. This defect appears generally in ionic crystals in which anion is much larger in size than the cation, e.g., AgBr, ZnS.

In Schottky defect, density decreases while in Frenkel defect it remains the same. In both the defects, electrical conductivity is observed to some extent. The overall chemical composition of the substance does not change. However, there are other defects in which there is change in overall chemical combination. Such defects are termed **non-stoichiometric defects**. In such crystals, there is excess of either positive particles or negative particles. However, the crystal is neutral in nature.

Positive particle excess defects: (i) A negative ion may be missing from the lattice site which is occupied by an extra electron. (ii) An extra positive particle is present in the interstitial position. To maintain neutrality, an extra electron also occupies a place in the interstitial space. Such crystals are usually coloured and semiconductors.

Positive particle deficiency defect: One of the positive particles may be missing from its lattice site. The extra negative charge may be balanced if a nearby positive particle acquires extra positive charge. Such crystals are also semiconductors. Examples are FeO, FeS, NiO, etc.

Certain defects in crystals arise due to presence of chemical impurities. These are known as impurity defects.

Questions

1. Matrix Match Type Questions:

[A] Match the crystalline solids in Column-I with the coordination number of their ions in Column-II:

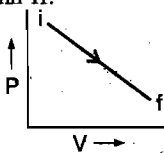
Column-I

- (a) CsCl
(b) CaF_2
(c) ZnS
(d) Na_2O

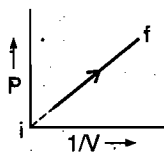
Column-II

- (p) Coordination number of cation = 8
(q) Coordination number of anion = 4
(r) Coordination number of cation = 4
(s) Coordination number of anion = 8

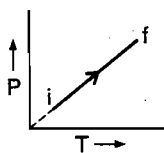
[B] The diagrams below depict the different processes for a given amount of an ideal gas. Match the Column-I and Column-II:



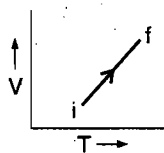
(i)



(ii)



(iii)



(iv)

i → initial state,

f → final state

Column-I

- (a) Fig. (i) : System proceeding from initial state to final state
(b) Fig. (ii) : System from initial state to final state
(c) Fig. (iii) : System proceeding from initial state to final state
(d) Fig. (iv) : System proceeding from initial state to final state

Column-II

- (p) Temperature will remain constant
(q) Pressure will decrease
(r) Volume will be constant
(s) Temperature may increase or decrease or may first increase and then decrease

[C] Match Column-I with Column-II for ideal gases:

Column-I

- (a) If temperature of given gas is increased
(b) If the pressure of a given gas is increased at constant temperature
(c) If the density of a given gas is lowered at constant temperature
(d) If the volume of a given gas is increased at constant temperature

Column-II

- (p) Average speed of gas will increase
(q) Root mean square speed of gas molecules will increase
(r) Most probable speed of gas molecules will increase
(s) Speed of gas molecules will not change

[D] Match the Column-I with Column-II:

Column-I

- (a) Boyle's temperature
(b) $\frac{1}{2}$ (Inversion temperature)
(c) Critical temperature
(d) Critical pressure

Column-II

- (p) a/Rb
(q) $8a/27Rb$
(r) The gas cannot be liquefied above this temperature, on applying pressure
(s) $a/27b^2$

[E] Match the Column-I with Column-II:

Column-I

- (a) Real gas at high pressure
(b) Force of attraction among gas molecules is negligible
(c) At high temperature and low pressure
(d) Real gas at N.T.P.

Column-II

- (p) $PV = RT + Pb$
(q) $PV = nRT$
(r) $Z = 1$
(s) $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

[F] Match the Column-I with Column-II:

Column-I

- (a) Internal energy of gas
(b) Translational kinetic energy of gas molecules
(c) The temperature at which there is no molecular motion
(d) The lowest possible temperature at which gas molecules have no heat

Column-II

- (p) $\frac{3}{2}RT$
(q) $\frac{5}{2}RT$
(r) -273°C
(s) 3.716 kJ at 298 K

[G] Match the Column-I with Column-II:

Column-I

- (a) NaCl
(b) ZnS
(c) AgBr
(d) KCl

Column-II

- (p) Schottky defect
(q) Frenkel defect
(r) Develops yellow colour on heating due to F-centre
(s) Develops blue/violet colour on heating due to F-centre

[H] Match the crystalline solids in Column-I with packing arrangement in Column-II:

Column-I**Column-II**

- | | |
|---------------------------|-------------------------------------|
| (a) CaF_2 | (p) Cations are in ccp arrangement |
| (b) NaCl | (q) Anions are in tetrahedral voids |
| (c) ZnS | (r) Anions are in ccp arrangement |
| (d) Na_2O | (s) Cations are in octahedral voids |

[I] Match the crystal system in Column-I with unit cell dimensions in Column-II:

Column-I**Column-II**

- | | |
|------------------|---|
| (a) Cubic | (p) $a = b = c$ |
| (b) Rhombohedral | (q) $\alpha = \beta = \gamma = 90^\circ$ |
| (c) Orthorhombic | (r) $a \neq b \neq c$ |
| (d) Triclinic | (s) $\alpha \neq \beta \neq \gamma \neq 90^\circ$ |

[J] Match the crystal system in Column-I with Bravais lattice in Column-II:

Column-I
(Crystal System)**Column-II**
(Bravais lattice)

- | | |
|------------------|---|
| (a) Cubic | (p) Primitive only |
| (b) Hexagonal | (q) Primitive, body centred |
| (c) Tetragonal | (r) Primitive, face centred, body centred |
| (d) Orthorhombic | (s) Primitive, face centred, body centred and end centred |

[K] Match the Column-I with Column-II:

Column-I**Column-II**

- | | |
|---|-------------------------------|
| (a) Root mean square velocity | (p) $\sqrt{\frac{3P}{d}}$ |
| (b) Average velocity | (q) $\sqrt{\frac{3RT}{m}}$ |
| (c) Most probable velocity | (r) $\sqrt{\frac{8P}{\pi d}}$ |
| (d) Velocity possessed by maximum fraction of molecules | (s) $\sqrt{\frac{2RT}{m}}$ |

Answers

1. [A] (a — p, s); (b — p, q); (c — q, r); (d — r, s)
 [B] (a — s); (b — p); (c — r); (d — q)
 [C] (a — p, q, r); (b — s); (c — p, q, r); (d — s)
 [D] (a — p); (b — p); (c — q, r); (d — s)
 [E] (a — p); (b — p); (c — q, r); (d — s)
 [F] (a — p, q, s); (b — p, s); (c — r); (d — r)

- [G] (a — p, r); (b — q); (c — p, q); (d — p, s)
 [H] (a — p, q); (b — r, s); (c — q); (d — q)
 [I] (a — p, q); (b — p); (c — q, r); (d — r, s)
 [J] (a — r); (b — p); (c — q); (d — s)
 [K] (a — p, q); (b — r); (c — s); (d — s)

● PRACTICE PROBLEMS ●

1. A gas occupies a volume of 250 cm^3 at 745 torr and 25°C . What additional pressure is required to reduce the gas volume to 200 cm^3 at the same temperature?

[Ans. 186.25 torr]

2. A vessel of 120 cm^3 contains a certain mass of a gas at 20°C and 750 torr pressure. The gas was transferred to a vessel of volume 180 cm^3 . Calculate the pressure of the gas at the same temperature.

[Ans. 500 torr]

3. A gaseous system has a volume of 580 cm^3 at a certain pressure. If its pressure is increased by 0.96 atm, its volume becomes 100 cm^3 . Determine the pressure of the system.

[Ans. 0.2 atm]

[Hint: $P \times 580 = (P + 0.96)100$]

4. A gas filled freely collapsible balloon is pushed from the surface level of a lake to a depth of 50 m. Approximately what per cent of its original volume will the balloon finally have, assuming that the gas behaves ideally and temperature is same at the surface and at 50 m depth?

[Ans. 17.13]

[Hint: P_1 = Pressure at the surface = 1 atm
 $= 76.0 \times 13.6 \times 981 \text{ dyne/cm}^2$

$$P_2 = \text{Pressure at a depth of 50 m} \\ = 76.0 \times 13.6 \times 981 + (50 \times 100) \times 1 \times 981 \text{ dyne/cm}^2 \\ = 981[76.0 \times 13.6 + 5000] \\ = 981 \times (6033.6) \text{ dyne/cm}^2$$

Now apply Boyle's law, $P_1V_1 = P_2V_2$
 or $\frac{V_2}{V_1} = \frac{P_1}{P_2} = \frac{76.0 \times 13.6 \times 981}{981 \times 6033.6} = 0.1713$
 $\% = 0.1713 \times 100 = 17.13$

5. A sample of gas at room temperature is placed in an evacuated bulb of volume 0.51 dm^3 and is found to exert a pressure of 0.24 atm. The bulb is connected to another evacuated bulb whose volume is 0.63 dm^3 . What is the new pressure of the gas at room temperature?

[Ans. 0.1074 atm]

6. It is desired to increase the volume of 800 cm^3 of a gas by 20% keeping the pressure constant. To what temperature should the gas be heated, if the initial temperature is 22°C ?

[Ans. 81°C]

7. A chamber of constant volume contains hydrogen gas. When the chamber is immersed in a bath of melting ice (0°C) the pressure of the gas is 800 torr. What pressure will be indicated when the chamber is brought to 100°C ?

[Ans. 1093 torr]

8. Calculate the volume occupied by 4.045×10^{23} molecules of oxygen at 27°C and having a pressure of 700 torr.

[Ans. 17.97 dm^3]

[Hint: No. of moles ' n ' = $\frac{4.045 \times 10^{23}}{6.023 \times 10^{23}} = 0.672$; $P = \frac{700}{760} \text{ atm}$

Now use the gas equation, $PV = nRT$]

9. Calculate the moles of hydrogen present in a 500 cm^3 sample of hydrogen gas at a pressure of 760 mm of Hg and 27°C .

[Ans. $2.03 \times 10^{-2} \text{ mol}$]

[Hint: $500 \text{ cm}^3 = 0.5 \text{ L}$, 760 mm of Hg = 1 atm. Now apply the gas equation, $n = \frac{PV}{RT}$]

10. Calculate the volume occupied by 4 mole of an ideal gas at $2.5 \times 10^5 \text{ Nm}^{-2}$ pressure and 300 K temperature.

[Ans. 39.9 dm^3]

[Hint: $V = \frac{nRT}{P}$, Given, $n = 4$; $R = 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1}$;

$T = 300$; $P = 2.5 \times 10^5 \text{ Nm}^{-2}$]

11. What is the volume occupied by 11 g of carbon dioxide at 27°C and 780 mm of Hg pressure?

[Ans. 6 litre]

[Hint: 780 mm of Hg = $\frac{780}{760} \text{ atm}$; $w = 11 \text{ g}$; $M = 44 \text{ g mol}^{-1}$.

Now apply $V = \frac{w}{M} \cdot \frac{RT}{P}$]

12. A certain quantity of a gas occupies 200 mL when collected over water at 15°C and 745 mm pressure. It occupies 182.6 mL in dry state at NTP. Find the vapour pressure of water at 15°C .

[Ans. 13 mm]

13. The density of a gas is found to be 2.07 g L^{-1} at 30°C and 2 atmospheric pressure. What is its density at NTP?

[Ans. 1.149 g L^{-1}]

[Hint: Apply $P_1 = \frac{D_1}{M} RT_1$, $P_2 = \frac{D_2}{M} RT_2$

So, $\frac{P_1}{D_1 T_1} = \frac{P_2}{D_2 T_2}$]

14. At the top of a mountain, the thermometer reads 0°C and the barometer reads 700 mm Hg. At the bottom of the mountain the thermometer reads 30°C and the pressure 760 mm Hg. Compare the density of the air at the top with that at the bottom.

[Ans. 1.02 : 1]

[Hint: Density is inversely proportional to volume.

$$\frac{d_{\text{top}}}{d_{\text{bottom}}} = \frac{V_b}{V_t} = \frac{T_b P_t}{T_t P_b} = \frac{303 \times 700}{273 \times 760} = \frac{1.02}{1}]$$

15. Calculate the volume occupied by 5 g of acetylene gas at 50°C and 740 mm of pressure. (IIT 1991)

[Ans. 5.23 litre]

16. Calculate the volume occupied by 7 g of nitrogen gas at 27°C and 750 mm Hg pressure. (MLNR 1992)

[Ans. 6.24 litre]

17. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 20 atm and 27°C . The cylinder can hold 2.82 litre of water at NTP. Calculate the number of balloons that can be filled up. (MLNR 1991)

[Ans. 10]

[Hint: Volume of one balloon

$$= \frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} \times \left(\frac{21}{2}\right)^3 = 4851 \text{ cm}^3$$

$$= 4.851 \text{ litre}$$

Let n balloons be filled; thus, total volume of hydrogen used in filling balloons

$$= 4.851 \times n \text{ litre}$$

Total volume of hydrogen in the cylinder at NTP,

$$V = \frac{20 \times 2.82 \times 273}{300 \times 1} = 51.324 \text{ litre}$$

Actual volume of H_2 to be transferred to balloons

$$= 51.324 - 2.82 \text{ (2.82 litre retained in the cylinder)}$$

$$= 48.504 \text{ litre}$$

$$\text{No. of balloons filled 'n' = } \frac{48.504}{4.851} = 10]$$

18. An open vessel at 27°C is heated until three-fifth of the air in it has been expelled. Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated? (MLNR 1990)

[Ans. 477°C]

[Hint: Both volume and pressure are constant as the vessel is open,

$$\text{i.e., } n_1 RT_1 = n_2 RT_2$$

$$\text{or } \frac{n_1}{n_2} = \frac{T_2}{T_1}$$

$$\text{If } n_1 = 1, n_2 = 1 - \frac{3}{5} = \frac{2}{5}$$

$$\text{So, } \frac{5}{2} = \frac{T_2}{300} \text{ or } T_2 = 750 \text{ K} = 477^\circ\text{C}]$$

19. A gaseous mixture of He and O_2 is found to have a density of 0.518 g L^{-1} at 25°C and 720 torr. What is the per cent by mass of helium in this mixture?

[Ans. 19.88]

[Hint: First determine the average molecular mass and then number of moles of helium and oxygen.

$$\text{Moles of helium} = 0.665; \text{ Moles of oxygen} = 0.335$$

$$\text{Mass per cent of helium} = \frac{4 \times 0.665}{4 \times 0.665 + 32 \times 0.335} \times 100$$

$$= 19.88]$$

20. A sample of natural gas is 85.2% methane and 14.8% ethane by mass. What is the density of this mixture at 18°C and 748 mm Hg?

[Ans. 0.74 g L^{-1}]

[Hint: Molecular mass of mixture,

$$M = \frac{85.2}{100} \times 16 + \frac{14.8}{100} \times 30 = 13.632 + 4.44 = 18.07$$

$$PM = dRT$$

$$d = \frac{PM}{RT} = \frac{748}{760} \times \frac{18.07}{0.0821 \times 291} = 0.74 \text{ g L}^{-1}$$

21. 125 mL of a gas A of pressure 500 mm is mixed with 200 mL of another gas B at a pressure of 300 mm in a vessel of 150 mL capacity. What will be the total pressure of the resulting mixture if the temperature is kept constant?

[Ans. 816.67 mm]

22. Two vessels whose volumes are in the ratio 2 : 1 contain nitrogen and oxygen at 800 mm and 680 mm pressures respectively, when they are connected together what will be the pressure of the resulting mixture?

[Ans. 760 mm]

23. A 10 litre flask at 298 K contains a gaseous mixture of CO and CO₂ at a total pressure of 2 atm. If 0.20 mole of CO is present, find its partial pressure and also that of CO₂.

[Ans. Partial pressure of CO = 0.49 atm; partial pressure of CO₂ = 1.51 atm]

24. Calculate the total pressure in a mixture of 4 g of oxygen and 3 g of hydrogen confined in a total volume of one litre at 0°C.

(MLNR 1991)

[Ans. 25.18 atm]

[Hint: Determine total number of moles and then apply

$$PV = n_{\text{total}} RT]$$

25. A gas cylinder contains 55% nitrogen, 20% oxygen and 25% carbon dioxide by mass, at 760 mm pressure. Calculate the partial pressure of each gas.

[Ans. 472.8 mm, 150.44 mm, 136.74 mm]

26. The density of a mixture of N₂ and O₂ at NTP is 1.3 g L⁻¹. Calculate partial pressure of O₂.

[Ans. 0.28 atm]

[Hint: Let n_1 and n_2 moles of N₂ and O₂ be present in the mixture respectively.

$$\text{Average molecular mass of the mixture} = \frac{28n_1 + 32n_2}{n_1 + n_2} \quad \dots (i)$$

Average molecular mass from general gas equation,

$$M = \frac{D}{P} \times RT = \frac{1.3}{1} \times 0.0821 \times 273 = 29.137 \quad \dots (ii)$$

$$\text{So, } \frac{28n_1 + 32n_2}{n_1 + n_2} = 29.137 \text{ or } \frac{4n_2}{n_1 + n_2} = 1.137$$

$$\text{or } \frac{n_2}{n_1 + n_2} = 0.28 = \text{mole fraction of oxygen}$$

$$\text{Partial pressure of O}_2 = 0.28 \times 1 = 0.28 \text{ atm}]$$

27. At a definite pressure and temperature, 100 mL of hydrogen diffused in 20 minute. How long will 40 mL of oxygen take to diffuse under similar conditions?

[Ans. 32 minute]

28. At a given temperature and pressure, 20 mL of air diffused through a porous membrane in 15 second. Calculate the volume of carbon dioxide which will diffuse in 10 second if the vapour density of air is 14.48.

[Ans. 10.8 mL]

29. At room temperature, ammonia gas at one atmospheric pressure and hydrogen chloride at P atmospheric pressure are allowed to effuse through identical pinholes from opposite ends of a glass tube of one metre length and uniform cross reaction. NH₄Cl is first formed at a distance of 60 cm from the end through which HCl gas is sent in. What is the value of P ?

[Ans. 2.198 atm]

$$[\text{Hint: } \frac{r_{\text{HCl}}}{r_{\text{NH}_3}} = \sqrt{\frac{M_{\text{NH}_3}}{M_{\text{HCl}}} \times \frac{P_{\text{HCl}}}{P_{\text{NH}_3}}]$$

30. The rate of effusion of an unknown gas (X) through a pinhole is found to be 0.279 times the rate of effusion of hydrogen gas through the same pinhole, if both are at STP. What is the molecular mass of the unknown gas? [CEE (Bihar) 1991]

[Ans. 25.69]

31. In a 2 m long narrow tube, HCl is allowed to diffuse in the tube from one end and NH₃ from the other end. If diffusion is started at the same time, predict at what point the white fumes of NH₄Cl will form?

[Ans. NH₄Cl will form at 1.1886 m from the NH₃ end of the tube]

32. The composition of air is approximately 80% N₂ and 20% O₂ by mass. Calculate density of air at 293 K and 76 cm Hg pressure.

[Ans. 1.19 g L⁻¹]

[Hint: Determine first average molecular mass of air and then apply $D = \frac{P \times M_{\text{av}}}{RT}$]

33. Calculate the internal energy of one gram mole of nitrogen at 150°C assuming it to be an ideal gas.

[Ans. 5.275×10^{10} erg]

34. Calculate the kinetic energy of 5 mole of a gas at 27°C in erg and calorie.

[Ans. 1.8706×10^{11} erg, 4477 cal]

35. A glass tumbler containing 243 mL of air at 100 kPa and 20°C is turned upside down and immersed in a water bath to a depth of 20.5 metre. The air in the glass is compressed by the weight of water above it. Calculate the volume of air in the glass assuming the temperature and the barometric pressure have not changed.

[Ans. 80.7 mL]

[Hint: Hydrostatic pressure = $h \times d \times g$

$$= 20.5 \times 1 \times 9.81$$

$$= 201.105 \text{ kPa}$$

Inside the water bath atmospheric pressure and hydrostatic pressure acts:

$$P_{\text{total}} = 100 + 201.105 = 301.105 \text{ kPa}$$

$$P_1 V_1 = P_2 V_2$$

$$100 \times 243 = 301.105 \times V_2$$

$$V_2 = 80.70 \text{ mL}]$$

36. Calculate the rms speed of the molecules of ethane gas of volume 1.5 litre at 750 mm of Hg pressure.

[Ans. 1.225×10^4 cm/sec]

37. The density of a gas at 1.5 atm is 1.52 g L⁻¹. Calculate the rms speed of the molecules of the gas.

[Ans. 5.476×10^4 cm/sec]

38. At what temperature will the rms speed of hydrogen be the same as that of oxygen at 25°C?

[Ans. 18.62 K or -254.38°C]

39. Calculate the average rms and most probable speed of SO₂ molecules at 27°C.

[Ans. 3.15×10^4 cm/sec, 3.419×10^4 cm/sec,
 2.792×10^4 cm/sec]

40. The average speed at temperature T_1 and most probable speed at T_2 of CO₂ gas is 9×10^4 cm/sec. Calculate the values of T_1 and T_2 .

[Ans. 1682.5 K, 2143.4 K]

41. How many times would the average molecular speed of nitrogen increase as its temperature is raised from -73°C and 127°C?

[Ans. 1.414 times]

42. A 4 : 1 molar mixture of He and CH₄ is contained in a vessel at 20 bar pressure. Due to hole in the vessel the gas mixture leaks out. What is the composition of the mixture effusing out initially? (IIT 1994)

[Ans. 8 : 1]

[Hint: Partial pressure ratio of He and CH₄ is 16 : 4.

For diffusion $\frac{r_{\text{He}}}{r_{\text{CH}_4}} = \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} \times \frac{P_{\text{He}}}{P_{\text{CH}_4}}$

$$\frac{n_{\text{He}}}{n_{\text{CH}_4}} = \sqrt{\frac{16}{4}} \times \frac{16}{4} = 8$$

i.e., mole ratio of diffusion for He and CH₄ is 8 : 1.]

43. Pure O₂ diffuses through an aperture in 224 second, whereas mixture of O₂ and another gas containing 80% O₂ diffuses from the same in 234 second. What is the molecular mass of gas?

[Ans. 46.6]

44. 56 g of nitrogen are confined to a 6 litre flask at 37°C. Calculate its pressure using van der Waals' equation for nitrogen. $a = 4.17$ atm litre² mol⁻² and $b = 0.037$ litre mol⁻¹.

[Ans. 8.1175 atm]

45. One mole of carbon dioxide was found to occupy a volume of 1.32 litre at 48°C under a pressure of 16.4 atm. Calculate the pressure that would have been expected from:

(i) the ideal gas equation,

(ii) van der Waals' equation.

$$(a = 3.59 \text{ atm litre}^2 \text{ mol}^{-1}; b = 4.27 \times 10^{-3} \text{ litre mol}^{-1})$$

and $R = 0.0821$ litre-atm K⁻¹ mol⁻¹)

[Ans. (i) 19.96 atm (ii) 18.64 atm]

46. Calculate the compressibility factor for SO₂, if 1 mole of it occupies 0.35 litre at 300 K and 50 atm pressure. Comment on the result.

[Hint: $Z = \frac{PV}{nRT} = \frac{50 \times 0.35}{1 \times 0.0821 \times 300} = 0.711$

Since, $Z < 1$; the gas SO₂ will be more compressible than ideal gas.]

47. The average velocity of gas molecules is 400 m/sec. Calculate its rms velocity at the same temperature. (IIT 2003)

[Ans. 434 m/sec]

48. A chamber contains monoatomic 'He' at STP, determine its number density.

[Ans. $2.68 \times 10^{25} \text{ m}^{-3}$]

[Hint: Number density = $\frac{P}{kT}$

(where, k = Boltzmann constant)

$$PV = nRT$$

$$= (n \times N) \frac{R}{N} T$$

$$= (n \times N) kT$$

$$\frac{P}{kT} = \frac{n \times N}{V} = \text{number density}$$

$$\therefore \text{Number density} = \frac{1.01 \times 10^5}{1.38 \times 10^{-23} \times 273} = 2.68 \times 10^{25} \text{ m}^{-3}$$

49. Two perfect gases at absolute temperature T_1 and T_2 are mixed. There is no loss of energy. Find the temperature of the mixture if masses of molecules are m_1 and m_2 and the number of moles of the gases are n_1 and n_2 respectively.

[Ans. $T = \frac{n_1 T_1 + n_2 T_2}{n_1 + n_2}$]

[Hint: Let final temperature is T

$$\frac{3}{2} n_1 R T_1 + \frac{3}{2} n_2 R T_2 = \frac{3}{2} (n_1 + n_2) R T$$

$$T = \frac{n_1 T_1 + n_2 T_2}{n_1 + n_2}$$

50. van der Waals' constant 'b' for oxygen is 32 cm³/mol. Assume b is four times the actual volume of a mole of "billiard-ball" O₂ molecules and compute the diameter of an O₂ molecule.

51. The speed of ten particles in metre/sec are 0, 1, 2, 3, 3, 3, 4, 4, 5 and 6. Find (a) average speed (b) the root mean square speed (c) most probable speed.

[Ans. $c_{av} = 3.1 \text{ m sec}^{-1}$, $c_{rms} = 12.5 \text{ m sec}^{-1}$, $c_{mp} = 3 \text{ m sec}^{-1}$]

52. Using van der Waals' equation, calculate the constant 'a' when two moles of a gas confined in a four litre flask exerts a pressure of 11 atm at a temperature of 300 K. The value of 'b' is 0.05 litre mol⁻¹. (IIT 1998)

[Ans. 6.46 atm litre² mol⁻²]

53. (a) Calculate the pressure exerted by 5 moles of CO₂ in one litre vessel at 47°C using van der Waals' equation. Also, report the pressure of the gas if it behaves ideally in nature. Given that $a = 3.592$ atm litre² mol⁻², $b = 0.0427$ litre mol⁻¹.

(IIT 2002)

(b) If volume occupied by CO₂ molecule is negligible, then calculate the pressure exerted by one mol of CO₂ gas at 273 K.

(IIT 2000)

[Ans. (a) 77.218 atm, 131.36 atm and (b) 0.9922 atm]

54. A compound alloy of gold and copper crystallises in a cubic lattice in which gold atoms occupy corners of cubic unit cell and copper atoms occupy the centre of faces of cube. What is formula of alloy compound?

[Ans. AuCu₃]

55. A compound formed by elements A and B crystallises in the cubic structure where A atoms are at the corners of the cube

and B atoms at the centre of the cube. What is the formula of the compound?

[Ans. AB]

56. A fcc element (atomic mass = 60) has a cell edge of 400 pm. What is its density?

[Ans. 6.23 g cm^{-3}]

[Hint: Apply density = $\frac{Z \times M}{N_0 \times V}$, $Z = 4$ and $V = (4 \times 10^{-8})^3$

cm^3 ($1 \text{ pm} = 10^{-12} \text{ m} = 10^{-10} \text{ cm}$)]

57. The face-centred unit cell of nickel has an edge length of 352.39 pm. The density of nickel is 8.9 g cm^{-3} . Calculate the value of Avogadro's number. The atomic mass of nickel is 58.7 and 1 pm is equal to 10^{-10} cm .

[Ans. 6.029×10^{23}]

58. The unit cell of aluminium is a cube with an edge length of 405 pm. The density of aluminium is 2.70 g cm^{-3} . What type of unit cell of aluminium is?

[Ans. The unit cell is face-centred]

[Hint: Apply the formula, density = $\frac{Z \times M}{N_0 \times V}$ and find the value of Z .]

59. A substance forms face-centred cubic crystals. Its density is 1.984 g cm^{-3} and the edge length of the unit cell is 630 pm. Calculate the molar mass of the substance.

[Ans. 74.70 g mol^{-1}]

60. Molybdenum forms body-centred cubic crystals whose density is 10.3 g cm^{-3} . Calculate the edge length of the unit cell. The molar mass of Mo is 95.94 g mol^{-1} .

[Ans. 313.9 pm]

61. An element crystallises in a structure having a fcc unit cell of an edge 200 pm. Calculate its density if 200 g of this element contains 24×10^{23} atoms.

[Ans. 4.166 g cm^{-3}]

[Hint: Molar mass = $\frac{200}{24 \times 10^{23}} \times 6.023 \times 10^{23} = 50.19 \text{ g mol}^{-1}$

For fcc, $Z = 4$, $V = a^3 = (200 \times 10^{-10})^3$

Apply density = $\frac{ZM}{N_0 \times V}$]

62. The element chromium exists in bcc lattice with unit cell edge $2.88 \times 10^{-10} \text{ m}$. The density of chromium is $7.2 \times 10^3 \text{ kg m}^{-3}$. How many atoms does $52 \times 10^{-3} \text{ kg}$ of chromium contain?

[Ans. 6.04×10^{23}]

63. A cubic solid is made up of two elements P and Q . Atoms Q are present at the corners of the cube and atoms P at the body-centre. What is the formula of the compound? What are the coordination numbers of P and Q ?

[Ans. PQ , 8, 8]

64. A metallic element crystallises into a lattice containing a sequence of layers of $AB AB AB \dots$. Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space? (IIT 1996)

[Ans. 26%]

65. A lead(II) sulphide crystal has an NaCl structure. What is its density? The edge length of the unit cell is 500 pm. $N_0 = 6.023 \times 10^{23}$; atomic mass: Pb = 207.2, S = 32.

[Ans. 12.708 g cm^{-3}]

66. The unit cell of metallic gold is face-centred cubic.

(a) How many atoms occupy the gold unit cell?

(b) What is the mass of a gold unit cell?

[Ans. (a) 4 atoms (b) $1.308 \times 10^{-21} \text{ g}$]

67. Polonium crystallises in a simple cubic unit cell. It has atomic mass 209 and density 91.5 kg m^{-3} . What is the edge length of its unit cell?

[Ans. $15.59 \times 10^{-8} \text{ cm}$]

68. The unit cell of nickel is a face-centred cube. The length of its side is 0.352 nm. Calculate the atomic radius of nickel.

[Ans. 0.124 nm]

69. Determine the simplest formula of an ionic compound in which cations are present at the corners and the anions occur at the centre of each face.

[Ans. AB_3 ; A and B are cation and anion respectively.]

70. Sodium metal crystallises in a body-centred cubic lattice with cell edge, $a = 4.29 \text{ \AA}$. What is the radius of sodium atom? (IIT 1994)

[Ans. $1.8576 \text{ \AA}$]

[Hint: $4r = \sqrt{3}a$]

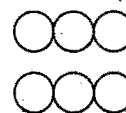
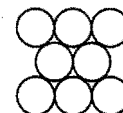
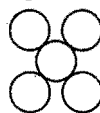
71. If three elements P , Q and R crystallise in a cubic type lattice with P atoms at the corners, Q atoms at the cube centre and R atoms at the edges, then write the formula of the compound.

[Ans. PQR_3]

72. The first order reflection of the beam of X-ray from a given crystal occurs at $5^\circ 15'$. At what angle will be the third order reflection?

[Ans. $15^\circ 56'$]

73. The figures given below show the location of atoms in three crystallographic planes in a fcc lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. (IIT 2000)



OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

- At constant temperature, the product of pressure and volume of a given amount of a gas is constant. This is:
 - Gay-Lussac law
 - Charles' law
 - Boyle's law
 - Pressure law
- A curve drawn at constant temperature is called an isotherm. This shows the relationship between:
 - P and $\frac{1}{V}$
 - PV and V
 - V and $\frac{1}{P}$
 - P and V
- Charles' law is represented mathematically as:
 - $V_t = KV_0t$
 - $V_t = \frac{KV_0}{t}$
 - $V_t = V_0 \left(1 + \frac{273}{t}\right)$
 - $V_t = V_0 \left(1 + \frac{t}{273}\right)$
- Correct gas equation is: [UGET (Manipal Medical) 2006]
 - $\frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$
 - $\frac{V_1T_2}{P_1} = \frac{V_2T_1}{P_2}$
 - $\frac{P_1T_1}{V_1} = \frac{P_2T_2}{V_2}$
 - $\frac{V_1V_2}{T_1T_2} = P_1P_2$
- In general gas equation, $PV = nRT$, V is the volume of:
 - n moles of a gas
 - any amount of a gas
 - one mole of a gas
 - one gram of a gas
- In the equation of state of an ideal gas $PV = nRT$, the value of universal gas constant would depend only on: (CPMT 1991)
 - the nature of the gas
 - the units of measurement
 - the pressure of the gas
 - the temperature of the gas
- The value of gas constant per degree per mol is approximately:
 - 1 cal
 - 2 cal
 - 3 cal
 - 4 cal
- Which one of the following is not the value of R ?
 - 1.99 cal $K^{-1} \text{ mol}^{-1}$
 - 0.0821 litre-atm $K^{-1} \text{ mol}^{-1}$
 - 9.8 kcal $K^{-1} \text{ mol}^{-1}$
 - 8.3 J $K^{-1} \text{ mol}^{-1}$
- One litre of a gas collected at NTP will occupy at 2 atmospheric pressure and 27°C :
 - $\frac{300}{2 \times 273}$ litre
 - $\frac{2 \times 300}{273}$ litre
 - $\frac{273}{2 \times 300}$ litre
 - $\frac{2 \times 273}{300}$ litre
- 10 g of a gas at atmospheric pressure is cooled from 273°C to 0°C keeping the volume constant; its pressure would become:
 - $\frac{1}{2}$ atm
 - $\frac{1}{273}$ atm
 - 2 atm
 - 273 atm
- 56 g of nitrogen and 96 g of oxygen are mixed isothermally and a total pressure of 10 atm. The partial pressures of oxygen and nitrogen (in atm) are respectively: [PET (Kerala) 2010]
 - 4, 6
 - 5, 5
 - 2, 8
 - 8, 2

[Hint: $n_{N_2} = \frac{56}{28} = 2$; $n_{O_2} = \frac{96}{32} = 3$

$$P_{N_2} = x_{N_2} \times P_{\text{Total}}$$

$$= \frac{2}{2+3} \times 10 = 4 \text{ atm,}$$

$$P_{O_2} = 10 - 4 = 6 \text{ atm}]$$

- 273 mL of a gas at STP was taken to 27°C and 600 mm pressure. The final volume of the gas would be: (CPMT 1992)
 - 273 mL
 - 300 mL
 - 380 mL
 - 586 mL
- The density of the gas is equal to: (CBSE 1991)
 - nP
 - MP/RT
 - P/RT
 - M/V

[P = Pressure; V = Volume; T = Temperature; R = Gas constant; n = number of mole; M = molecular mass]
- The density of a gas is 1.964 g dm^{-3} at 273 K and 76 cm Hg. The gas is: (KCET 2006)
 - CH_4
 - C_2H_6
 - CO_2
 - Xe
- Compressed oxygen is sold at a pressure of 100 atmosphere in a cylinder of 49 litre. The number of moles of oxygen in the cylinder is:
 - 400
 - 100
 - 300
 - 200

[Hint: One mole occupies a volume approximately 24.5 litre under ordinary atmospheric conditions.]
- If the pressure and absolute temperature of 2 litre of carbon dioxide are doubled, the volume of carbon dioxide would become: (CBSE 1991)
 - 7 litre
 - 5 litre
 - 4 litre
 - 2 litre
- One gram mole of a gas at NTP occupies 22.4 litre as volume. This fact was derived from:
 - Dalton's theory
 - Avogadro's hypothesis
 - Berzelius hypothesis
 - law of gaseous volumes
- 4.4 g of CO_2 contains how many litre of CO_2 at STP? (AFMC 2004)
 - 2.4 litre
 - 2.24 litre
 - 44 litre
 - 22.4 litre
- Five gram each of the following gases at 87°C and 750 mm pressure are taken. Which of them will have the least volume? (MLNR 1991)
 - HF
 - HCl
 - HBr
 - HI
- If molecular mass of O_2 and SO_2 are 32 and 64 respectively. If one litre of O_2 at 15°C and 750 mm pressure contains N molecules, the number of molecules in two litre of SO_2 under the same conditions of temperature and pressure will be: (MLNR 1991)
 - $2N$
 - N
 - $N/2$
 - $4N$
- Rate of diffusion of a gas is:
 - directly proportional to its density
 - directly proportional to its molecular mass
 - directly proportional to the square of its molecular mass
 - inversely proportional to the square root of its molecular mass
- The rate of diffusion of hydrogen is about: (CPMT 1991)
 - one-half that of helium
 - 1.4 times that of helium
 - twice that of helium
 - four times that of helium

23. The rate of diffusion of methane at a given temperature is twice that of gas X . The molecular mass of gas X is:
(IIT 1990; MLNR 1995)
(a) 64.0 (b) 32.0 (c) 4.0 (d) 8.0
24. Some moles of O_2 diffuse through a small opening in 18 second. Same number of moles of an unknown gas diffuse through the same opening in 45 second. Molecular mass of the unknown gas is:
(a) $32 \times \frac{(45)^2}{(18)^2}$ (b) $32 \times \frac{(18)^2}{(45)^2}$
(c) $(32)^2 \times \frac{45}{18}$ (d) $(32)^2 \times \frac{18}{45}$
25. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both the ends. The white ring first formed will be:
(a) at the centre of the tube
(b) near the ammonia bottle
(c) near the HCl bottle
(d) throughout the length of the tube
26. 0.5 mole of each H_2 , SO_2 and CH_4 are kept in a container. A hole was made in the container. After 3 hours, the order of partial pressures in the container will be :
[CET (Karnataka) 2009]
(a) $p_{SO_2} > p_{CH_4} > p_{H_2}$ (b) $p_{H_2} > p_{SO_2} > p_{CH_4}$
(c) $p_{H_2} > p_{CH_4} > p_{SO_2}$ (d) $p_{SO_2} > p_{H_2} > p_{CH_4}$
27. The mass of 6.02×10^{23} molecules of CO is:
(a) 28 g (b) 14 g (c) 7.0 g (d) 56 g
28. 10 g of hydrofluoric acid occupy 5.6 litre of volume at NTP. The empirical formula of the gas is HF. The molecular formula of the gas will be (At. mass of fluorine = 19):
(a) H_4F_4 (b) HF
(c) H_3F_3 (d) H_2F_2
29. A fire extinguisher contains 4.4 kg of CO_2 . The volume of CO_2 delivered by this fire extinguisher at room temperature is:
(a) 24.5 litre (b) 100×24.5 litre
(c) 10×24.5 litre (d) 1000×24.5 litre
30. The number of moles of H_2 in 0.224 litre of hydrogen gas at STP is:
(MLNR 1994)
(a) 1 (b) 0.1 (c) 0.01 (d) 0.001
31. A gas has a vapour density 11.2. The volume occupied by 1 g of the gas at NTP is:
(a) 1 L (b) 11.2 L (c) 22.4 L (d) 4 L
32. "The total pressure exerted by a number of non-reacting gases is equal to the sum of partial pressures of the gases under the same conditions" is known as:
(a) Boyle's law (b) Dalton's law
(c) Avogadro's law (d) Charles' law
33. Equal masses of methane and oxygen are mixed in an empty container at $25^\circ C$. The fraction of the total pressure exerted by oxygen is:
(a) $\frac{1}{3}$ (b) $\frac{1}{2}$ (c) $\frac{2}{3}$ (d) $\frac{1}{3} \times \frac{273}{298}$
34. Equal masses of methane and hydrogen are mixed in an empty container at $25^\circ C$. The fraction of the total pressure exerted by hydrogen is:
(a) $\frac{1}{2}$ (b) $\frac{8}{9}$
(c) $\frac{1}{9}$ (d) $\frac{16}{17}$
35. A gaseous mixture of 2 moles of A , 3 moles of B , 5 moles of C and 10 moles of D is contained in a vessel. Assuming that gases are ideal and the partial pressure of C is 1.5 atm, the total pressure is:
(a) 3 atm (b) 6 atm (c) 9 atm (d) 15 atm
[Hint: 5 moles of C produce pressure 1.5 atm; therefore partial pressures of $D = 3$ atm, $B = \frac{1.5}{5} \times 3 = 0.9$ atm and $A = \frac{1.5}{5} \times 2 = 0.6$ atm]
36. 50 mL of a gas A diffuse through a membrane in the same time as for the diffusion of 40 mL of gas B under identical conditions of pressure and temperature. If the molecular mass of A is 64; that of B would be: (CBSE 1992)
(a) 100 (b) 250 (c) 200 (d) 80
37. 3.2 g of oxygen (At. mass = 16) and 0.2 g of hydrogen (At. mass = 1) are placed in a 1.12 litre flask at $0^\circ C$. The total pressure of the gas mixture will be: (CBSE 1992)
(a) 1 atm (b) 2 atm (c) 3 atm (d) 4 atm
38. Select the correct statement:
In the gas equation, $PV = nRT$ (CBSE 1992)
(a) n is the number of molecules of a gas
(b) n moles of the gas have volume V
(c) V denotes volume of one mole
(d) P is the pressure of the gas when only one mole of gas is present
39. The density of a gas at $27^\circ C$ and 1 atm is d . Pressure remaining constant, at which of the following temperatures will its density become $0.75d$? (CBSE 1992)
(a) $20^\circ C$ (b) $30^\circ C$ (c) 400 K (d) 300 K
40. If 4 g of oxygen diffuse through a very narrow hole, how much hydrogen would have diffused under identical conditions?
(a) 16 g (b) 1 g (c) $\frac{1}{4}$ g (d) 64 g
[Hint: $\frac{w/2}{4/32} = \sqrt{\frac{M_{O_2}}{M_{H_2}}}$]
41. A closed vessel contains equal number of hydrogen and nitrogen molecules. The total pressure is 740 mm of Hg. If N_2 molecules are removed, the pressure would become/remains:
(a) double of 740 mm of Hg
(b) one-ninth of 740 mm of Hg
(c) unchanged
(d) one-half of 740 mm of Hg
42. The pressure P exerted by a mixture of three gases having partial pressures P_1 , P_2 and P_3 is given by:
(a) $P = P_1 + P_2 - P_3$ (b) $P = \sqrt{P_1 + P_2 + P_3}$
(c) $P = P_1 - P_2 + P_3$ (d) $P = P_1 + P_2 + P_3$
43. Two sealed containers of same capacity at the same temperature are filled with 44 g of hydrogen gas in one and 44 g of CO_2 in the other. If the pressure of CO_2 is 1 atm, what is the pressure in the hydrogen container?
(a) 1 atm (b) Zero atm (c) 22 atm (d) 44 atm

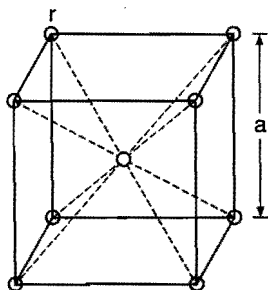
44. Absolute zero is the temperature where all gases are expected to have:
 (a) different volumes (b) same volume
 (c) zero volume (d) none of these
45. If a gas is heated at constant pressure, its density:
 (a) will decrease (b) will increase
 (c) may increase or decrease (d) will remain unchanged
46. Density of neon will be highest at:
 (a) STP (b) 0°C , 2 atm
 (c) 273°C , 1 atm (d) 273°C , 2 atm
47. Equal masses of ethane and hydrogen are mixed in an empty container at 25°C . The fraction of the total pressure exerted by hydrogen is: (IIT 1993)
 (a) 1 : 2 (b) 1 : 1 (c) 1 : 16 (d) 15 : 16
48. According to kinetic theory of gases:
 (a) there are intermolecular attractions
 (b) molecules have considerable volume
 (c) there is no intermolecular attraction
 (d) speed of molecules decreases for each collision
49. Postulate of kinetic theory is:
 (a) atom is indivisible
 (b) gases combine in simple ratio
 (c) there is no influence of gravity on the molecules of the gas
 (d) none of the above
50. Which of the following statements is not consistent with the postulates of kinetic theory of gases?
 (a) Gases consist of large number of tiny particles
 (b) Particles are in constant motion
 (c) All the particles have same speed
 (d) Pressure is due to hits recorded by particles against the walls of containing vessel
51. A helium atom is two times heavier than a hydrogen molecule. At 298 K , the average kinetic energy of a helium atom is:
 (a) two times that of a hydrogen molecule
 (b) four times that of a hydrogen molecule
 (c) half that of a hydrogen molecule
 (d) same as that of a hydrogen molecule
52. The kinetic theory of gases predicts that total kinetic energy of a gas depends on:
 (a) pressure of the gas
 (b) temperature of the gas
 (c) volume of the gas
 (d) pressure, temperature and volume of the gas
53. If a gas is allowed to expand at constant temperature then:
 (a) number of molecules of the gas decreases
 (b) the kinetic energy of the gas molecules decreases
 (c) the kinetic energy of the gas molecules increases
 (d) the kinetic energy of the gas molecules remains the same
54. Gases deviate from ideal behaviour because molecules:
 (a) are colourless (b) are spherical
 (c) attract each other (d) have high speeds
55. Deviations from ideal behaviour will be more if the gas is subjected to:
 (a) low temperature and high pressure
 (b) high temperature and low pressure
 (c) low temperature
 (d) high temperature
56. In a closed vessel, a gas is heated from 300 K to 600 K ; the kinetic energy becomes/remains:
 (a) double (b) half (c) same (d) four times
57. A mixture contains 56 g of nitrogen, 44 g of CO_2 and 16 g of methane. The total pressure of the mixture is 720 mm Hg . The partial pressure of methane is: (EAMCET 1991)
 (a) 180 mm (b) 360 mm (c) 540 mm (d) 720 mm
58. The root mean square speed of an ideal gas at 27°C is 0.3 m/sec . Its rms velocity at 927°C is: (EAMCET 1991)
 (a) 3.0 m/sec (b) 2.4 m/sec (c) 0.9 m/sec (d) 0.6 m/sec
59. The rms speed at NTP of the species can be calculated from the expression: (EAMCET 1990)
 (a) $\sqrt{\frac{3P}{d}}$ (b) $\sqrt{\frac{3PV}{M}}$ (c) $\sqrt{\frac{3RT}{M}}$ (d) all of these
60. At constant volume, for a fixed number of mole of a gas, the pressure of the gas increases with rise of temperature due to:
 (a) increase in average molecular speed
 (b) increased rate of collisions amongst molecules
 (c) increase in molecular attraction
 (d) decrease in mean free path
61. Non-ideal gases approach ideal behaviour: (IIT 1999; KCET 2004)
 (a) high temperature and high pressure
 (b) high temperature and low pressure
 (c) low temperature and high pressure
 (d) low temperature and low pressure
62. The ratio of root mean square speed and average speed of a gas molecule, at a particular temperature, is:
 (a) 1 : 1.086 (b) 1.086 : 1
 (c) 2 : 1.086 (d) 1.086 : 2
63. Most probable speed, average speed and rms speed are related as:
 (a) 1 : 1.224 : 1.128 (b) 1.128 : 1 : 1.224
 (c) 1 : 1.128 : 1.224 (d) 1.224 : 1.128 : 1
64. In a closed flask of 5 litre , 1.0 g of H_2 is heated from $300\text{--}600\text{ K}$. Which statement is not correct? (CBSE 1991)
 (a) The rate of collision increases
 (b) The energy of gaseous molecules increases
 (c) The number of mole of the gas increases
 (d) Pressure of the gas increases
65. The root mean square speed is expressed as:
 (a) $\left[\frac{3}{2} \frac{RT}{M}\right]^{1/2}$ (b) $\left[\frac{2RT}{M}\right]^{1/2}$
 (c) $\left[\frac{3RT}{M}\right]$ (d) $\left[\frac{3RT}{M}\right]^{1/2}$
66. The rms speed of hydrogen molecules at room temperature is 2400 m s^{-1} . At room temperature the rms speed of oxygen molecules would be:
 (a) 400 ms^{-1} (b) 300 ms^{-1}
 (c) 600 ms^{-1} (d) 1600 ms^{-1}
- [Hint: $\frac{C_{\text{O}_2}}{C_{\text{H}_2}} = \sqrt{\frac{M_{\text{H}_2}}{M_{\text{O}_2}}}$]

67. The molecules of which of the following gas have highest speed?
 (a) Hydrogen at -50°C (b) Methane at 298 K
 (c) Nitrogen at 1000°C (d) Oxygen at 0°C
68. Which one of the following is an ideal gas?
 (a) Hydrogen (b) Nitrogen
 (c) Carbon dioxide (d) None of these
69. van der Waals' equation explains the behaviour of:
 (a) ideal gases (b) real gases
 (c) mixture of gases (d) diatomic gases
70. The critical temperature of a gas is that temperature:
 (a) above which it can no longer remain in the gaseous state
 (b) above which it cannot be liquefied by pressure
 (c) at which it solidifies
 (d) at which the volume of the gas becomes zero
71. The van der Waals' equation for a real gas is:
 (a) $\left(P + \frac{a}{V^2}\right)(V - b) = nRT$
 (b) $\left(P + \frac{an^2}{V^2}\right)(V - b) = nRT$
 (c) $\left(P + \frac{a}{V^2}\right)(V + b) = nRT$
 (d) $P = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}$
72. In van der Waals' equation of state for a non-ideal gas the term that accounts for intermolecular force is:
 (a) $\left(P + \frac{a}{V^2}\right)$ (b) $(V - b)$ (c) RT (d) $\frac{1}{RT}$
73. The units of 'a' in van der Waals' equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$
 are:
 (a) $\text{atom litre}^2 \text{ mol}^{-2}$ (b) $\text{atom litre mol}^{-2}$
 (c) $\text{atom litre mol}^{-1}$ (d) $\text{atom litre}^2 \text{ mol}^{-1}$
74. If 1000 mL of gas A at 600 torr and 500 mL of gas B at 800 torr are placed in a 2 litre flask, the final pressure will be:
 (a) 2000 torr (b) 1000 torr
 (c) 500 torr (d) 400 torr
75. Two samples of gases A and B are at the same temperature. The molecules of A are travelling four times faster than the molecules of B. The ratio of m_A/m_B of their masses will be:
 (a) 16 (b) 4 (c) 1/4 (d) 1/16
 [Hint. $\frac{m_A}{m_B} = \frac{C_2^2}{C_1^2}$]
76. The root mean square speed of a certain gas at 27°C is $3 \times 10^4 \text{ cm s}^{-1}$. The temperature at which the velocity will be $6 \times 10^4 \text{ cm s}^{-1}$ is:
 (a) 54°C (b) 108°C (c) 1200 K (d) 600 K
77. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called: (IIT 1991)
 (a) critical temperature (b) Boyle temperature
 (c) inversion temperature (d) reduced temperature
78. The value of van der Waals' constant 'a' for gases O_2 , N_2 , NH_3 and CH_4 are 1.360, 1.390, 4.170 and $2.253 \text{ litre}^2\text{-atm mol}^{-2}$ respectively. The gas which can be most easily liquefied is:
 (a) O_2 (b) N_2 (c) NH_3 (d) CH_4
79. According to kinetic theory of gases for a diatomic molecule:
 (a) the pressure exerted by the gas is proportional to the mean square speed of the molecules
 (b) the pressure exerted by the gas is proportional to the root mean square speed of the molecules
 (c) the root mean square speed is inversely proportional to the temperature
 (d) the mean translational KE of the molecule is directly proportional to the absolute temperature
80. A real gas obeying van der Waals' equation will resemble an ideal gas if the:
 (a) constants a and b are small
 (b) a is large and b is small
 (c) a is small and b is large
 (d) constants a and b are large
81. When the universal gas constant (R) is divided by Avogadro's number (N), their ratio is called:
 (a) Planck's constant (b) Rydberg's constant
 (c) Boltzmann's constant (d) van der Waals' constant
82. The compressibility factor of a gas is defined as $Z = \frac{PV}{RT}$. The compressibility factor of an ideal gas is: [PMT (MP) 2004]
 (a) 0 (b) 1 (c) -1 (d) infinity
83. An ideal gas is one which obeys:
 (a) gas laws (b) Boyle's law
 (c) Charles' law (d) Avogadro's law
84. A mixture of three gases X (density 1.0), Y (density 0.2) and Z (density 0.4) is enclosed in a vessel at constant temperature. When the equilibrium is established, the gas/gases:
 (a) X will be at the top of the vessel
 (b) Y will be at the top of the vessel
 (c) Z will be at the top of the vessel
 (d) will mix homogeneously throughout the vessel
85. 16 g of oxygen and 3 g of hydrogen are mixed and kept at 760 mm pressure at 0°C . The total volume occupied by the mixture will be nearly: [CMC (Vellore) 1991]
 (a) 22.4 litre (b) 33.6 litre (c) 44800 mL (d) 4480 mL
86. Which of the following expressions does not represent Boyle's law?
 (a) $PV = \text{constant}$ (b) $V \propto \frac{1}{P}$
 (c) $V_1T_2 = V_2T_1$ (d) $P_1V_1 = P_2V_2$
87. When an ideal gas undergoes unrestricted expansion, no cooling occurs because the molecules:
 (a) exert no attractive forces on each other
 (b) do work equal to loss of kinetic energy
 (c) collide without loss of energy
 (d) are above the inversion temperature
88. Which of the following mixture of gases at room temperature does not follow Dalton's law of partial pressures?

- (a) NO_2 and O_2 (b) NH_3 and HCl
 (c) CO and CO_2 (d) SO_2 and O_2
89. The speed possessed by most of the gaseous molecules is:
 (a) most probable speed (b) average speed
 (c) root mean square speed (d) none of these
90. In which of the following pairs the gaseous species diffuse through a porous plug along with the same rate of diffusion? (EAMCET 1990)
 (a) NO , CO (b) NO , CO_2
 (c) NH_3 , PH_3 (d) NO , C_2H_6
91. Which of the following statements is correct?
 (a) $3PV = mnc^2$ is the expression for real gases
 (b) At normal temperature and pressure most gases behave nearly as ideal gases
 (c) The molecules of real gases have both volume and mutual attraction
 (d) Pressure depends on number of molecules and volume
92. For one gram molecule of an ideal gas:
 (a) $\frac{PV}{T} = \frac{3}{2} \text{ cal}$ (b) $\frac{PV}{T} = 2 \text{ cal}$
 (c) $\frac{PV}{T} = 8.31 \text{ cal}$ (d) $\frac{PV}{T} = 0.0821 \text{ cal}$
93. When helium is allowed to expand into vacuum, heating effect is observed. This is due to the fact that:
 (a) helium is an inert gas
 (b) helium is a noble gas
 (c) helium is an ideal gas
 (d) the inversion temperature of helium is very low
94. At STP, the order of mean square velocity of molecules of H_2 , N_2 , O_2 and HBr is: (CBSE 1991)
 (a) $\text{H}_2 > \text{N}_2 > \text{O}_2 > \text{HBr}$ (b) $\text{HBr} > \text{O}_2 > \text{N}_2 > \text{H}_2$
 (c) $\text{HBr} > \text{H}_2 > \text{O}_2 > \text{N}_2$ (d) $\text{N}_2 > \text{O}_2 > \text{H}_2 > \text{HBr}$
95. At constant temperature in a given mass of an ideal gas: (CBSE 1991)
 (a) the ratio of pressure and volume always remains constant
 (b) volume always remains constant
 (c) pressure always remains constant
 (d) the product of pressure and volume always remains constant
96. The non-compressible volume of a gas is . . . times the actual volume of gas molecules:
 (a) 2 (b) 4 (c) 3 (d) 2.5
97. One mole of an ideal monoatomic gas is mixed with 1 mole of an ideal diatomic gas. The molar specific heat of the mixture at constant volume is:
 (a) 3 cal (b) 4 cal (c) 5 cal (d) 8 cal
98. In an experiment during the analysis of a carbon compound, 145 mL of H_2 was collected at 760 mm Hg pressure and 27°C . The mass of H_2 is nearly:
 (a) 10 mg (b) 6 g (c) 12 mg (d) 12 g
 [Hint: Apply $PV = \frac{w}{M} RT$; $1 \times 0.145 = \frac{w}{2} \times 0.0821 \times 300$]
99. The kinetic energy of N molecules of O_2 is x joule at -123°C . Another sample of O_2 at 27°C has a kinetic energy of $2x$ joule. The latter sample contains:
 (a) N molecules of O_2 (b) $2N$ molecules of O_2
 (c) $\frac{N}{2}$ molecules of O_2 (d) $\frac{N}{4}$ molecules of O_2
100. A balloon filled with N_2O is pricked with a sharper point and plunged into a tank of CO_2 under the same pressure and temperature. The balloon will:
 (a) be enlarged (b) shrink
 (c) collapse completely (d) remain unchanged in size
101. The three states of matter are solid, liquid and gas. Which of the following statements is true about them?
 (a) Gases and liquids have viscosity as a common property
 (b) The molecules in all the three states possess random translational motion
 (c) Gases cannot be converted into solids without passing through the liquid phase
 (d) Solids and liquids have pressure as a common property
102. Strong intermolecular forces exist in:
 (a) gases (b) liquids
 (c) amorphous solids (d) crystalline solids
103. Association of molecules in water is due to:
 (a) covalent bonding (b) hydrogen bonding
 (c) ionic bonding (d) van der Waals' forces
104. Which of the following statements is wrong?
 (a) Evaporation is a spontaneous process
 (b) Evaporation is a surface phenomenon
 (c) Vapour pressure decreases with increase of temperature
 (d) The vapour pressure of a solution is always less than the vapour pressure of a pure solvent
105. Normal boiling point of a liquid is that temperature at which vapour pressure of the liquid is equal to:
 (a) zero (b) 380 mm of Hg
 (c) 760 mm of Hg (d) 100 mm of Hg
106. Water boils at lower temperature on high altitudes because:
 (a) atmospheric pressure is low there
 (b) atmospheric pressure is high there
 (c) water is weakly hydrogen bonded there
 (d) water in pure form is found there
107. When a student was given a viscometer, the liquid was sucked with difficulty; the liquid may be:
 (a) benzene (b) toluene (c) water (d) glycerine
108. Mark the statement which is correct:
 (a) surface tension of a liquid increases with temperature
 (b) addition of chemicals reduces the surface tension of a liquid
 (c) stalagmometer is used for measuring viscosity of the liquid
 (d) viscosity of the liquid does not depend on intermolecular forces
109. With the increasing molecular mass of a liquid, the viscosity: (Jiwaji 1990)
 (a) decreases (b) increases
 (c) no effect (d) all are wrong
110. The viscosity of which liquid is the maximum?
 (a) water (b) glycol
 (c) acetone (d) ethanol

111. The rise of a liquid in a capillary tube is due to:
 (a) viscosity (b) osmosis
 (c) diffusion (d) surface tension
112. With increase in temperature, the fluidity of liquids:
 (a) increases (b) decreases
 (c) remains constant (d) may increase or decrease
113. If η_1 and η_2 are the coefficients of viscosity of two liquids, d_1 and d_2 their densities and t_1 and t_2 the flow times in Ostwald viscometer, then:
 (a) $\frac{\eta_1}{\eta_2} = \frac{d_1 t_2}{d_2 t_1}$ (b) $\frac{\eta_1}{\eta_2} = \frac{d_2 t_2}{d_1 t_1}$
 (c) $\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$ (d) $\frac{\eta_1}{\eta_2} = \frac{d_2 t_1}{d_1 t_2}$
114. Which of the following expressions regarding the unit of coefficient of viscosity is not true?
 (a) dyne cm⁻² sec (b) dyne cm² sec⁻¹
 (c) Nm⁻² sec (d) 1 poise = 10⁻¹ Nm⁻² sec
115. The boiling points of water, ethyl alcohol and diethyl ether are 100°C, 78.5°C and 34.6°C respectively. The intermolecular forces will be in the order of:
 (a) water > ethyl alcohol > diethyl ether
 (b) ethyl alcohol > water > diethyl ether
 (c) diethyl ether > ethyl alcohol > water
 (d) diethyl ether > water > ethyl alcohol
116. The unit cell in a body centered cubic lattice is given in the figure. Each sphere has a radius, r and the cube has a side, a . What fraction of the total cube volume is empty. (TIFR 2010)



- (a) $1 - \frac{8}{3}\pi \frac{r^3}{a^3}$ (b) $\frac{4}{3}\pi \frac{r^3}{a^3}$
 (c) $\frac{r}{a}$ (d) $2 - \frac{4}{3}\pi \frac{r^3}{a^3}$
117. Which one is not the property of crystalline solid?
 (a) Isotropic
 (b) Sharp melting point
 (c) A definite and regular geometry
 (d) High intermolecular forces
118. The number of crystal systems known is:
 (a) 7 (b) 8 (c) 6 (d) 4
119. Tetragonal crystal system has the following unit cell dimensions:
 [PMT (MP) 1993]
 (a) $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$
 (b) $a = b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$
 (c) $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$
 (d) $a = b \neq c$ and $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

120. A match box exhibits: [PET (MP) 1993]
 (a) cubic geometry (b) monoclinic geometry
 (c) orthorhombic geometry (d) tetragonal geometry
121. In the crystal of CsCl, the nearest neighbours of each Cs ion are: [PET (MP) 1993]
 (a) six chloride ions (b) eight Cs ions
 (c) six Cs ions (d) eight chloride ions
122. How many chloride ions are there around sodium ion in sodium chloride crystal?
 (a) 3 (b) 8 (c) 4 (d) 6
123. The number of atoms contained in one face-centred cubic unit cell of monoatomic substance is:
 [PMT (Vellore) 2006; PET (MP) 2007]
 (a) 1 (b) 2 (c) 4 (d) 3
124. The number of close neighbours in a body-centred cubic lattice of identical spheres is:
 (a) 4 (b) 12 (c) 6 (d) 8
125. The coordination number of each sphere in (bcc) arrangement is:
 (a) 8 (b) 12 (c) 6 (d) 4
126. Bragg's law is given by the equation: (BHU 1990)
 (a) $n\lambda = 2\theta \sin \theta$ (b) $n\lambda = 2d \sin \theta$
 (c) $2n\lambda = d \sin \theta$ (d) $n \frac{\theta}{2} = \frac{d}{2} \sin \theta$
127. In Bragg's equation for diffraction of X-rays, ' n ' represents:
 (a) the number of mole (b) quantum number
 (c) the order of reflection (d) Avogadro's number
128. The coordination number for an atom in a primitive cubic unit cell is:
 (a) 6 (b) 8 (c) 10 (d) 12
129. The number of atoms per unit cell in a simple cubic, face-centred cubic and body-centred cubic are respectively:
 (a) 1, 4, 2 (b) 4, 1, 2
 (c) 2, 4, 1 (d) 4, 8, 2
130. In a solid lattice, the cation has left a lattice site and is located at interstitial position, the lattice defect is: (VITEEE 2007)
 (a) interstitial defect (b) vacancy defect
 (c) Frenkel defect (d) Schottky defect
131. Schottky defects occur mainly in ionic compounds where : (VITEEE 2008)
 (a) positive and negative ions are of different size
 (b) positive and negative ions are of same size
 (c) positive ions are small and negative ions are big
 (d) positive ions are big and negative ions are small
132. What type of crystal defect is indicated in the diagram below?
 $\begin{array}{cccccc} \text{Na}^+ & \text{Cl}^- & \text{Na}^+ & \text{Cl}^- & \text{Na}^+ & \text{Cl}^- \\ \text{Cl}^- & & \text{Cl}^- & & \text{Na}^+ & \\ \text{Na}^+ & \text{Cl}^- & & \text{Cl}^- & \text{Na}^+ & \text{Cl}^- \\ \text{Cl}^- & \text{Na}^+ & \text{Cl}^- & \text{Na}^+ & & \text{Na}^+ \end{array}$ (AIEEE 2004)
 (a) Frenkel defect (b) Schottky defect
 (c) Interstitial defect (d) Frenkel and Schottky defects
133. In a closed packed array of N spheres, the number of tetrahedral holes is:
 (a) $N/2$ (b) N
 (c) $4N$ (d) $2N$

134. In a closed packed array of N spheres, the octahedral holes are:
 (a) $N/2$ (b) $2N$ (c) $4N$ (d) N
135. AB crystallizes in a body centred cubic lattice with edge length ' a ' equal to 387 pm. The distance between two oppositely charged ions in the lattice is: [CBSE (PMT) 2010]
 (a) 335 pm (b) 250 pm
 (c) 200 pm (d) 300 pm
 [Hint : Distance between two oppositely charged ions

$$(r^+ + r^-) = \frac{a\sqrt{3}}{2} = \frac{387 \times \sqrt{3}}{2}$$

$$= 335.14 \text{ pm}]$$
136. Germanium or silicon becomes semiconductor due to:
 (a) Schottky defect (b) chemical impurity
 (c) Frenkel defect (d) none of these
137. A particular solid is very hard and has a high melting point. In solid state it is a non conductor and its melt is a conductor of electricity. Classify the solid: [CMC Vellore (Med.) 2008]
 (a) metallic (b) molecular
 (c) network (d) ionic
 (e) amorphous
138. Which one has the highest melting point?
 (a) Ionic crystal (b) Molecular crystal
 (c) Covalent crystal (d) Metallic crystal
139. For an ionic crystal of general formula AX and coordination number 6, the value of radius ratio will be: [PMT (MP) 1993]
 (a) greater than 0.73 (b) in between 0.73 and 0.41
 (c) in between 0.41 and 0.22 (d) less than 0.22
140. The Ca^{2+} and F^- are located in CaF_2 crystal respectively at face-centred cubic lattice points and in: (AIIMS 2006)
 (a) tetrahedral voids (b) half of tetrahedral voids
 (c) octahedral voids (d) half of octahedral voids
141. In calcium fluoride structure, the coordination numbers of calcium and fluoride ions are:
 (a) 8 and 4 (b) 6 and 8
 (c) 4 and 4 (d) 4 and 8
142. The unit cell of a binary compound of A and B metals has a ccp structure with A atoms occupying the corners and B atoms occupying the centres of each faces of the cubic unit cell. If during the crystallisation of this alloy, in the unit cell two A atoms are missed, the overall composition per unit cell is: [CET (J&K) 2009]
 (a) AB_6 (b) AB_4 (c) AB_8 (d) A_6B_{24}
 [Hint : Number of atoms of $A = 6 \times \frac{1}{8} = \frac{3}{4}$
 Number of atoms of $B = 6 \times \frac{1}{2} = 3$

$$A : B = \frac{3}{4} : 3 = 1 : 4$$

$$\therefore \text{Composition of alloy} = AB_4]$$
143. In a solid lattice, the cation has left a lattice site and is located at an interstitial position. The lattice defect is : [BHU (screening) 2008]
 (a) interstitial defect (b) vacancy defect
 (c) Frenkel defect (d) Schottky defect
144. Which of the following statements is incorrect about amorphous solids? (KCET 2004)
 (a) They are anisotropic
 (b) They are rigid and incompressible
 (c) They melt over a wide range of temperature
 (d) There is no orderly arrangement of particles
145. Which defect causes decrease in the density of a crystal?
 (a) Frenkel (b) Schottky
 (c) Interstitial (d) F -centre
146. For tetrahedral coordination number, the radius ratio r_c^+/r_a^- is: (KCET 2008)
 (a) 0.732 – 1.0 (b) 0.225 – 0.414
 (c) 0.414 – 0.732 (d) 0.155 – 0.225
147. What is the total number of ions present in one unit cell of sodium chloride lattice? (EAMCET 2006)
 (a) 2 (b) 6 (c) 12 (d) 8
148. The formula for determination of density of cubic unit cell is:
 (a) $\frac{a^3 N_0}{Z \times M} \text{ g cm}^{-3}$ (b) $\frac{Z \times N_0}{M \times a^3} \text{ g cm}^{-3}$
 (c) $\frac{a^3 \times M}{Z \times N_0} \text{ g cm}^{-3}$ (d) $\frac{Z \times M}{N_0 \times a^3} \text{ g cm}^{-3}$
149. The closest-packing sequence $ABAB \dots$ represents:
 (a) primitive cubic packing
 (b) body-centred cubic packing
 (c) face-centred cubic packing
 (d) hexagonal packing
150. The closest-packing sequence $ABCABC \dots$ represents:
 (a) primitive cubic packing
 (b) body-centred cubic packing
 (c) face-centred cubic packing
 (d) hexagonal packing
151. The edge length of face centred cubic cell of an ionic substance is 508 pm. If the radius of cation is 110 pm, the radius of anion is: (AIEEE 2010)
 (a) 618 pm (b) 144 pm
 (c) 288 pm (d) 398 pm
 [Hint : Edge length = $2(r^+ + r^-)$

$$508 = 2(110 + r^-)$$

$$r^- = 144 \text{ pm}]$$
152. Close packing is maximum in the crystal lattice of:
 (a) face-centred cubic (b) body-centred cubic
 (c) simple-centred cubic (d) none of these
153. The ratio between the root mean square speed of H_2 at 50 K and that of O_2 at 800 K is: (IIT 1996)
 (a) 4 (b) 2 (c) 1 (d) $1/4$
154. X mL of H_2 gas effused through a hole in a container in 5 second. The time taken for the effusion of the same volume of the gas specified below under identical conditions is: (IIT 1996)
 (a) 10 second : He (b) 20 second : O_2
 (c) 25 second : CO (d) 55 second : CO_2
155. The energy of a gas per litre is 300 joule. Its pressure will be:
 (a) $3 \times 10^5 \text{ N/m}^2$ (b) $6 \times 10^5 \text{ N/m}^2$
 (c) 10^5 N/m^2 (d) $2 \times 10^5 \text{ N/m}^2$
156. If the universal gas constant is $8.3 \text{ joule mol}^{-1} \text{ K}^{-1}$ and the Avogadro's number is 6×10^{23} . The mean kinetic energy of the oxygen molecules at 327°C will be:

- (a) 415×10^{-23} joule (b) 2490×10^{-22} joule
(c) 1245×10^{-23} joule (d) 830×10^{-22} joule
157. If increase in temperature and volume of an ideal gas is two times, then initial pressure of P changes to:
[JEE (Orissa) 2006]
(a) $4P$ (b) $2P$ (c) P (d) $3P$
158. The average kinetic energy of one molecule of an ideal gas at 27°C and 1 atm pressure is: (EAMCET 2009)
(a) $900 \text{ cal K}^{-1} \text{ mol}^{-1}$
(b) $6.21 \times 10^{-21} \text{ J K}^{-1} \text{ molecule}^{-1}$
(c) $336.7 \text{ J K}^{-1} \text{ molecule}^{-1}$
(d) $3741.3 \text{ J K}^{-1} \text{ mol}^{-1}$
[Hint : $\text{KE} = \frac{3}{2} \frac{R}{N} T$
 $= \frac{3}{2} \times \frac{8.314}{6.023 \times 10^{23}} \times 300$
 $= 6.21 \times 10^{-21} \text{ J K}^{-1} \text{ molecule}^{-1}$]
159. The respective speeds of five molecules are 2, 1.5, 1.6, 1.6 and 1.2 km/sec. The most probable speed in km/sec will be:
(a) 2 (b) 1.58 (c) 1.6 (d) 1.31
160. If one mole of a monoatomic gas ($\gamma = \frac{5}{3}$) is mixed with one mole of diatomic gas ($\gamma = \frac{7}{5}$), the value of γ for the mixture is:
(a) 1.40 (b) 1.50 (c) 1.53 (d) 3.07
161. The root mean square speed of hydrogen molecule of an ideal hydrogen gas kept in a gas chamber at 0°C is 3180 metre/second. The pressure on the hydrogen gas is: (density of hydrogen gas is $8.99 \times 10^{-2} \text{ kg/m}^3$, 1 atmosphere = $1.01 \times 10^5 \text{ N/m}^2$)
(a) 1.0 atmosphere (b) 1.5 atmosphere
(c) 2.0 atmosphere (d) 3.0 atmosphere
162. CH_4 diffuses two times faster than a gas X . The number of molecules present in 32 g of gas X is: (N is Avogadro number) [EAMCET (Engg.) 2010]
(a) N (b) $\frac{N}{2}$ (c) $\frac{N}{4}$ (d) $\frac{N}{16}$
[Hint: $\frac{r_{\text{CH}_4}}{r_{\text{gas}}} = \sqrt{\frac{m_{\text{gas}}}{m_{\text{CH}_4}}}$
 $2 = \sqrt{\frac{m_{\text{gas}}}{16}}$
 $m_{\text{gas}} = 64$
Number of molecules = $\frac{w}{\text{molar mass}} \times N$
 $= \frac{32}{64} \times N = \frac{N}{2}$]
163. At what temperature would the rms speed of a gas molecule have twice its value at 100°C ?
(a) 4192 K (b) 1492 K
(c) 9142 K (d) 2491 K
164. Find the rms speed of an argon molecule at 27°C (Molecular weight of argon = 40 gm/mol):
(a) 234.2 m/s (b) 342.2 m/s
(c) 432.2 m/s (d) 243.2 m/s
165. At a temperature T K, the pressure of 4 g argon in a bulb is P . The bulb is put in a bath having a temperature higher by 50 K than the first one. 0.8 g of argon gas had to be removed to maintain original pressure. The temperature T is equal to: (IIT 1999)
(a) 510 K (b) 200 K
(c) 100 K (d) 73 K
166. At 25°C and 730 mm pressure, 380 mL of dry oxygen was collected. If the temperature is constant, what volume will the oxygen occupy at 760 mm pressure? (CBSE 1999)
(a) 265 mL (b) 365 mL (c) 569 mL (d) 621 mL
167. Which of the following solids shows electrical conduction? (CBSE 1999)
(a) Graphite (b) Potassium chloride
(c) Diamond (d) Sodium chloride
168. Schottky defect in solids is due to: [PMT (Vellore) 2006; VITEEE 2006]
(a) a pair of cation and anion vacancies
(b) occupation of interstitial site by a pair of cation and anion
(c) occupation of interstitial site by a cation
(d) occupation of interstitial site by an anion
169. Copper crystallises in face-centred cubic lattice with a unit cell length of 361 pm. What is the radius of copper atom in pm? [CBSE (PMT) 2009; AIEEE 2009]
(a) 108 (b) 128 (c) 157 (d) 181
[Hint : $a\sqrt{2} = 4r$
 $361 \times \sqrt{2} = 4r$
 $r = 128 \text{ pm}$]
170. The second order Bragg diffraction of X-rays with $\lambda = 1 \text{ \AA}$ from a set of parallel planes in a metal occurs at an angle of 60° . The distance between the scattering planes in the crystal is: (CBSE 1998)
(a) 0.575 $\text{\AA}$ (b) 1.00 $\text{\AA}$
(c) 2.00 $\text{\AA}$ (d) 1.15 $\text{\AA}$
171. According to Graham's law at a given temperature, the ratio of the rates of diffusion r_A / r_B of gases A and B is given by: (IIT 1998)
(a) $\frac{P_A}{P_B} \cdot \left(\frac{M_A}{M_B}\right)^{1/2}$ (b) $\frac{M_A}{M_B} \cdot \left(\frac{P_A}{P_B}\right)^{1/2}$
(c) $\frac{P_A}{P_B} \cdot \left(\frac{M_B}{M_A}\right)^{1/2}$ (d) $\frac{M_A}{M_B} \cdot \left(\frac{P_B}{P_A}\right)^{1/2}$
172. The root mean square velocity of an ideal gas at constant pressure varies with density as: [IIT (Screening) 2000]
(a) d^2 (b) d (c) $\sqrt{d}$ (d) $1/\sqrt{d}$
173. Match the following:
List-I List-II
(A) Inversion temperature (i) a/Rb
(B) Boyle's temperature (ii) $8a/27Rb$
(C) Critical temperature (iii) $2a/Rb$
(a) A—(i), B—(ii), C—(iii) (b) A—(iii), B—(ii), C—(i)
(c) A—(iii), B—(i), C—(ii) (d) A—(i), B—(iii), C—(ii)

174. For three different gases values of van der Waals' constant 'a' and 'b' are given. What is the correct order of liquefaction of gases?

Gases	a	b
X_2	1.3	0.090
Y_2	4.1	0.023
Z_2	2.2	0.075

- (a) $X_2 > Y_2 > Z_2$ (b) $Y_2 > Z_2 > X_2$
 (c) $Z_2 > Y_2 > X_2$ (d) $X_2 > Z_2 > Y_2$
175. Match the following:
- | | |
|---------------|-----------------|
| List-I | List-II |
| (A) P_c | (i) $3b$ |
| (B) V_c | (ii) $8a/27bR$ |
| (C) T_c | (iii) $a/27b^2$ |
- (a) A—(i), B—(ii), C—(iii) (b) A—(iii), B—(ii), C—(i)
 (c) A—(ii), B—(iii), C—(i) (d) A—(iii), B—(i), C—(ii)
176. By what factor does the average velocity of a gaseous molecule increases when the absolute temperature is doubled? (DUMET 2010)
- (a) 1.4 (b) 2 (c) 2.8 (d) 4.0
177. The van der Waals' constant 'a' for different gases have been given as :

Gas	a (atm L ² mol ⁻²)
O ₂	1.36
N ₂	1.39
CH ₄	2.25
NH ₃	4.17

The gas that can be most easily liquefied is :

[JEE (Orissa) 2010]

- (a) O₂ (b) N₂ (c) CH₄ (d) NH₃

178. Match the following:

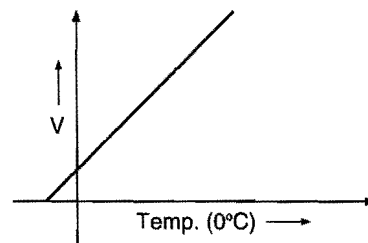
List-I	List-II
(A) U_{rms}/U_{av}	(i) 1.22
(B) U_{av}/U_{mp}	(ii) 1.13
(C) U_{rms}/U_{mp}	(iii) 1.08

(a) A—(iii), B—(ii), C—(i) (b) A—(i), B—(ii), C—(iii)
 (c) A—(iii), B—(i), C—(ii) (d) A—(ii), B—(iii), C—(i)

179. Joule-Thomson coefficient is zero at:
- (a) critical temperature (b) inversion temperature
 (c) absolute temperature (d) Boyle's temperature
180. At a constant pressure, what should be the percentage increase in temperature for a 10% increase in volume?
- (a) 10% (b) 11% (c) 8.9% (d) 12.5%
181. 5 g of unknown gas has pressure P at a temperature T K in a vessel. On increasing the temperature by 50°C, 1 g of the gas was given out to maintain the pressure P . The original temperature was:
- (a) 73 K (b) 100 K
 (c) 200 K (d) none of these
182. Which of the following expressions correctly represents the relationship between the average molar kinetic energy, KE of CO and N₂ molecules at the same temperature? [CBSE (PMT) 2000]
- (a) $\overline{KE}_{CO} = \overline{KE}_{N_2}$
 (b) $\overline{KE}_{CO} > \overline{KE}_{N_2}$
 (c) $\overline{KE}_{CO} < \overline{KE}_{N_2}$

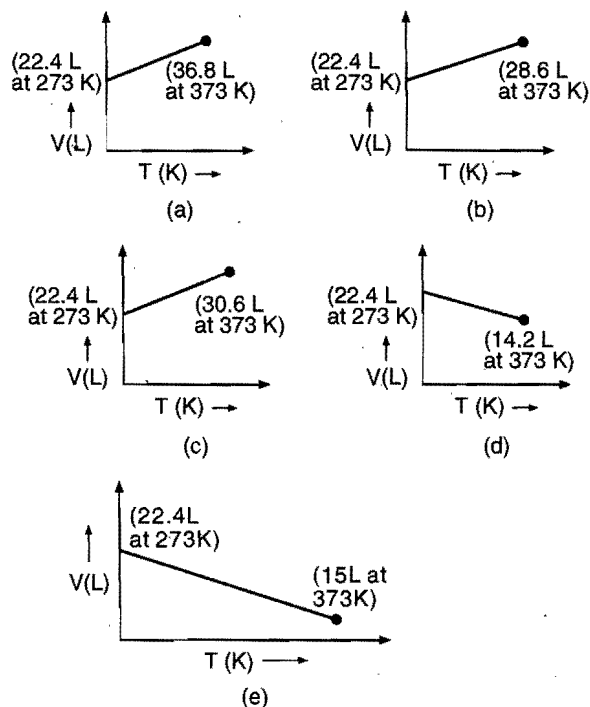
- (d) Cannot be predicted unless the volumes of the gases are given

183. Which of the following exhibits the weakest intermolecular forces? (AIIMS 2000)
- (a) NH₃ (b) HCl (c) He (d) H₂O
184. The compressibility of a gas is less than unity at STP. Therefore: [IIT 2000; PMT (MP) 2004]
- (a) $V_m > 22.4$ litre (b) $V_m < 22.4$ litre
 (c) $V_m = 22.4$ litre (d) $V_m = 44.8$ litre
185. The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If T is the temperature of the gas: (IIT 2000)
- (a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$
 (c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7}T(N_2)$
186. The kinetic energy of any gas molecule at 0°C is:
- (a) zero (b) 3408 J
 (c) 2 cal (d) 5.66×10^{-21} J
187. Densities of two gases are in the ratio 1 : 2 and their temperatures are in the ratio 2 : 1; then the ratio of their respective pressures is: (BHU 2000)
- (a) 1 : 1 (b) 1 : 2 (c) 2 : 1 (d) 4 : 1
188. Gas equation $PV = nRT$ is obeyed by: (BHU 2000)
- (a) only isothermal process (b) only adiabatic process
 (c) both (a) and (b) (d) none of these
189. An ideal gas will have maximum density when: (CPMT 2000)
- (a) $P = 0.5$ atm, $T = 600$ K (b) $P = 2$ atm, $T = 150$ K
 (c) $P = 1$ atm, $T = 300$ K (d) $P = 1.0$ atm, $T = 500$ K
190. The following graph illustrates: (JIPMER 2000)



- (a) Dalton's law (b) Charles' law
 (c) Boyle's law (d) Gay-Lussac's law
191. 4.4 g of a gas at STP occupies a volume of 2.24 L. The gas can be: [CET (Haryana) 2000]
- (a) O₂ (b) CO (c) NO₂ (d) CO₂
192. At 0°C and one atm pressure a gas occupies 100 cc. If the pressure is increased to one and a half times and temperature is increased by one-third of absolute temperature, then final volume of the gas will be: (DCE 2000)
- (a) 80 cc (b) 88.9 cc (c) 66.7 cc (d) 100 cc
193. Pressure of a mixture of 4 g of O₂ and 2 g of H₂ confined in a bulb of 1 litre at 0°C is: (AIIMS 2000)
- (a) 25.215 atm (b) 31.205 atm
 (c) 45.215 atm (d) 15.210 atm
194. Density ratio of O₂ and H₂ is 16 : 1. The ratio of their rms velocities will be: (AIIMS 2000)
- (a) 4 : 1 (b) 1 : 16 (c) 1 : 4 (d) 16 : 1

195. The rate of diffusion of a gas having molecular weight just double of nitrogen gas is 56 mL s^{-1} . The rate of diffusion of nitrogen will be: (CPMT 2000)
 (a) 79.19 mL s^{-1} (b) 112.0 mL s^{-1}
 (c) 56 mL s^{-1} (d) 90.0 mL s^{-1}
196. The density of air is 0.00130 g/mL . The vapour density of air will be: (DCE 2000)
 (a) 0.00065 (b) 0.65 (c) 14.4816 (d) 14.56
197. If 300 mL of a gas at 27°C is cooled to 7°C at constant pressure, its final volume will be: (AIIMS 2000)
 (a) 135 mL (b) 540 mL (c) 350 mL (d) 280 mL
198. For an ideal gas, number of moles per litre in terms of its pressure P , gas constant R and temperature T is: (AIEEE 2002)
 (a) PT/R (b) PRT (c) P/RT (d) RT/P
199. The van der Waals' equation reduces itself to the ideal gas equation at: [MEE (Kerala) 2001; CBSE (PMT) 2002]
 (a) high pressure and low temperature
 (b) low pressure and low temperature
 (c) low pressure and high temperature
 (d) high pressure alone
200. Which of the following volume (V), temperature (T) plots represents the behaviour of an ideal gas at one atmospheric pressure? [IIT (Screening) 2002; PET (Kerala) 2007]



201. The following is a method to determine the surface tension of liquids: [CET (J&K) 2007]
 (a) single capillary method (b) refractometric method
 (c) polarimetric method (d) boiling point method
202. The crystalline structure of NaCl is: [CET (J&K) 2007]
 (a) hexagonal close packing (b) face-centred cubic
 (c) square planar (d) body-centred cubic

203. A crystal lattice with alternate +ve and -ve ions has radius ratio 0.524, its coordination number is: [PMT (Manipal) 2002]
 (a) 4 (b) 3 (c) 6 (d) 12
204. The major binding force of diamond, silicon and quartz is: [MEE (Kerala) 2002]
 (a) electrostatic force (b) electrical attraction
 (c) covalent bond force (d) non-covalent bond force
 (e) van der Waals' force
205. A compound is formed by elements A and B . This crystallizes in the cubic structure when atoms A are at the corners of the cube and atoms B are at the centre of the body. The simplest formula of the compound is: (DPMT 2009)
 (a) AB (b) AB_2 (c) A_2B (d) AB_4
206. The coordination number of a metal crystallizing in a hexagonal close packed (hcp) structure is: [PET (MP) 2004]
 (a) 6 (b) 12 (c) 8 (d) 4
207. The crystal system of a compound with unit cell dimensions $a = 0.387$, $b = 0.387$, $c = 0.504 \text{ nm}$ and $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ is: (AIIMS 2004)
 (a) cubic (b) hexagonal
 (c) orthorhombic (d) rhombohedral
208. The maximum number of molecules is present in: [CBSE (PMT) 2004]
 (a) 15 L of H_2 gas at STP (b) 5 L of N_2 gas at STP
 (c) 0.5 g of H_2 gas (d) 10 g of O_2 gas
209. The root mean square velocity of one mole of a monoatomic gas having molar mass M is U_{rms} . The relation between average kinetic energy (E) of the gas and U_{rms} is: [IIT (S) 2004]

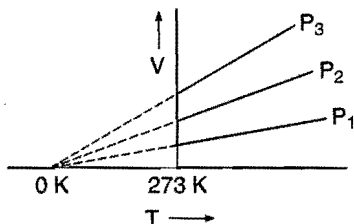
$$(a) U_{\text{rms}} = \sqrt{\frac{3E}{2M}} \quad (b) U_{\text{rms}} = \sqrt{\frac{2E}{3M}}$$

$$(c) U_{\text{rms}} = \sqrt{\frac{2E}{M}} \quad (d) U_{\text{rms}} = \sqrt{\frac{E}{3M}}$$

210. Which of the following is not a property of liquid state? [BHU (Pre) 2005]
 (a) Intermolecular force of attraction in a liquid is quite large
 (b) All liquids accompanied by cooling on evaporation
 (c) Lower the boiling point of a liquid, greater is its vapour pressure at room temperature
 (d) A liquid boils at higher temperature at the top of a mountain than at the sea level
211. A certain sample of a gas has a volume of 0.2 litre measured at 1 atm pressure and 0°C . At the same pressure but 273°C , its volume will be: [BHU (Pre) 2005]
 (a) 0.4 L (b) 0.8 L (c) 27.8 L (d) 55.6 L
212. When electrons are trapped into the crystal in anion vacancy, the defect is known as: [BHU (Pre) 2005]
 (a) Schottky defect (b) Frenkel defect
 (c) stoichiometric defect (d) F -centres
213. In the equation of state of an ideal gas $PV = nRT$, the value of the universal gas constant R would depend only on the: (KCET 2005)
 (a) nature of the gas (b) pressure of the gas
 (c) units of the measurement (d) none of these

214. If Z is the number of atoms in the unit cell that represents the closest packing sequence $ABC\ ABC\ \dots$, the number of tetrahedral voids in the unit cell is equal to: (AIIMS 2005)
- (a) Z (b) $2Z$ (c) $\frac{Z}{2}$ (d) $\frac{Z}{4}$
215. Equation of Boyle's law is: (DPMT 2005)
- (a) $\frac{dP}{P} = -\frac{dV}{V}$ (b) $\frac{dP}{P} = +\frac{dV}{V}$
 (c) $\frac{d^2P}{P} = -\frac{dV}{dT}$ (d) $\frac{d^2P}{P} = +\frac{d^2V}{dt}$
- [Hint: $PV = \text{constant}$
 $P dV + V dP = 0$
 $\frac{dP}{P} = -\frac{dV}{V}$]
216. In a face-centred cubic unit cell, edge length is: (DPMT 2005)
- (a) $\frac{4}{\sqrt{3}} r$ (b) $\frac{4}{\sqrt{2}} r$ (c) $2r$ (d) $\frac{\sqrt{3}}{2} r$
217. If v_{rms} is $30R^{1/2}$ at 27°C , then calculate the molar mass of the gas in kilogram: (DPMT 2005)
- (a) 1 (b) 2 (c) 4 (d) 0.001
- [Hint: $v_{\text{rms}} = \sqrt{\frac{3RT}{m}}$
 $30R^{1/2} = \sqrt{\frac{3 \times R \times 300}{m}}$
 $m = 0.001 \text{ kg}$]
218. The pressure exerted by 1 mole of methane in a 0.25 litre container at 300 K using van der Waals' equation (given $a = 2.253 \text{ atm L}^2 \text{ mol}^{-2}$, $b = 0.0428 \text{ L mol}^{-1}$) is: [JEE (Orissa) 2005]
- (a) 82.82 atm (b) 152.51 atm
 (c) 190.52 atm (d) 70.52 atm
219. An ionic compound has a unit cell consisting of ' A ' ions at the corners of a cube and ' B ' ions on the centres of the faces of the cube. The empirical formula for this compound would be: [AIEEE 2005; CET (Karnataka) 2009]
- (a) AB (b) A_2B
 (c) AB_3 (d) A_3B
220. Which one of the following statements is not true about the effect of an increase in temperature on the distribution of molecular speeds in a gas?
- (a) The most probable speed increases
 (b) The fraction of the molecules with most probable speed increases
 (c) The distribution becomes broader
 (d) The area under the distribution curve remains the same as under the lower temperature
221. A gas can be liquefied: (AFMC 2005)
- (a) above its critical temperature
 (b) at its critical temperature
 (c) below its critical temperature
 (d) at any temperature
222. If the absolute temperature of a gas is doubled and the pressure is reduced to one-half, the volume of the gas will: [PET (Kerala) 2005]
- (a) remain unchanged (b) be doubled
 (c) increase fourfold (d) be halved
 (e) be reduced to one-fourth
- [Hint: Use $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$]
223. To what temperature must a neon gas sample be heated to double the pressure, if the initial volume of a gas at 75°C is decreased by 15%? [PET (Kerala) 2005]
- (a) 319°C (b) 592°C (c) 128°C (d) 60°C
 (e) 90°C
- [Hint: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
 $\frac{PV}{348} = \frac{2P \times 85V}{T_2 \times 100}$
 $T_2 = 591.6 \text{ K}$
 $t_2 = 318.6^\circ\text{C}$]
224. The surface tension of which of the following liquids is maximum? [CBSE (Pre) 2005]
- (a) $\text{C}_2\text{H}_5\text{OH}$ (b) CH_3OH (c) H_2O (d) C_6H_6
- [Hint: (c) Due to hydrogen bonding, H_2O has the highest intermolecular force, hence its surface tension is also maximum.]
225. An element (with atomic mass = 250 g) crystallises in a simple cube. If the density of unit cell is 7.2 g cm^{-3} , what is the radius of the element? [JEE (Orissa) 2006]
- (a) $1.93 \times 10^{-6} \text{ cm}$ (b) $1.93 \times 10^{-8} \text{ cm}$
 (c) $1.93 \times 10^{-8} \text{ \AA}$ (d) $1.93 \times 10^{-8} \text{ m}$
- [Hint: $Z = \frac{l^3 \times \rho \times N_A}{M}$
 $1 = \frac{l^3 \times 7.2 \times 6.023 \times 10^{23}}{250}$
 $l = 3.86 \times 10^{-8} \text{ cm}$
 $l = 2r$ (for simple cubic unit cell)
 $r = \frac{l}{2} = \frac{3.86 \times 10^{-8}}{2} = 1.93 \times 10^{-8} \text{ cm}$]
226. Dominance of strong repulsive forces among the molecules of the gas (Z = compressibility factor): (AIIMS 2006)
- (a) depends on Z and indicated by $Z = 1$
 (b) depends on Z and indicated by $Z > 1$
 (c) depends on Z and indicated by $Z < 1$
 (d) is independent of Z
- [Hint: When $Z > 1$, the gas is less compressible than ideal gas and the repulsive forces dominate.]
227. Total volume of atoms present in a face-centred cubic unit cell of a metal is (r is atomic radius): (AIEEE 2006)
- (a) $\frac{20}{3} \pi r^3$ (b) $\frac{24}{3} \pi r^3$ (c) $\frac{12}{3} \pi r^3$ (d) $\frac{16}{3} \pi r^3$
228. If we know the ionic radius ratio in a crystal of ionic solid, what can be known of the following? [CET (Gujarat) 2006]
- (a) Magnetic property
 (b) Nature of chemical bond
 (c) Type of defect
 (d) Geometrical shape of crystal

229. If a volume containing gas is compressed to half, how many moles of gas remained in the vessel? (DCE 2006)
 (a) Just double (b) Just half
 (c) Same (d) More than double
230. The volume-temperature graphs of a given mass of an ideal gas at constant pressures are shown below. What is the correct order of pressures? (EAMCET 2006; AIIMS 2008)



- (a) $P_1 > P_3 > P_2$ (b) $P_1 > P_2 > P_3$
 (c) $P_2 > P_3 > P_1$ (d) $P_2 > P_1 > P_3$
231. If NaCl is doped with 10^{-4} mol % of SrCl_2 , the concentration of cation vacancies will be ($N_A = 6.023 \times 10^{23}$): [CBSE (Medical) 2007]
 (a) $6.02 \times 10^{16} \text{ mol}^{-1}$ (b) $6.02 \times 10^{17} \text{ mol}^{-1}$
 (c) $6.02 \times 10^{14} \text{ mol}^{-1}$ (d) $6.02 \times 10^{15} \text{ mol}^{-1}$
232. Coordination number of NaCl crystal will be: [PET (MP) 2007]
 (a) 8:8 (b) 6:6 (c) 4:4 (d) 2:2
233. The unit cell of Al (molar mass 27 g mol^{-1}) has an edge length of 405 pm. Its density is 2.7 g cm^{-3} . The cubic unit cell is: [PET (Kerala) 2007]
 (a) face-centred (b) body-centred (c) primitive
 (d) edge-centred (e) simple
- [Hint: $Z = \frac{a^3 \times d \times N_A}{M} = \frac{(405 \times 10^{-10})^3 \times 2.7 \times 6.023 \times 10^{23}}{27} = 4$
 $\therefore$ It is a face-centred cubic unit cell.]
234. The 8:8 type packing is present in: (VITEEE 2007)
 (a) MgF_2 (b) CsCl (c) KCl (d) NaCl
235. Equal masses of methane and oxygen are mixed in an empty container at 25°C . The fraction of the total pressure exerted by oxygen is: [AIEEE 2007; EAMCET (Med.) 2010]
 (a) $\frac{1}{2}$ (b) $\frac{2}{3}$ (c) $\frac{1}{3} \times \frac{273}{298}$ (d) $\frac{1}{3}$
236. Percentage of free space in a body centred cubic unit cell is: [CBSE (PMT) 2008]
 (a) 34% (b) 28% (c) 30% (d) 32%
237. Which of the following statement is not correct? [CBSE (PMT) 2008]
 (a) The number of carbon atoms in a unit cell of diamond is 4.
 (b) The number of Bravais lattices in which a crystal can be categorized is 14.
 (c) The fraction of the total volume occupied by the atoms in a primitive cell is 0.48.
 (d) Molecular solids are generally volatile.
238. If a stands for the edge length of the cubic systems: simple cubic, body centred cubic and face centred cubic, then the ratio of radii of the spheres in these systems will be respectively: [CBSE (PMT) 2008]

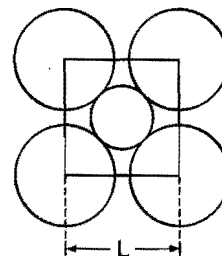
- (a) $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{2}}{2}a$ (b) $1a : \sqrt{3}a : \sqrt{2}a$
 (c) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$ (d) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$

[Hint: Simple unit cell, $r = a/2$

Body centred unit cell, $r = \frac{a\sqrt{3}}{4}$

Face centred unit cell, $r = \frac{a}{2\sqrt{2}}$]

239. The term that corrects for the attractive forces present in a real gas in the van der Waals' equation is: (IIT 2009)
 (a) nb (b) $\frac{an^2}{V^2}$ (c) $\frac{-an^2}{V^2}$ (d) $-nb$
240. Which is not the correct statement for ionic solids in which positive and negative ions are held by strong electrostatic attractive forces? (DCE 2009)
 (a) The ratio $\frac{r^+}{r^-}$ increases as coordination number increases
 (b) As the difference in size of ions increases coordination number increases
 (c) When coordination number is eight, the $\frac{r^+}{r^-}$ ratio lies between 0.225 – 0.414
 (d) In ionic solid of the type AX (ZnS , Wurtzite) the coordination number of Zn^{2+} and S^{2-} respectively are 4 and 4
241. The packing efficiency of the two-dimensional square unit cell shown below is: (IIT 2010)



- (a) 39.27% (b) 68.02%
 (c) 74.05% (d) 78.54%

[Hint: $a\sqrt{2} = 4r$

$$a = 2\sqrt{2}r$$

$$\text{Packing fraction} = \frac{\text{Occupied area}}{\text{Total area}} \times 100$$

$$= \frac{2\pi r^2}{(2\sqrt{2}r)^2} \times 100 = 78.5\%$$

Set-2: The questions given below may have more than one correct answers

1. If force of attraction between the molecules is negligible, van der Waals' equation (for one mole) will become:
 (a) $PV = RT + Pb$ (b) $P = \frac{RT}{V-b} - \frac{a}{V^2}$
 (c) $PV = RT + a/V$ (d) $PV = RT - a/V$

2. van der Waals' equation for:

- A. High pressure (i) $PV = RT + Pb$
 B. Low pressure (ii) $PV = RT - a/V$
 C. Force of attraction is negligible (iii) $PV = RT + a/V$
 D. Volume of molecules is negligible (iv) $\left(P + \frac{a}{V^2}\right)(V - b) = RT$
- (a) A (iv), B (ii), C (i), D (iii)
 (b) A (i), B (ii), C (iii), D (iv)
 (c) A (iv), B (iii), C (ii), D (i)
 (d) A (iv), B (ii), C (iii), D (i)

3. van der Waals' constants for three different gases are given:

Gases	a	b
X	3.0	0.025
Y	10.0	0.030
Z	6.0	0.035

Which is correct?

- (a) Maximum critical temperature—Y
 (b) Most ideal behaviour—X
 (c) Maximum molecular volume—Z
 (d) All are correct
4. What is the ratio of mean speed of an O_3 molecule to the rms speed of an O_2 molecule at the same T ?
 (a) $(3\pi/7)^{1/2}$ (b) $(16/9\pi)^{1/2}$
 (c) $(3\pi)^{1/2}$ (d) $(4\pi/9)^{1/2}$
5. Boyle's law may be represented as:
 (a) $\left(\frac{dP}{dV}\right)_T = K/V$ (b) $\left(\frac{dP}{dV}\right)_T = -\frac{K}{V}$
 (c) $\left(\frac{dP}{dV}\right) = -\frac{K}{V^2}$ (d) $\left(\frac{dP}{dV}\right)_T = \frac{K}{V^2}$
- where, $K = \text{constant}$.
6. If pressure of a gas is increased by 1% when heated by 1°C , its initial temperature must be (if volume remains constant):
 (a) 100 K (b) 100°C (c) 250 K (d) 250°C
7. Which of the following are not the units of gas constant, R ?
 (a) $\text{dyne K}^{-1} \text{mol}^{-1}$ (b) $\text{erg deg}^{-1} \text{mol}^{-1}$
 (c) $\text{cm}^3 \text{K}^{-1} \text{mol}^{-1}$ (d) $\text{kPa dm}^3 \text{K}^{-1} \text{mol}^{-1}$

8. According to Charles' law:

- (a) $V \propto \frac{1}{T}$ (b) $\left(\frac{dV}{dT}\right)_P = K$
 (c) $\left(\frac{dT}{dV}\right)_P = K$ (d) $\left(\frac{1}{T} - \frac{V}{T^2}\right)_P = 0$

9. In the following statements :

- (A) ideal gases are liquefied only at very low temperatures
 (B) ideal gases can not be liquefied
 (C) ideal gas behaviour is observed by real gases at low pressures
 (D) ideal gases do not exist

The correct statements are :

(ISAT 2010)

- (a) A, B, C and D (b) A, B and C
 (c) B, C and D (d) C and D

10. Which of the following relationships is/are not true?

- (a) Most probable velocity = $\sqrt{\frac{2RT}{M}}$
 (b) $PV = \frac{3}{2} kT$
 (c) Compressibility factor $Z = \frac{PV}{nRT}$
 (d) Average kinetic energy of gas = $\frac{1}{2} kT$

11. According to kinetic theory of gases: (IIT 1991)

- (a) the pressure exerted by a gas is proportional to mean square velocity of the molecules
 (b) the pressure exerted by the gas is proportional to the root mean square velocity of the molecules
 (c) the root mean square velocity is inversely proportional to the temperature
 (d) the mean translational KE of the molecule is directly proportional to the absolute temperature

12. A gas described by van der Waals' equation : (IIT 2008)

- (a) behaves similar to an ideal gas in the limit of large molar volume
 (b) behaves similar to an ideal gas in the limit of large pressures
 (c) is characterised by van der Waals' constant that are dependent on identity of the gas but are independent of the temperature.
 (d) has the pressure that is lower than the pressure exerted by the same behaving ideally.

Assertion-Reason TYPE QUESTIONS**Set-1**

The questions given below consist of an 'Assertion' (A) and the 'Reason' (R). Use the following keys to choose the appropriate answer:

- (a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).
 (b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).
 (c) If (A) is correct, but (R) is incorrect.

(d) If (A) is incorrect, but (R) is correct.

1. (A) The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
 (R) The volume occupied by the molecules of an ideal gas is zero. (IIT 2000)
2. (A) The pressure of a fixed amount of an ideal gas is proportional to its temperature.
 (R) Frequency of collisions and their impact both increase in proportion of the square root of temperature. (IIT 2000)

3. (A) $C_p - C_v = R$ for an ideal gas.
(R) $\left(\frac{\partial E}{\partial V}\right)_T = 0$ for an ideal gas.
4. (A) A lighter gas diffuses more rapidly than a heavier gas.
(R) At a given temperature, the rate of diffusion of a gas is inversely proportional to the square root of its density.
5. (A) On cooling, the brown colour of nitrogen dioxide disappears.
(R) On cooling, NO_2 undergoes dimerisation resulting in the pairing of the odd electrons in NO_2 .
6. (A) The value of the van der Waals' constant 'a' is larger for ammonia than for nitrogen.
(R) Hydrogen bonding is present in ammonia.
7. (A) The Joule-Thomson coefficient for the ideal gas is zero.
(R) There are no intermolecular attractive forces in an ideal gas.
8. (A) At 27°C , the kinetic energy of 8 gram of methane is equal to the kinetic energy of 16 gram of oxygen.
(R) The total heat change in a reaction is the same whether the chemical reaction takes place in one single step or in several steps. (EAMCET 2006)
9. (A) A closed cylinder containing high pressure gas tends to rise against gravity when the gas is allowed to escape through an orifice at the bottom.
(R) The velocity of escaping gas develops an upward thrust proportional to the area of cross-section of the orifice. (SCRA 2007)
[Hint: Assertion is correct but reason is wrong as the velocity of escaping gas is inversely proportional to the area of cross-section of orifice.]
10. (A) Meniscus of a liquid disappears at the critical temperature.
(R) Density of liquid and its gaseous phase become equal at the critical temperature. [BHU (Screening) 2008]
11. (A) Graphite is soft while diamond is hard.
(R) Graphite has three dimensional structure while diamond has planar. [BHU (Screening) 2008]
12. (A) White tin is an example of tetragonal system.
(R) For tetragonal system $a = b = c$ and $\alpha = \beta = \gamma \neq 90^\circ$.
16. (A) Under similar conditions of temperature and pressure, O_2 diffuses 1.4 times faster than SO_2 .
(R) Density of SO_2 is 1.4 times greater than that of O_2 .
17. (A) On compressing a gas to half the volume, the number of moles is halved.
(R) The number of moles present decreases with decrease in volume.
18. (A) The plot of volume (V) versus pressure (P) at constant temperature is a hyperbola in the first quadrant.
(R) $V \propto 1/P$ at constant temperature.
19. (A) At constant temperature, if pressure on the gas is doubled, density is also doubled.
(R) At constant temperature, molecular mass of a gas is directly proportional to the density and inversely proportional to the pressure.
20. (A) If H_2 and Cl_2 enclosed separately in the same vessel exert pressures of 100 and 200 mm respectively, their mixture in the same vessel at the same temperature will exert a pressure of 300 mm.
(R) Dalton's law of partial pressures states that total pressure is the sum of partial pressures.
21. (A) Most probable velocity is the velocity possessed by maximum fraction of molecules at the same temperature.
(R) On collision, more and more molecules acquire higher speed at the same temperature.
22. (A) Compressibility factor (Z) for non-ideal gases is always greater than 1.
(R) Non-ideal gases always exert higher pressure than expected.
23. (A) van der Waals' equation is applicable only to non-ideal gases.
(R) Ideal gases obey the equation $PV = nRT$.
24. (A) Helium shows only positive deviations from ideal behaviour.
(R) Helium is an inert gas.
25. (A) Gases are easily absorbed on the surface of metals, especially transition metals.
(R) Transition metals have free valencies.
26. (A) SO_2 gas is easily liquefied while H_2 is not.
(R) SO_2 has low critical temperature while H_2 has high critical temperature.
27. (A) Diffusion is used in the enrichment of U^{235} .
(R) A lighter gas diffuses more rapidly than a heavier gas.
28. (A) Crystalline solids can cause X-rays to diffract.
(R) Interatomic distance in crystalline solids is of the order of 0.1 nm. (AIIMS 2004)
29. (A) The effusion rate of oxygen is smaller than that of nitrogen.
(R) Molecular size of nitrogen is smaller than that of oxygen. (AIIMS 2004)
30. (A) The compressibility factor for hydrogen varies with pressure with positive slope at all pressures.
(R) Even at low pressures, the repulsive forces dominate in hydrogen gas. (AIIMS 2005)
31. (A) Graphite is an example of tetragonal crystal system.
(R) For a tetragonal system $a = b \neq c$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. (AIIMS 2006)
32. (A) No compound has both Schottky and Frenkel defects.
(R) Both defects change the density of the solid. (AIIMS 2008)

Set-2

The questions given below consist of two statements each printed as 'Assertion' (A) and 'Reason' (R). While answering these questions you are required to choose any one of the following four responses:

- (a) If both (A) and (R) are true and (R) is the correct explanation for (A).
- (b) If both (A) and (R) are true but (R) is not the correct explanation for (A).
- (c) If (A) is true but (R) is false.
- (d) If both (A) and (R) are false.
13. (A) Sulphur dioxide and chlorine are both bleaching agents.
(R) Both are reducing agents. (AIIMS 1994)
14. (A) Nitrogen is unreactive at room temperature but becomes reactive at elevated temperatures (on heating or in the presence of catalysts).
(R) In nitrogen molecule, there is extensive delocalisation of electrons. (AIIMS 1996)
15. (A) Noble gases can be liquefied.
(R) Attractive forces can exist between non-polar molecules. (AIIMS 1998)

Answers : OBJECTIVE QUESTIONS

● Set-1

- | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (c) | 2. (d) | 3. (d) | 4. (a) | 5. (a) | 6. (b) | 7. (b) | 8. (c) |
| 9. (a) | 10. (a) | 11. (a) | 12. (c) | 13. (b) | 14. (c) | 15. (d) | 16. (d) |
| 17. (b) | 18. (b) | 19. (d) | 20. (a) | 21. (d) | 22. (b) | 23. (a) | 24. (a) |
| 25. (c) | 26. (a) | 27. (a) | 28. (d) | 29. (b) | 30. (c) | 31. (a) | 32. (b) |
| 33. (a) | 34. (b) | 35. (b) | 36. (a) | 37. (d) | 38. (b) | 39. (c) | 40. (b) |
| 41. (d) | 42. (d) | 43. (c) | 44. (c) | 45. (a) | 46. (b) | 47. (d) | 48. (c) |
| 49. (c) | 50. (c) | 51. (d) | 52. (b) | 53. (d) | 54. (c) | 55. (a) | 56. (a) |
| 57. (a) | 58. (d) | 59. (d) | 60. (a) | 61. (b) | 62. (b) | 63. (c) | 64. (c) |
| 65. (d) | 66. (c) | 67. (a) | 68. (d) | 69. (b) | 70. (b) | 71. (d) | 72. (a) |
| 73. (a) | 74. (c) | 75. (d) | 76. (c) | 77. (b) | 78. (c) | 79. (d) | 80. (a) |
| 81. (c) | 82. (b) | 83. (a) | 84. (d) | 85. (c) | 86. (c) | 87. (a) | 88. (b) |
| 89. (a) | 90. (d) | 91. (c) | 92. (b) | 93. (d) | 94. (a) | 95. (d) | 96. (b) |
| 97. (b) | 98. (c) | 99. (a) | 100. (d) | 101. (a) | 102. (d) | 103. (b) | 104. (c) |
| 105. (c) | 106. (a) | 107. (d) | 108. (b) | 109. (b) | 110. (b) | 111. (d) | 112. (a) |
| 113. (c) | 114. (b) | 115. (a) | 116. (d) | 117. (a) | 118. (a) | 119. (b) | 120. (c) |
| 121. (d) | 122. (d) | 123. (c) | 124. (d) | 125. (b) | 126. (b) | 127. (c) | 128. (a) |
| 129. (a) | 130. (c) | 131. (b) | 132. (a) | 133. (d) | 134. (d) | 135. (a) | 136. (b) |
| 137. (d) | 138. (c) | 139. (b) | 140. (a) | 141. (a) | 142. (b) | 143. (c) | 144. (a) |
| 145. (b) | 146. (c) | 147. (c) | 148. (d) | 149. (d) | 150. (c) | 151. (b) | 152. (a) |
| 153. (c) | 154. (b) | 155. (d) | 156. (c) | 157. (c) | 158. (b) | 159. (d) | 160. (b) |
| 161. (d) | 162. (b) | 163. (b) | 164. (c) | 165. (b) | 166. (b) | 167. (a) | 168. (a) |
| 169. (b) | 170. (d) | 171. (c) | 172. (d) | 173. (c) | 174. (b) | 175. (d) | 176. (a) |
| 177. (d) | 178. (b) | 179. (a) | 180. (a) | 181. (b) | 182. (a) | 183. (c) | 184. (b) |
| 185. (c) | 186. (d) | 187. (a) | 188. (c) | 189. (b) | 190. (b) | 191. (d) | 192. (b) |
| 193. (a) | 194. (c) | 195. (a) | 196. (d) | 197. (d) | 198. (c) | 199. (c) | 200. (c) |
| 201. (a) | 202. (b) | 203. (c) | 204. (c) | 205. (a) | 206. (b) | 207. (b) | 208. (a) |
| 209. (b) | 210. (d) | 211. (a) | 212. (d) | 213. (c) | 214. (b) | 215. (a) | 216. (a) |
| 217. (d) | 218. (a) | 219. (c) | 220. (b) | 221. (c) | 222. (c) | 223. (a) | 224. (c) |
| 225. (b) | 226. (b) | 227. (d) | 228. (d) | 229. (c) | 230. (b) | 231. (b) | 232. (b) |
| 233. (a) | 234. (a) | 235. (d) | 236. (d) | 237. (c) | 238. (c) | 239. (b) | 240. (c) |
| 241. (d) | | | | | | | |

● Set-2

- | | | | | | | | |
|--------|---------|------------|------------|--------|--------|-----------|--------------|
| 1. (a) | 2. (a) | 3. (d) | 4. (b) | 5. (a) | 6. (a) | 7. (a, c) | 8. (b, c, d) |
| 9. (c) | 10. (d) | 11. (b, d) | 12. (a, c) | | | | |

Answers : ASSERTION-REASON TYPE QUESTIONS

- | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (c) | 3. (b) | 4. (a) | 5. (a) | 6. (a) | 7. (a) | 8. (b) |
| 9. (c) | 10. (a) | 11. (c) | 12. (c) | 13. (c) | 14. (c) | 15. (a) | 16. (c) |
| 17. (d) | 18. (a) | 19. (c) | 20. (d) | 21. (c) | 22. (d) | 23. (b) | 24. (b) |
| 25. (a) | 26. (c) | 27. (b) | 28. (c) | 29. (c) | 30. (a) | 31. (d) | 32. (d) |

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

The following questions have single correct option:

1. Which of the following graphs is not a straight line for an ideal gas?

(a) $V \rightarrow T$ (b) $T \rightarrow P$ (c) $n \rightarrow \frac{1}{T}$ (d) $n \rightarrow \frac{1}{P}$

2. The quantity $(PV / k_B T)$ represents the:

- (a) number of molecules in the gas
(b) mass of the gas
(c) number of moles of the gas
(d) translational energy of the gas

[Hint: $PV = nRT$

$$n = \frac{PV}{RT}$$

$$\begin{aligned} \text{Number of molecules} &= N_A \frac{PV}{RT} \\ &= \frac{PV}{(R/N_A)T} = \frac{PV}{k_B T} \end{aligned}$$

where, k_B = Boltzmann constant.]

3. 1 litre of N_2 and $7/8$ litre of O_2 at the same temperature and pressure were mixed together. What is the relation between the masses of the two gases in the mixture?

- (a) $M_{N_2} = 3M_{O_2}$ (b) $M_{N_2} = 8M_{O_2}$
(c) $M_{N_2} = M_{O_2}$ (d) $M_{N_2} = 16M_{O_2}$

[Hint: $PV = \frac{M}{m} RT$

$$P \times 1 = \frac{M_{N_2}}{28} RT \quad \dots (i)$$

$$P \times \frac{7}{8} = \frac{M_{O_2}}{32} RT \quad \dots (ii)$$

Dividing eq. (i) by eq. (ii), we get

$$M_{N_2} = M_{O_2}$$

4. A box is divided into two equal compartments by a thin partition and they are filled with gases X and Y respectively. The two compartments have a pressure of 250 torr each. The pressure after removing the partition will be equal to:

- (a) 125 torr (b) 500 torr (c) 250 torr (d) 750 torr

5. The density of a gas A is twice that of a gas B at the same temperature. The molecular mass of gas B is thrice that of A . The ratio of the pressures acting on A and B will be:

- (a) 6 : 1 (b) 7 : 8 (c) 2 : 5 (d) 1 : 4

[Hint: $Pm = dRT$

$$\frac{P_A m_A}{P_B m_B} = \frac{d_A RT}{d_B RT}$$

$$\frac{P_A}{P_B} \times \frac{1}{3} = 2$$

$$P_A : P_B = 6 : 1]$$

6. In the corrections made to the ideal gas equation for real gases, the reduction in pressure due to attractive forces is directly proportional to:

- (a) n/V (b) nb (c) $\frac{n^2}{V^2 b}$ (d) $\frac{n^2}{V^2}$

[Hint: Pressure correction = $a \frac{n^2}{V^2}$

$\therefore$ Pressure correction $\propto \frac{n^2}{V^2}$]

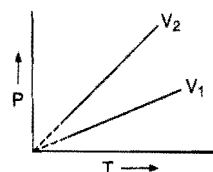
7. Which of the following conditions is favourable for liquefaction of gas?

- (a) $T > T_c; P > P_c$ (b) $T < T_c; P > P_c$
(c) $T = T_c; P = P_c$ (d) $T = T_c; P < P_c$

8. An ideal gas of certain mass is heated in a small vessel and then in a large vessel, such that their volume remains unchanged. The $P-T$ curves are:

- (a) parabolic with same curvature
(b) parabolic with different curvatures
(c) linear with same slope
(d) linear with different slopes

[Hint:



Straight lines with different slopes will be obtained.]

9. A spherical air bubble is rising from the depth of a lake when pressure is P atm and temperature is T K. The percentage increase in its radius when it comes to the surface of a lake will be: (Assume temperature and pressure at the surface to be respectively $2T$ K and $P/4$.)

- (a) 100% (b) 50% (c) 40% (d) 200%

[Hint: $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$; V_1 = initial volume, V_2 = final volume

$$\frac{P V_1}{T} = \frac{P}{4} \times \frac{V_2}{2T}$$

$$V_1 = \frac{V_2}{8}$$

$$V_2 = 8V_1$$

$$V_2 = 8 \times \frac{4}{3} \pi r^3 = \frac{4}{3} \pi (8r)^3$$

New radius = $2r$ ($\therefore$ 100% radius will increase)]

10. It is easier to liquefy oxygen than hydrogen because:

- (a) oxygen has a higher critical temperature and lower inversion temperature than hydrogen
(b) oxygen has a lower critical temperature and higher inversion temperature than hydrogen

- (c) oxygen has a higher critical temperature and a higher inversion temperature than hydrogen
 (d) the critical temperature and inversion temperature of oxygen is very low

11. 2 mole 'He' is mixed with 2 gm of H_2 . The molar heat capacity at constant pressure for the mixture is:

- (a) $\frac{17R}{6}$ (b) $\frac{11R}{6}$ (c) $4R$ (d) $\frac{3R}{2}$

[Hint: C_{P1} for 'He' = $\frac{5}{2}R$; C_{P2} for H_2 = $\frac{7}{2}R$

$$n_{He} = 2; n_{H_2} = 1$$

$$C_P = \frac{n_1 C_{P1} + n_2 C_{P2}}{n_1 + n_2} = \frac{2 \times \frac{5}{2}R + 1 \times \frac{7}{2}R}{3} = \frac{17R}{6}$$

12. The van der Waals' constant 'a' for the gases O_2 , N_2 , NH_3 and CH_4 are 1.36, 1.39, 4.17 and 2.253 respectively, the gas which can be most easily liquefied is:

- (a) O_2 (b) N_2 (c) NH_3 (d) CH_4

[Hint: The van der Waals' constant 'a' is directly proportional to the intermolecular force; hence, the gas with greater value of 'a' can be most easily liquefied.]

13. At what temperature will the molar kinetic energy of 0.3 mole of 'He' be the same as that of 0.4 mole of argon at 400 K?

- (a) 700 K (b) 500 K (c) 800 K (d) 400 K

[Hint: $KE = \frac{3}{2} nRT$

$n = 1$, for molar kinetic energy

$$\left(\frac{3}{2} \times 1 \times R \times T \right)_{\text{Helium}} = \left(\frac{3}{2} \times 1 \times R \times 400 \right)_{\text{Argon}}$$

$$T = 400 \text{ K}]$$

14. Let P_s and P be the saturated partial pressure and partial pressure of water respectively. Then the relative humidity is given by:

- (a) $\frac{P_s + P}{P_s} \times 100$ (b) $\frac{P}{P_s} \times 100$
 (c) $\frac{P_s}{P} \times 100$ (d) $(P + P_s) \times 100$

15. Molar volume of a monoatomic gas at P_0 and T_0 is 0.5 times its molar volume at $10P_0$ and at the same temperature. Ignoring the value of the van der Waals' constant 'a', the radius of the gas molecules is given by:

- (a) $\frac{0.8RT_0}{P_0}$ (b) $\left(\frac{0.6RT_0}{P_0 N \pi} \right)^{1/3}$
 (c) $\left(\frac{3RT_0}{20P_0 N \pi} \right)^{1/3}$ (d) $\left(\frac{3RT_0}{20P_0 \pi} \right)^{1/3}$

where, N = Avogadro's number

16. A vessel is filled with a mixture of oxygen and nitrogen. At what ratio of partial pressures will the mass of gases be identical?

- (a) $P(O_2) = 0.785P(N_2)$ (b) $P(O_2) = 8.75P(N_2)$
 (c) $P(O_2) = 11.4P(N_2)$ (d) $P(O_2) = 0.875P(N_2)$

[Hint: $PV = nRT$

$$PV = \frac{w}{m} RT$$

$$P_{O_2} V = \frac{w}{32} RT \quad \dots (i)$$

$$P_{N_2} V = \frac{w}{28} RT \quad \dots (ii)$$

$$\frac{P_{O_2}}{P_{N_2}} = \frac{28}{32}$$

$$P_{O_2} = 0.875P_{N_2}]$$

17. KCl crystallises in the same type of lattice as does NaCl. Given that $r_{Na^+}/r_{Cl^-} = 0.55$ and $r_{K^+}/r_{Cl^-} = 0.74$. Calculate the ratio of the side of the unit cell for KCl to that of NaCl

[PET (Kerala) 2008]

- (a) 1.123 (b) 0.891 (c) 1.414 (d) 0.414
 (e) 1.732

[Hint: $\frac{r_{Na^+}}{r_{Cl^-}} = 0.55$, $\frac{r_{K^+}}{r_{Cl^-}} = 0.74$

$$\frac{r_{Na^+}}{r_{Cl^-}} + 1 = 1.55 \quad \dots (1)$$

$$\frac{r_{K^+}}{r_{Cl^-}} + 1 = 1.74 \quad \dots (2)$$

Dividing (2) by (1)

$$\frac{1.74}{1.55} = \frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} \times \frac{r_{Cl^-}}{r_{Na^+} + r_{Cl^-}}$$

$$\frac{r_{K^+} + r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = 1.122]$$

18. 8:8 coordination of CsCl is found to change into 6:6 coordination:

- (a) on increasing the pressure
 (b) on increasing the temperature
 (c) on decreasing the pressure
 (d) on decreasing the temperature

19. An alloy of Cu, Ag and Au is found to have copper constituting ccp lattice. If silver atoms occupy the edge-centres and gold is present at body-centre, the alloy has the formula:

- (a) Cu_4Ag_2Au (b) Cu_4Ag_4Au
 (c) Cu_4Ag_3Au (d) $CuAgAu$

[Hint: In ccp arrangement, Cu atoms occupy the corners and face-centres.

$$\therefore \text{Number of Cu atoms} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\begin{aligned} \text{Number of silver atoms} &= \text{Number of edge-centres} \times \frac{1}{4} \\ &= 12 \times \frac{1}{4} = 3 \end{aligned}$$

Number of gold atoms = 1 (at body-centre)

$$\therefore \text{Formula of alloy} = Cu_4Ag_3Au]$$

20. The anions (A) form hexagonal closest packing and atoms (M) occupy only two-third of octahedral voids in it; then the general formula of the compound is:

- (a) MA (b) A_2 (c) M_2A_3 (d) M_3A_2

21. In a face-centred cubic of A and B -atoms in which A atoms are at the corners of the unit cell and B -atoms at the face-centres, one of the A -atoms is missing from one corner in unit cell. The simplest formula of the compound is:

(a) A_7B_3 (b) AB_3 (c) A_7B_{24} (d) A_8B_{21}

[Hint: Number of A atoms = $\frac{1}{8} \times 7 = \frac{7}{8}$

Number of B atoms = $6 \times \frac{1}{2} = 3$

$A : B = \frac{7}{8} : 3 = 7 : 24$

Molecular formula = A_7B_{24}

22. Select the incorrect statement(s):
 (a) Schottky defect is not shown by CsCl
 (b) Frenkel defect is shown by ZnS
 (c) hcp and ccp structures have different coordination numbers
 (d) at high pressure, the coordination number increases
23. Select the incorrect statement:
 (a) In CsCl unit cell, $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{\sqrt{3}}{2} l$
 (b) In NaCl unit cell, $r_{\text{Na}^+} + r_{\text{Cl}^-} = \frac{l}{2}$
 (c) In CsCl unit cell, 68% space is void
 (d) In NaCl unit cell, 26% space is void
24. The ionic radii of Rb^+ and I^- are 1.46 and 2.16 Å respectively. The most probable type of structure exhibited by it is:
 (a) CsCl (b) NaCl (c) ZnS (d) CaF_2
25. Perovskite is a mineral with the formula CaTiO_3 . Which of the positive ions in the crystal is more likely to be packed in the octahedral holes?
 (a) Ti^{4+} (b) Ti^{2+} (c) Ca^{2+} (d) O_2^+
26. Which of the following is incorrect? [BHU (Screening) 2008]
 (a) A real gas behaves like ideal gas over a wide range of pressure (~ 100 atm) at Boyle point
 (b) A real gas behaves like an ideal gas over a wide range of pressure (~ 100 atm) at critical temperature of the gas.
 (c) $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for an ideal gas
 (d) $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$ for a real gas obeying van der Waal's equation
 [Hint: A real gas cannot behave like ideal gas at critical temperature.]
27. The number of atoms in 100 g of an fcc crystal with density $d = 10 \text{ g/cm}^3$ and cell edge as 200 pm is equal to:
 (a) 3×10^{25} (b) 5×10^{24} (c) 1×10^{25} (d) 2×10^{25}
28. In a ccp structure, the:
 (a) first and third layers are repeated
 (b) first and fourth layers are repeated
 (c) second and fourth layers are repeated
 (d) first, third and sixth layers are repeated

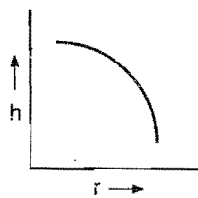
29. Which of the following compounds represents an inverse 2:3 spinel structure?

(a) $\text{Fe}^{\text{III}} [\text{Fe}^{\text{II}} \text{Fe}^{\text{III}}] \text{O}_4$ (b) PbO_2
 (c) Al_2O_3 (d) Mn_3O_4

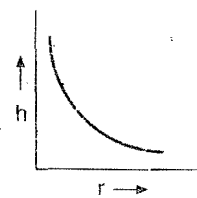
30. A solid solution of CdBr_2 in AgBr contains:

(a) Schottky defects
 (b) Frenkel defects
 (c) Colour centres
 (d) Frenkel as well as Schottky defects

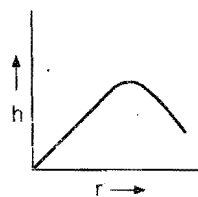
31. Which of the following correctly represents the relation between capillary rise ' h ' and capillary radius ' r '?



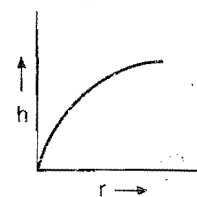
(a)



(b)



(c)



(d)

[Hint: Capillary rise decreases with increase in the radius of tube.]

32. There is a depression in the surface of the liquid in a capillary when:

(a) the cohesive force is smaller than the adhesive force
 (b) the cohesive force is greater than the adhesive force
 (c) the cohesive and adhesive forces are equal
 (d) none of the above is true

[Hint: Depression in the surface takes place when intermolecular attraction force of liquid called cohesive force dominates the force of attraction between the liquid and the capillary called adhesive force.]

33. Surface tension does not vary with:

(a) temperature (b) vapour pressure
 (c) the size of surface (d) concentration

34. Which among the following has the least surface tension?

(a) Benzene (b) Acetic acid
 (c) Diethyl ether (d) Chlorobenzene

35. The SI unit of the coefficient of viscosity is:

(a) $\text{N s}^{-1} \text{m}^{-1}$ (b) N s m^{-2} (c) $\text{N s}^{-2} \text{m}^{-2}$ (d) $\text{N s}^{-1} \text{m}^{-2}$

36. Compressibility factor for a gas under critical condition is:

(a) $3/8$ (b) $8/3$ (c) 1 (d) $1/4$

[Hint: $P_c V_c = \frac{3}{8} RT_c$

$$Z = \frac{P_c V_c}{RT_c} = \frac{3}{8}$$

37. Critical temperature of H_2O is greater than that of O_2 because H_2O molecules have:

(a) greater dipole moment
(b) V-shape
(c) lesser number of electrons
(d) it has only sigma bonds

38. For van der Waals' constants 'a' and 'b', the unit of the ratio $\frac{a}{b}$ will be:

(a) atm litre⁻¹ (b) litre-atm mol⁻¹
(c) litre-atm mol⁻² (d) litre mol⁻¹

[Hint: $P_{\text{correction}} = \frac{an^2}{V^2}$ Unit of $a = \text{atm litre}^2 \text{mol}^{-2}$

$V_{\text{correction}} = nb$ Unit of $b = \text{litre mol}^{-1}$

Unit of $\left(\frac{a}{b}\right) = \frac{\text{atm litre}^2 \text{mol}^{-2}}{\text{litre mol}^{-1}} = \text{atm litre mol}^{-1}$

39. Select the correct order of the following temperatures:

Boyle temp. Critical temp. Inversion temp.

(A) (B) (C)

(a) $A > C > B$ (b) $B > A > C$
(c) $A > B > C$ (d) $C > A > B$

[Hint: T_B (Boyle temp.) = $\frac{a}{Rb}$; T_i (Inversion temp.) = $\frac{2a}{Rb}$

T_c (Critical temp.) = $\frac{8a}{27Rb}$

$\therefore T_i > T_B > T_c$

40. The gas equation for a real gas is:

$P(V-b) = RT$

Here, the parameter 'b' is van der Waals' constant. The graph of pressure against temperature (isochore) will give straight line of slope:

(a) zero (b) $\frac{R}{(V-b)}$ (c) R/P (d) negative

41. A crystalline solid is made of X, Y and Z elements. Atoms of X form fcc packing; atoms of Y occupy octahedral voids while atoms of Z occupy tetrahedral voids. What will be the simplest formula of solid if atoms along one body diagonal are removed:

(a) $X_5Y_4Z_8$ (b) XYZ (c) $X_8Y_4Z_5$ (d) X_2YZ

[Hint: Number of atoms of X (at packing site, i.e., at corners and face-centres)

$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

Number of atoms of Y = 4

Number of atoms of Z = 8

Along one body diagonal there will be two X atoms, one Y atom and two Z atoms are found and are removed.

Number of atoms of X will be $= 4 - \frac{1}{8} \times 2 = \frac{15}{4}$

Number of atoms of Y will be $= 4 - 1 = 3$

Number of atoms of Z will be $= 8 - 2 = 6$

$X:Y:Z$

$\frac{15}{4}:3:6$

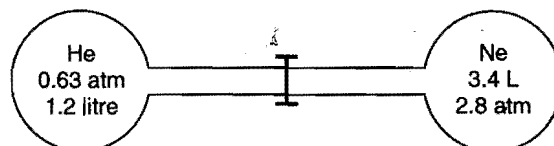
$5:4:8$

$\therefore$ Simplest formula will be $X_5Y_4Z_8$

42. Which of the following pattern has void fraction of 0.26?

(a) AAAA... (b) ABABAB...
(c) ABCABCABC... (d) ABCCBAABC...

43. Two gas bulbs are connected by a thin tube. Calculate the partial pressure of helium after the connective valve is opened at a constant temperature of 27°C :



(a) 1 atm (b) 0.328 atm (c) 1.64 atm (d) 0.166 atm

[Hint: $n_{\text{He}} = \frac{PV}{RT} = \frac{0.63 \times 1.2}{0.0821 \times 300} = 0.03$

$n_{\text{Ne}} = \frac{2.8 \times 3.4}{0.0821 \times 300} = 0.39$

$x_{\text{He}} = \frac{n_{\text{He}}}{n_{\text{He}} + n_{\text{Ne}}} = \frac{0.03}{0.03 + 0.39} = 0.0714$

Total pressure after connecting the bulbs will be:

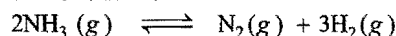
$P_1V_1 + P_2V_2 = P_R(V_1 + V_2)$

$0.63 \times 1.2 + 2.8 \times 3.4 = P_R(1.2 + 3.4)$

$P_R = 2.33 \text{ atm}$

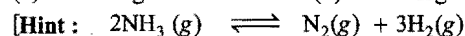
$P_{\text{He}} = x_{\text{He}} \times P_R = 0.0714 \times 2.33 = 0.166 \text{ atm}$

44. Ammonia gas at 76 cm Hg pressure was connected to a manometer. After sparking in the flask, ammonia is partially dissociated as follows:



the level in the mercury column of the manometer was found to show the difference of 18 cm. What is the partial pressure of $\text{H}_2(g)$ at equilibrium?

(a) 18 cm Hg (b) 9 cm Hg
(c) 27 cm Hg (d) 24 cm Hg.



t_0	76	0	0
t_{eq}	$76-2x$	x	$3x$

total pressure after dissociation = $76 - 2x + x + 3x = 76 + 2x$

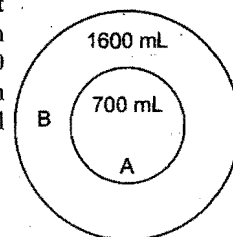
Increase in pressure = $2x = 18$

$x = 9 \text{ cm.}$

Partial pressure of $\text{H}_2 = 3x = 27 \text{ cm}$

45. Two balloons A and B are taken at 300K. Maximum capacity of balloon A and balloon B are 800 mL and 1800 mL respectively. When the balloon system is heated; which one will burst first?

(a) Inner balloon (A)
(b) Outer balloon (B)
(c) Both balloons simultaneously
(d) Cannot be predicted



[Hint : For balloon A :

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

$$\frac{700}{300} = \frac{800}{T_2}$$

$$T_2 = 342.85 \text{ K}$$

For balloon B :

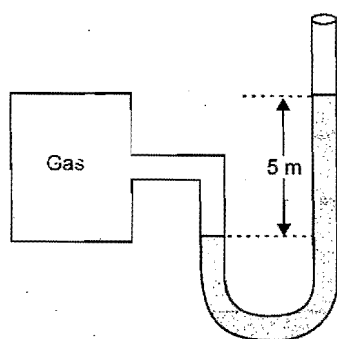
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{1600}{300} = \frac{1800}{T_2}$$

$$T_2 = 337.5 \text{ K}$$

Thus, outer balloon B will burst first.]

46.



A gas jar of 10 litre volume filled with O_2 at 300 K is connected to glycerine manometer. The manometer shows 5 m difference in the level as shown in figure. What will be the number of moles of O_2 in the gas jar ?

(Give $d_{\text{glycerine}} = 2.72 \text{ g/mL}$; $d_{\text{mercury}} = 13.6 \text{ g/mL}$.)

(a) 0.64 mol (b) 0.4 mol (c) 0.94 mol (d) 0.36 mol

[Hint : $(h \times d \times g)_{\text{Hg}} = (h \times d \times g)_{\text{glycerine}}$

$$(h \times 13.6)_{\text{Hg}} = (5 \times 2.72)_{\text{glycerine}}$$

$$h_{\text{Hg}} = 1 \text{ m}$$

$$P_{\text{gas}} = (1 + 0.76) \text{ m}$$

$$= 1760 \text{ mm Hg}$$

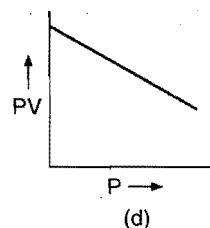
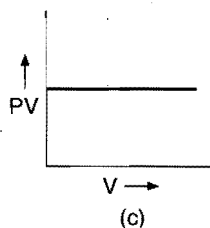
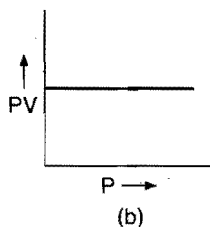
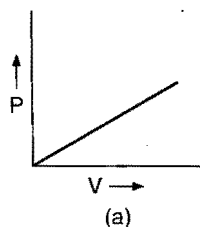
$$PV = nRT$$

$$\frac{1760}{760} \times 10 = n \times 0.0821 \times 300$$

$$n = 0.94 \text{ mol}]$$

Following questions may have more than one correct options:

1. Which of the following graphs represent Boyle's law?



2. Which of the following equation(s) is/are correct on the basis of ideal gas equation?

(a) $PV = \frac{N}{N_A} RT$

(b) $PV = Nk_B T$

(c) $PV = \frac{d}{m} RT$

(d) $PV = dRT$

where, N = number of molecules, N_A = Avogadro's number, k_B = Boltzmann constant

3. A gas can be easily liquefied:

- (a) when its inversion temperature equals the Boyle's temperature
 (b) under reversible adiabatic expansion
 (c) under pressure when it is cooled below the critical temperature
 (d) at low pressure and above critical temperature

[Hint: (i) Reversible adiabatic expansion lowers the temperature hence facilitates the liquefaction of gas. (ii) A gas can be liquefied below the critical temperature by increasing the pressure.]

4. Which of the following quantities are same for all ideal gases at the same temperature?

- (a) The kinetic energy of 1 mole
 (b) The kinetic energy of 1 g
 (c) The number of molecules in 1 mole
 (d) The number of molecules in 1 g

[Hint: (i) 1 mole of a gas always contains 6.023×10^{23} molecules.

(ii) Kinetic energy of ideal gases depends only on temperature.]

5. Which of the following statements are correct?

- (a) Helium diffuses at a rate 8.65 times as fast as CO does
 (b) Helium diffuses at a rate 2.65 times as fast as CO does
 (c) Helium diffuses at a rate of 4 times faster than CO_2
 (d) Helium diffuses at a rate 4 times as fast as SO_2 does

6. The viscosity of a liquid molecule depends on:

- (a) the volume of the liquid
 (b) the temperature of the liquid
 (c) the surface area of the liquid
 (d) the structure of the molecule

7. Viscosity is the property of:

- (a) liquids (b) gases (c) solids (d) all of these

8. Which of the following crystals have 6 : 6 coordination?

- (a) NH_4I (b) MgO (c) MnO (d) ZnS

9. Which of the following compounds represent a normal 2 : 3 spinel structure?

- (a) $\text{Mg}^{II} \text{Al}_2^{\text{III}} \text{O}_4$ (b) $\text{Co}^{II} (\text{Co}^{\text{III}})_2 \text{O}_4$
 (c) $\text{Zn}(\text{TiZn}) \text{O}_4$ (d) $\text{Ni}(\text{CO})_4$

10. Which type of crystals contain only one Bravais lattice?

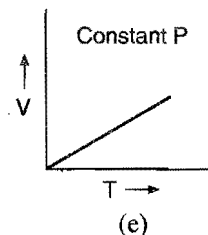
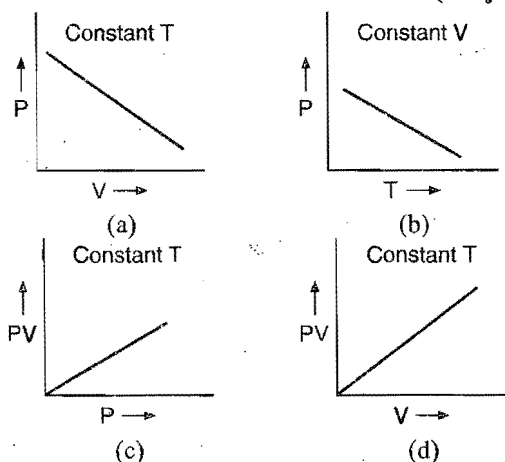
- (a) Hexagonal (b) Triclinic
 (c) Rhombohedral (d) Monoclinic

11. At which temperature, is a ferrimagnetic solid converted to a ferromagnetic solid?

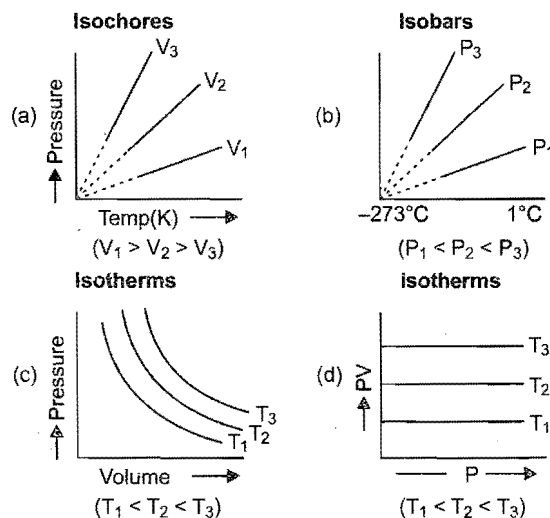
- (a) 850 K (b) 300 K (c) 400 K (d) 600 K
12. In NaCl structure, all the:
- octahedral sites are occupied
 - tetrahedral sites are unoccupied
 - octahedral as well as tetrahedral sites are unoccupied
 - octahedral as well as tetrahedral sites are occupied
13. The density of a certain solid AB (formula mass = 119) is 2.75 g/cm³. The edge of the unit cell is 654 pm long. What is/are true about the solid AB?
- It has bcc unit cell
 - There are four constituents per unit cell
 - Unit cell constituted by anion is fcc
 - Structure is similar to ZnS

[Hint: $Z = \frac{a^3 \times d \times N}{M}$
 $= \frac{(654 \times 10^{-10})^3 \times 2.75 \times 6.023 \times 10^{23}}{119} \approx 4$]

14. The unit cell of a crystalline solid is bounded by f (faces), e (edges) and c (interfacial angle). Which of the following relations is correct?
- $f + e = c + 2$
 - $f + c = e + 2$
 - $c + e = f + 2$
 - None of these
15. Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas? (T is measured in K)
- [PMT (Kerala) 2007; CMS Vellore (Med.) 2008; CET (Punjab) 2008]



16. Molar mass of Ne atom is ten times of H₂ molecule. Which of the following statement is/are true?
- Both these gases have same Kinetic Energy at 27°C
 - H₂ molecule will travel 10 times faster than Ne atom at same temperature
 - Pressure of 1 mol Ne atom and 1 mole H₂ molecules will be same
 - Ten mole of H₂ and 1 mole of Ne will have same volume at a temperature of 27°C
17. Select the correct conditions indicated below the following plots:



Answers

• Single correct option

- | | | | | | | | |
|---------|---------|---------|---------|---------|------------|---------|---------|
| 1. (d) | 2. (a) | 3. (c) | 4. (c) | 5. (a) | 6. (d) | 7. (b) | 8. (d) |
| 9. (a) | 10. (c) | 11. (a) | 12. (c) | 13. (d) | 14. (b) | 15. (c) | 16. (d) |
| 17. (a) | 18. (b) | 19. (c) | 20. (c) | 21. (c) | 22. (a, c) | 23. (c) | 24. (b) |
| 25. (a) | 26. (c) | 27. (b) | 28. (b) | 29. (a) | 30. (d) | 31. (b) | 32. (b) |
| 33. (c) | 34. (c) | 35. (b) | 36. (a) | 37. (a) | 38. (b) | 39. (d) | 40. (b) |
| 41. (a) | 42. (c) | 43. (d) | 44. (c) | 45. (b) | 46. (c) | | |

• One or more than one correct options

- | | | | | | | | |
|---------------|---------------|-----------|------------|------------|-----------|-----------|---------------|
| 1. (b, c) | 2. (a, b) | 3. (b, c) | 4. (a, c) | 5. (a, d) | 6. (b, d) | 7. (a, b) | 8. (a, b) |
| 9. (a, b) | 10. (a, b, c) | 11. (a) | 12. (a, b) | 13. (b, c) | 14. (b) | 15. (e) | 16. (a, b, c) |
| 17. (a, c, d) | | | | | | | |

Integer Answer TYPE QUESTIONS

This section contains 14 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :

X	Y	Z	W
0	0	0	0
1	1	1	1
2	2	2	2
3	3	3	3
4	4	4	4
5	5	5	5
6	6	6	6
7	7	7	7
8	8	8	8
9	9	9	9

1. A substance A_xB_y crystallises in a face centred cubic lattice. Atoms 'A' occupy each corner of unit cell and atoms of 'B' occupy centre of each face of the cube. Total number of atoms of A and B in one unit cell will be
2. In KBr crystal structure, the number of second nearest neighbour of K^+ ions are
3. Density of lithium atom is 0.53 g/cm^3 . The edge length of Li is $3.5 \text{ \AA}$. The number of lithium atoms in a unit cell will be (Atomic mass of lithium is 6.94)
4. A cubic solid is made up of two elements P and Q. Atoms of Q are present at the corners of the cube and atoms of P at the body centre. The coordination number of P and Q will be
5. If there are 3 moles of atoms present in the packing of pattern ABC ABC ABC The number of moles of tetrahedral voids is equal to
6. The number of atoms in HCP unit cell is
7. How many effective Na^+ ions are present in rock salt NaCl? If ions along one axis joining opposite faces are removed?
8. How many moles of SO_2 will occupy a volume of 10 litre at a pressure of 15 atm and temperature 624 K? ($a = 6.71 \text{ atm L}^2 \text{ mol}^{-2}$; $b = 0.0564 \text{ litre mol}^{-1}$)

9. 3.2 g of oxygen and 0.2 g of hydrogen are placed in 1.12 litre flask at 0°C . The total pressure in atm of the gas mixture will be
10. A mixture of non reacting gases exert a pressure of 5 atm. If one of the gases occupy 40% volume of the mixture, what would be its partial pressure in atm?
11. A gas is found to have the formula $(C_3O_2)_n$. Its vapour density is 34. The value of n will be
12. The weight of hydrogen gas obtained from 42 g of CaH_2 by treatment with water is gm.
13. The stop cock containing two bulbs of volume 5 litre and 10 litre containing an ideal gas at 9 atm and 60 atm respectively is opened. What is the final pressure in atm if the temperature remains the same?
14. At 400 K, the root mean square (rms) speed of gas X (molecular mass = 40) is equal to the most probable speed of gas Y at 60 K. The molecular mass of the gas Y is

(IIT 2009)

[Hint : $\left(\sqrt{\frac{3RT}{m}}\right)_X = \left(\sqrt{\frac{2RT}{m}}\right)_Y$

$$\sqrt{\frac{3R400}{40}} = \sqrt{\frac{2R60}{m}}$$

$$\sqrt{30} = \sqrt{\frac{4 \times 30}{m}}$$

$$m = 4]$$

Answers

- | | | | | | | | |
|--------|---------|---------|---------|---------|---------|--------|--------|
| 1. (4) | 2. (12) | 3. (2) | 4. (8) | 5. (6) | 6. (6) | 7. (3) | 8. (3) |
| 9. (4) | 10. (2) | 11. (1) | 12. (4) | 13. (7) | 14. (4) | | |

● LINKED COMPREHENSION TYPE QUESTIONS ●

● Passage 1

The gases which strictly follow the general equation ($PV = nRT$) are called ideal or perfect gases. Actually, there is no gas which is perfect or ideal. A real gas is one which actually exists, whether it obeys gas laws strictly or not. Under ordinary conditions, only those gases nearly behave as ideal or perfect which have very low boiling points such as nitrogen, hydrogen, etc. The most easily liquefiable and highly soluble gases such as ammonia, carbon dioxide, sulphur dioxide show large deviations.

A very convenient method of studying deviation of real gases from ideal behaviour is through a compressibility factor (Z).

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

(i) $Z = 1$, for ideal gases.

(ii) $Z \neq 1$, for real gases.

Answer the following questions:

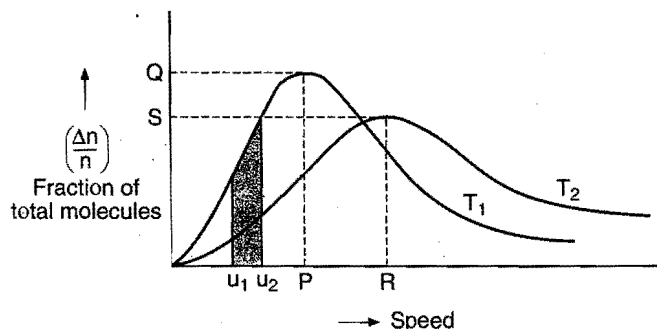
- Consider the equation $Z = \frac{PV}{nRT}$; which of the following statements is correct?
 - When $Z > 1$, real gases are easier to compress than the ideal gas
 - When $Z = 1$, real gases get compressed easily
 - When $Z > 1$, real gases are difficult to compress
 - When $Z = 1$, real gases are difficult to compress
- The compressibility of a gas is less than unity at STP, therefore:
 - $V_m > 22.4 \text{ L}$
 - $V_m < 22.4 \text{ L}$
 - $V_m = 22.4 \text{ L}$
 - $V_m = 44.8 \text{ L}$
- At low pressure, the van der Waals' equation is reduced to:
 - $Z = \frac{PV_m}{RT} = 1 - \frac{aP}{RT}$
 - $Z = \frac{PV_m}{RT} = 1 + \frac{bP}{RT}$
 - $PV_m = RT$
 - $Z = \frac{PV_m}{RT} = 1 - \frac{a}{RT}$
- At Boyle's temperature, compressibility factor Z for a real gas is:
 - $Z = 1$
 - $Z = 0$
 - $Z > 1$
 - $Z < 1$

[Hint: At Boyle's temperature, the real gas behaves like an ideal gas.]
- The behaviour of a real gas is usually depicted by plotting compressibility factor Z versus pressure P at a constant temperature. At high temperature and pressure, Z is usually more than one. This fact can be explained by van der Waals' equation when:
 - the constant ' a ' is negligible but not ' b '
 - the constant ' b ' is negligible but not ' a '
 - both the constants ' a ' and ' b ' are negligible
 - both the constants ' a ' and ' b ' are not negligible
- The units of compressibility factor are:
 - atm L^{-1}
 - atm^{-1}
 - L^{-1}
 - unitless

● Passage 2

The gas molecules randomly move in all directions and collide with each other and with the wall of the container. It is difficult to determine the speed of an individual molecule but it has become possible to work out the distribution of molecules among different molecular speeds. This is known as Maxwell Boltzmann distribution.

Consider the following graph about Maxwell's distribution of speeds at two different temperatures T_1 and T_2 :



Answer the following questions:

- In the above graph the point ' P ' refers to:
 - root mean square speed at T_1
 - average speed at T_1
 - most probable speed at T_1
 - highest possible speed at T_1
- The shaded area represents:
 - number of molecules having speed between u_1 and u_2
 - number of molecules having speed less than the most probable speed
 - number of molecules having v_{rms} at T_1
 - fraction of total molecules having average speed
- The point Q refers to:
 - number of molecules with speed at P
 - fraction of total molecules with speed at P
 - root mean square speed
 - total kinetic energy of molecules at P
- Relation between T_1 and T_2 is:
 - $T_1 = T_2$
 - $T_1 > T_2$
 - $T_1 < T_2$
 - cannot be predicted
- Total area under the curve at T_1 is:
 - equal to that under curve at T_2
 - less than that under curve at T_2
 - greater than that under curve at T_2
 - can be greater or less than that under curve at T_2 , depending on the nature of the gas
- Select the correct statement(s):
 - Most probable speed increases with increase in temperature
 - Fraction of total molecules with most probable velocity decreases with increase in temperature
 - Area under the curve increases with increase in the temperature
 - none of the above

7. The curve has which of the following characteristics?
- It has symmetrical distribution of molecules against molecular velocity.
 - The area under the curve gives the total number of molecules.
 - The maxima of the curve shifts towards right as the temperature is raised.
 - The area under the curve is independent of temperature.
- Select the correct statements from the codes given below:
- (i), (ii)
 - (i), (ii) and (iii)
 - (ii), (iii) and (iv)
 - all are correct

● Passage 3

The essential conditions for liquefaction of gases were discovered by Andrews in 1869 as a result of his study of pressure-volume-temperature relationship for CO_2 . It was found that above a certain temperature, it was impossible to liquefy a gas whatever the pressure was applied. The temperature below which the gas can be liquefied by the application of pressure alone is called critical temperature (T_c). The pressure required to liquefy a gas at this temperature is called the critical pressure (P_c). The volume occupied by one mole of the substance at the critical temperature and pressure is called critical volume. Critical constants are related with van der Waals' constant as follows:

$$V_c = 3b, P_c = \frac{a}{27b^2}, T_c = \frac{8a}{27Rb}$$

Answer the following question:

- The relationship between P_c , V_c and T_c is:
 - $P_c V_c = RT$
 - $P_c V_c = 3RT_c$
 - $P_c V_c = \frac{3}{5} RT_c$
 - $P_c V_c = \frac{3}{8} RT_c$
 - Which of the following parameters is three times the van der Waals' constant 'b'?
 - Critical volume
 - Critical temperature
 - Vapour density
 - Critical pressure
 - The critical temperature of:
 - a substance means the temperature above which the substance is in vapour form
 - a gas is the temperature below which it can be liquefied by application of pressure
 - water is 100°C
 - none of the above
 - The pressure required to liquefy a gas at the critical temperature is called:
 - reduced pressure
 - critical pressure
 - vapour pressure
 - atmospheric pressure
- | Gases | A | B | C | D |
|-------------|-----|----|-----|-----|
| P_c (atm) | 2.2 | 14 | 35 | 45 |
| T_c (K) | 5.1 | 33 | 127 | 140 |
- Which of the above gases cannot be liquefied at 100 K and 50 atm?
- D only
 - A only
 - A and B
 - C and D
6. At critical point, the meniscus between liquid and vapour disappears due to:

- zero refractive index
 - zero surface tension
 - zero viscosity
 - zero critical temperature
7. Gas A can be liquefied at room temperature by applying pressure but gas B cannot. This reflects:
- critical temperature of B is less than that of A
 - critical temperature of B is greater than that of A
 - A and B have critical temperature greater than room temperature
 - critical temperatures of both are equal
8. The values of critical volumes of four gases A, B, C and D are 0.025 L, 0.312 L, 0.245 L and 0.432 L respectively. The gas with larger diameter will be:
- A
 - D
 - B
 - C

[Hint: $V_c = 3b = 3 \times 4N \times \frac{4}{3} \pi r^3$]

● Passage 4

Kinetic theory of gases is a generalization offered by Maxwell, Boltzmann, Clausius, etc., to explain the behaviour of ideal gases. This theory assumes that ideal gas molecules neither attract nor repel each other. Average kinetic energy of gas molecules is directly proportional to the absolute temperature. A gas equation called kinetic gas equation was derived on the basis of kinetic theory.

$$PV = \frac{1}{3} m n u^2$$

Answer the following question:

- Gas Density

A	0.82 g L ⁻¹
B	0.26 g L ⁻¹
C	0.51 g L ⁻¹

Pick up the correct statement/statements:

 - gas A will tend to lie at the bottom.
 - the number of atoms of various gases A, B and C are same.
 - the gases will diffuse to form homogeneous mixture.
 - average kinetic energy of each gas is same.
 - 2, 3
 - 1, 4
 - 1
 - 3, 4
- Select the incorrect statement(s) about the real gases:
 - The molecules attract each other.
 - They show deviation from Boyle's and Charles' law.
 - Volume of gas molecules are negligible.
 - The molecules have negligible mass.
 - 2, 3
 - 1, 4
 - 1
 - 3, 4
- The average kinetic energy per molecule of an ideal gas is equal to:
 - 0.5 kJ
 - 0.5RT
 - 1.5kT
 - 1.5RT²
- Which of the following do not pertain to the postulates of kinetic theory of gases?
 - The gas molecules are perfectly elastic
 - Speed of gas molecules are ever changing
 - Pressure exerted by the gas is due to the collision of molecules with the walls of the container
 - Kinetic energy of a gas is given by the sum of 273 and temperature in Celsius scale

SELF ASSESSMENT

ASSIGNMENT NO. 4

SECTION-I

Straight Objective Type Questions

This section contains 14 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

- Boyle's temperature of four gases are given below:

Gases	A	B	C	D
T_B	120 K	25 K	500 K	410 K

 which gas can be liquified most easily?
 (a) A (b) B (c) C (d) D
- A gas is enclosed in a vessel of volume V at temperature T_1 and pressure P ; the vessel is connected to another vessel of volume $V/2$ by a tube and a stop cock. The second vessel is initially evacuated. If the stop cock is opened, the temperature of second vessel becomes T_2 . The first vessel is maintained at a temperature T_1 . What is the final pressure P_1 in the apparatus?
 (a) $\frac{2PT_2}{2T_2 + T_1}$ (b) $\frac{2PT_2}{T_2 + 2T_1}$ (c) $\frac{PT_2}{2T_2 + T_1}$ (d) $\frac{2PT_2}{T_1 + T_2}$
- The ratio of rate of diffusion of gases A and B is 1 : 4. If the ratio of their masses present in the mixture is 2 : 3, what is the ratio of their mole fraction?
 (a) $\frac{1}{8}$ (b) $\frac{1}{12}$ (c) $\frac{1}{16}$ (d) $\frac{1}{24}$
- Density of a gas at STP is 2g / L while the expected density is 1.8 g / L assuming its ideal behaviour. Then:
 (a) gas behaves ideally
 (b) forces of attraction are dominant among gas molecules
 (c) forces of repulsion are dominant among gas molecules
 (d) none of the above
- In a crystalline solid, anions B are arranged in ccp lattice and cations A occupy 50% of the octahedral voids and 50% of the tetrahedral voids. What is the formula of the solid?
 (a) AB (b) A_3B_2 (c) A_2B_2 (d) A_2B_3
- In a compound XY_2O_4 , oxide ions are arranged in ccp and cations X are present in octahedral voids. Cations Y are equally distributed among octahedral and tetrahedral voids. The fraction of the octahedral voids occupied is:
 (a) $\frac{1}{4}$ (b) $\frac{1}{2}$ (c) $\frac{1}{6}$ (d) $\frac{1}{8}$
- An ideal gas:
 (a) can be liquified if its temperature is more than critical temperature
 (b) can be liquified if its pressure is more than critical pressure
 (c) cannot be liquified at any pressure and temperature
 (d) can be liquified if its temperature is more than Boyle's temperature
- A mineral is made of calcium, titanium and oxygen Ca^{2+} ions located at corners, Ti^{4+} ions at the body-centre and O^{2-} ions at face-centres of the unit cell. The molecular formula of the mineral is.....
 (a) $CaTi_3O_4$ (b) $CaTiO_3$ (c) $CaTiO_2$ (d) $CaTi_2O_3$

- If the graph is plotted for 1 mol gas in such a way that PV is plotted against P then intercept of the graph for real gas will be:
 (a) $RT + Pb + a$ (b) RT
 (c) $RT - Pb + a$ (d) $RT + Pb + ab + a$
- The ratio of Boyle's temperature and critical temperature for a gas is:
 (a) $\frac{8}{27}$ (b) $\frac{27}{8}$ (c) $\frac{1}{2}$ (d) $\frac{2}{1}$
- With which of the following elements silicon should be doped so as to give p -type semiconductor? [CBSE (PMT) 2008]
 (a) Selenium (b) Boron (c) Germanium (d) Arsenic
- Total volume of atoms present in a face centred cubic unit cell of a metal is (r is atomic radius): [JIPMER 2008]
 (a) $\frac{16}{3}\pi r^3$ (b) $\frac{20}{3}\pi r^3$ (c) $\frac{24}{3}\pi r^3$ (d) $\frac{12}{3}\pi r^3$
- How many effective Na^+ and Cl^- ions are present respectively in the rocksalt ($NaCl$). If ions along the axis joining opposite faces are removed?
 (a) 4, $\frac{7}{2}$ (b) $\frac{7}{2}$, $\frac{7}{2}$ (c) $\frac{7}{2}$, 4 (d) 3, 3
- Kinetic energy and pressure of a gas of unit mole are related as :
 (a) $P = 2E$ (b) $P = \frac{2}{3}E$ (c) $P = \frac{3}{2}E$ (d) $P = \frac{E}{2}$

SECTION-II

Multiple Answers Type Objective Questions

- Which of the following measure the deviation from ideal behaviour of gas?
 (a) Collision diameter (b) Collision frequency
 (c) Compressibility factor (d) van der Waals' constant 'a'
- In face-centred cubic unit cell:
 (a) face diagonal of the cube is $a\sqrt{2}$ or $4r$
 (a = edge length, r = radius of constituent units)
 (b) effective number of atoms in the unit cell is 4
 (c) 8 tetrahedral voids per unit cell
 (d) rank of the unit cell is 3
- Which of the following mixtures of gases at room temperature follow Dalton's law of partial pressures?
 (a) NO and O_2 (b) CO and CO_2
 (c) NH_3 and HCl (d) SO_2 and O_2
- A real gas can be liquified:
 (a) under adiabatic expansion
 (b) above critical temperature
 (c) when cooled below critical temperature under applied pressure
 (d) at temperature lower than critical temperature and pressure higher than critical pressure
- Which of the following statements is (are) correct?
 (a) In body-centred cubic unit cell, the coordination number is 12
 (b) The coordination number of each type of ion in CsCl is 8

- (c) A unit cell of an ionic crystal shares some of its ions with neighbouring unit cell
 (d) If $r_{\text{Na}^+} = 95 \text{ pm}$; $r_{\text{Cl}^-} = 181 \text{ pm}$; then edge length of unit cell of NaCl is 552 pm

SECTION-III

Assertion-Reason Type Questions

This section contains 6 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
 (c) Statement-1 is true; statement-2 is false.
 (d) Statement-1 is false; statement-2 is true.
20. **Statement-1:** The pressure inside the LPG cylinder remains constant even when it is in use at room temperature.

Because

Statement-2: Vapour pressure of any liquid is independent of its amount; it depends only on temperature.

21. **Statement-1:** If a gas has compressibility factor (Z) greater than unity, then repulsive forces are dominant.

Because

Statement-2: Value of Z decreases with increase in pressure.

22. **Statement-1:** The value of Boyle's temperature for a real gas is $\left(T_B = \frac{a}{Rb} \right)$.

Because

Statement-2: At Boyle's temperature, T_B , real gases behave ideally over a long range of pressure.

23. **Statement-1:** CaCO_3 shows polymorphism.

Because

Statement-2: CaCO_3 exists in two forms called aragonite and calcite.

24. **Statement-1:** Lead zirconate is piezoelectric solid.

Because

Statement-2: Lead zirconate crystals have no dipole moment.

25. **Statement-1:** Band gap in germanium is small.

Because

Statement-2: The energy spread of each germanium atomic energy level is infinitesimally small. (IIT 2007)

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched.

Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4×4 matrix should be as follows:

	p	q	r	s
a	☐	☐	☐	☐
b	☐	☐	☐	☐
c	☐	☐	☐	☐
d	☐	☐	☐	☐

26. Match the Column-I with Column-II:

Column-I

Column-II

- | | |
|----------------------------|-------------------------------|
| (a) High temperature | (p) $Z \neq 1$ |
| (b) Extremely low pressure | (q) $\text{Pb} < \frac{a}{V}$ |
| (c) Very high pressure | (r) $Z = 1$ |
| (d) Low pressure | (s) $\text{Pb} > \frac{a}{V}$ |

27. Match the Column-I with Column-II:

Column-I

Column-II

- | | |
|--|------------|
| (a) Constituent units occupy only corners | (p) 67.98% |
| (b) Constituent units occupy corners as well as face-centres | (q) 26.17% |
| (c) Constituent units occupy corners and body-centre | (r) 74.01% |
| (d) Constituent units occupy corners and edge-centres | (s) 52.33% |

28. Match the Column-I with Column-II: (IIT 2007)

Column-I

Column-II

- | | |
|---|---|
| (a) Simple cubic and face-centred cubic | (p) Have these cell parameters, $a = b = c$ and $\alpha = \beta = \gamma$ |
| (b) Cubic and rhombohedral | (q) Are two crystal systems |
| (c) Cubic and tetragonal | (r) Have only two crystallography angles of 90° |
| (d) Hexagonal monoclinic | (s) Belong to same crystal system |

Answers

- | | | | | | | | |
|---------------|-----------------------------------|-----------------------------|--------------------------------------|---------|---------|------------|---------------|
| 1. (c) | 2. (a) | 3. (b) | 4. (b) | 5. (b) | 6. (b) | 7. (c) | 8. (b) |
| 9. (b) | 10. (b) | 11. (b) | 12. (a) | 13. (d) | 14. (b) | 15. (c, d) | 16. (a, b, c) |
| 17. (a, b, d) | 18. (a, c, d) | 19. (b, c, d) | 20. (c) | 21. (c) | 22. (b) | 23. (a) | 24. (c) |
| 25. (c) | 26. (a-p) (b-p) (c-p, s) (d-p, q) | 27. (a-s) (b-r) (c-p) (d-q) | 28. (a-p, s) (b-p, q) (c-q) (d-q, r) | | | | |