Indira Gandhi National
Open University
School of Sciences

BCHCT-137

COORDINATION CHEMISTRY, STATES OF MATTER AND CHEMICAL KINETICS

VOL.

2

STATES OF MATTER AND CHEMICAL KINETICS

ignou
THE PEOPLE'S
UNIVERSITY

Indira Gandhi National
Open University
School of Sciences

BCHCT-137

COORDINATION CHEMISTRY, STATES OF MATTER AND CHEMICAL KINETICS

Block

3

STATES OF MATTER

Course Design Committee

Prof. Gurmeet Singh,
Department of Chemistry,
University of Delhi, Delhi

Dr. Sushmita Choudhury (Retd.),
Gargi College, University of Delhi
New Delhi

Dr Pritam Mukhopadhyay ,
Associate Professor, School of Physical Sciences, Jawaharlal Nehru University.
New Delhi

Dr. Vijay Sarda (Retd.)
Department of Chemistry
Zakir Husain Delhi College
University of Delhi, Delhi

Prof. B. S. Saraswat (Retd.)
School of Sciences, IGNOU,
New Delhi

School of Sciences,
IGNOU, New Delhi 110068

Prof. M.S. Nathawat
Prof. Sunita Malhotra
Prof. B.I. Fozdar
Prof. Javed A. Farooqi
Prof. Sanjiv Kumar
Prof. Lalita S. Kumar
Prof. Kamalika Banerjee

Block Preparation Team

Prof. Sanjiv Kumar (Unit 8 and 9)
School of Sciences, IGNOU
New Delhi-110068

Prof. Kamalika Banerjee (Unit 10,11 and 12)
School of Sciences, IGNOU
New Delhi-110068

Dr. Vijay Sarda (Retd.) (Editor)
Department of Chemistry,
Zakir Husain College
University of Delhi, Delhi

Course Coordinator: Prof. Kamalika Banerjee

PRINT PRODUCTION

Mr. Sunil Kumar
AR(P), SOS, IGNOU

Acknowledgements: Sh. Sarabjeet Singh for word processing and CRC preparation;
Sh. Deepak Kumar for word processing.
Unit 8 and 9 have been adapted from Unit 2 and 3 of Physical Chemistry Course (CHE-04).
The utilisation of portions of Units 3, 4, 5 of CHE-04 & Units 4, 5 of CHE 11(L) courses have been done for writing Units 10, 11 and 12 of this course.

October, 2021

ISBN:

Further information on Indira Gandhi National Open University courses may be obtained from the University's office at Maidan Garhi, New Delhi-110068 or IGNOU website www.ignou.ac.in

Printed and published on behalf of Indira Gandhi National Open University, New Delhi by the Registrar, MPDD, IGNOU.

Printed at:

BLOCK 3: STATES OF MATTER

In the previous volume of this course you have learnt about coordination chemistry. Matter generally exists in one of the three states, namely gas, liquid and solid. In this block you will study the main characteristics of the three states of matter.

In Unit 8, titled, 'Kinetic Theory of Gases' we would recall the gas laws and the ideal gas equation before stating the postulates of kinetic theory of gases. This is used to derive an expression for the pressure of the gas which in turn is used in calculating the parameters like pressure, average kinetic energy etc. of the gas molecules. The unit also covers the principle of equipartition of energy, the distribution of molecular speeds, collision number and the mean free path of the gases.

Unit 9 deals with 'real gases and their liquefaction'. It discusses the deviation of the behaviour of real gases from ideal gas behaviour which is accommodated in the van der Waals equation. We would discuss critical phenomena and the relationships between critical constants and van der Waals constants. The unit also deals with the liquefaction of gases besides the concept of viscosity of gases and the effects of pressure and temperature on it.

Unit 10 is on liquids. It gives a glimpse of the structure and the properties of liquids. Also, intermolecular forces and the properties of liquids to such as surface tension and viscosity have been discussed.

Unit 11 gives the details of different types of solids, mainly crystalline and amorphous. The symmetry elements, crystal forms, Bravais lattice and crystal systems have been discussed and also the laws of crystallography, and crystal planes along with Miller indices are discussed in this unit.

In the last Unit 12 discussion on X-rays diffraction and Bragg's Law along with characteristics of cubic unit cells have been done. Thereafter discussions on defects in crystals, glasses and liquid crystals have been done.

We expect that after studying this block, you should be able to:

- state postulates of kinetic theory of gases and derive the equation for pressure of a gas;
- explain the distribution of molecular speeds and calculate the most probable speed, average speed and the root mean square speed for a gas;
- define, explain and calculate the collision number and mean free path of molecules in a gaseous sample;
- explain the pressure and volume correction terms to the ideal gas equation; and deduce van der Waals equation;

- define critical temperature, critical pressure and critical volume and derive the relationships between the critical constants and van der Waals constants;
- explain the concept of viscosity and derive the relation between the coefficient of viscosity and mean free path of a gas;
- discuss the effect of temperature and pressure on the viscosity of gases;
- compare liquids with gases and solids;
- discuss the intermolecular forces and explain the model of structure of liquids;
- state the significance of surface tension, viscosity of liquids and their determination;
- differentiate between amorphous and crystalline solids;
- describe the symmetry elements;
- define lattice, basis and unit cell;
- describe the fourteen Bravais lattices and the seven crystal systems;
- state and explain the laws of crystallography;
- denote the crystal planes in terms of Weiss and Miller indices;
- state Bragg's law;
- describe the determination of crystal structure by X-ray diffraction method;
- describe the characteristics of different types of cubic unit cell;
- explain the defects in crystals; and
- describe glasses and liquid crystals.

UNIT 8

KINETIC THEORY OF GASES

Structure

8.1 INTRODUCTION

Chemistry may be defined as the study of matter in terms of its structure, composition and properties. You know that under ordinary conditions of pressure and temperature, matter exists in three states, viz., solid, liquid and gas. For example, at ordinary pressures, H_2O can exist as ice, water or steam depending on the temperature. The behaviour of matter in these three states is quite different due to the extent of interaction between the constituent species. The gases behave quite different from solids and liquids in which these interactions are relatively stronger. The solids and liquids are sometimes referred to as condensed states. It is important to note that the physical properties of different gases are generally similar and can be expressed in terms of simple laws.

In this and the next unit you would learn about the behaviour of gases from kinetic theory approach. This approach considers a gas to be a collection of a large number of identical particles (atoms or molecules), that are in constant, and random motion. This theory is based on a set of postulates and explains the macroscopic properties like, pressure, volume and temperature of the gas.

We would begin the unit by recalling different gas laws formulated on the basis of extensive experimental studies of gases. These laws provide interrelationships between different properties of gases and can be combined to formulate an equation of state for ideal gases. Having done so, we would introduce the kinetic theory of gases in terms of its postulates. These would then be used to derive an expression for the pressure of the gas in terms of molecular velocities and collisions between the molecules. This equation is quite useful in calculating the parameters such as pressure, average kinetic energy etc. of the gas molecules. The principle of equipartition of energy and the distribution of molecular speeds and the dependence of molecular speeds on temperature will also be discussed. Finally, the equations for calculating the collision number and the mean free path of molecules of a gaseous sample will be derived. In the next unit, the deviation from ideal behaviour and the behaviour of real gases shall be taken up for discussion.

Expected Learning Outcomes

After studying this unit, you should be able to:

- state and explain the gas laws;
- derive the ideal gas equation from gas laws;
- calculate one of the unknowns amongst pressure, volume, temperature or amount of a gas using the ideal gas equation;
- state Dalton's law of partial pressures;
- state postulates of kinetic theory of gases and derive the equation $pV = \frac{1}{3} mN\,\bar{u}^2$;
- explain the distribution of molecular speeds;
- calculate the most probable speed, the average speed and the root mean square speed of the molecules of a gas;
- state and explain the principle of equipartition of energy;
- derive an expression to calculate the collision number between gas molecules; and
- define mean free path and calculate the mean free path of molecules in a gaseous sample.

8.2 RECAPITULATING GAS LAWS

Some of the earliest experimental measurements on pressure, volume and temperature (*p*-*V*-*T*) were made on air at atmospheric pressure and room temperature. Fortunately, under these conditions air behaves nearly as an

ideal gas. This helped a lot in the formulation of the gas laws. You would have studied Boyle's law, Charles' law and Avogadro's law in your previous classes. These provide quantitative relationship between different properties of gases. These properties are recognised in terms of four physical quantities viz., pressure, temperature, volume and amount of the gas. We shall recapitulate the gas laws after stating the SI units of pressure, volume and temperature.

Pressure: The SI unit of pressure is pascal (Pa). It is the pressure of one newton per square metre (N m^{-2}), or, in terms of SI base units, it equals one kilogram per metre per second squared (1 *k*g $m^{-1}s^{-2}$).It's equivalence with other units of pressure is as follows:

1 bar = 10^5 Pa

1 atmosphere = 1 atm = 760 mm Hg = 760 Torr

= 1.0132×10^5 Pa = 1.0132 bar

Volume: The SI unit of volume is cubic metre or metre cube (m^3). Other equivalent units are given below:

1 m^3 = 10^3 dm^3 = 10^3 L = 10^6 cm^3 = 10^6 mL

In the above expression 'L' stands for litre.

Temperature: The SI unit of temperature is kelvin (K). To convert temperature from Celsius scale into Kelvin scale, 273.15 is to be added to the former e.g., 25°C would be 298.15 K.

Let us now state and explain the gas laws.

8.2.1 Boyle's Law

It is a relation between pressure and volume of a gas at a given temperature formulated by the physicist Robert Boyle in 1662. It states that at constant temperature *T*, the volume, *V*, of a fixed amount of gas varies inversely as its pressure, *p*.

i.e., $V \propto \frac{1}{p}\ (T, n = \text{constant})$ …(8.1)

or $pV = K_1\ (T, n = \text{constant})$ …(8.2)

Here K_1 is a constant at a given temperature for a fixed amount of the gas. This implies that for a given amount of gas at a constant temperature the product of pressure and volume is a constant. This can be represented as

$p_1V_1 = p_2V_2$. …(8.3)

This type of behaviour of a gas is shown graphically in Fig. 8.1.The *p* versus *V* plot (Fig. 8.1 (a)) at constant temperature is called an **isotherm** and resembles a hyperbola. You may note that doubling the pressure reduces the volume to half.

Alternatively, the graphical representation of Boyle's law can be done in terms of a plot between pressure and 1/*V* as shown in Fig. 8.1 (b)) which gives a straight line.

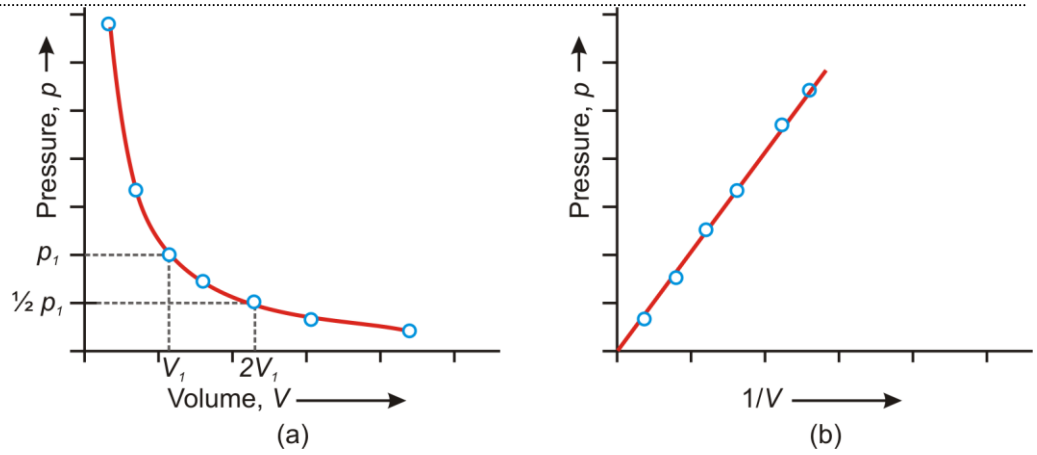


Fig. 8.1: *p-V* isotherms: a) variation of the volume of a gas with the pressure exerted on the gas, at constant temperature and b) *p* versus 1/*V* plot for a gas at constant temperature.

8.2.2 Charles' Law

It relates the volume and temperature of a gas at constant pressure and was discovered in 1787 by the French physicists Jacques Charles. The law states that for a certain amount of gas at a constant pressure, its volume (V) is directly proportional to its absolute temperature (T).

i.e., $V \propto T$ (p, n = constant) …(8.4)

or $V = K_2 T$ or $\frac{V}{T}$ = constant or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ …(8.5)

where K_2 is constant for a given pressure and amount of gas and it does not depend on the identity of the gas. The variation of volume with temperature at different constant pressures is given in Fig. 8.2. For a given pressure the plot is a straight line and is known as an **isobar**.

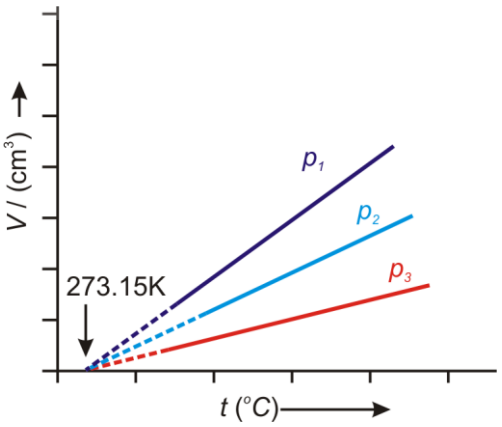


Fig. 8.2: Isobars relating volume of a gas with temperature at different pressures.

The law implies that if you increase the volume of a certain amount of gas at constant pressure then it must be accompanied by an increase in the temperature. Although most gases follow Charles's law to a good extent however they deviate from it at high pressures and low temperatures. You may also note that all the isobars extrapolate to a constant temperature of -273.15 °C i.e., the absolute zero.

8.2.3 Gay Lussac's Law

The Gay-Lussac's law (or **Amonton's law**) relates the pressure of a gas with its absolute temperature at constant volume. Sometimes this law is called pressure law and it states that the pressure of a given mass of gas varies directly with the absolute temperature of the gas when the volume is kept constant i.e.,

$$p \propto T \ (V, m = \text{constant}) \quad \text{or} \quad p = K_3 T \qquad \ldots(8.6)$$

Thus, if we increase the temperature of a gas keeping the mass and volume of the gas constant then its pressure would also increase.

8.2.4 Avogadro's Law

According to Avogadro's hypothesis equal volumes of all the gases contain equal number of molecules under the same conditions of temperature and pressure. In other words,

$$V \propto N \quad (T, p = \text{constant}) \qquad \ldots(8.7)$$

Avogadro number is equal to 6.022×10^{23} and has no units. Avogadro constant is equal to $6.022 \times 10^{23}\ \text{mol}^{-1}$.

where N is the number of molecules in a volume V. We know that the number of moles (n) is related to the number of molecules (N) as per the following equation,

$$n = \frac{N}{N_A} \qquad \ldots(8.8)$$

Where, N_A is Avogadro constant ($6.022 \times 10^{23}\ \text{mol}^{-1}$). Using Eq. 8.7 and Eq.8.8, we can write that at constant temperature and pressure,

$$V \propto n \quad \text{or} \quad V = K \times n \ (p, T = \text{constant}) \qquad \ldots(8.9)$$

This gives us the **Avogadro's law** which states that at constant temperature and pressure, the volume of a gas is proportional to the number of moles of the gas. In other words, equal amount of two gases would occupy same volume at the same temperature and pressure.

The constant of proportionality in Eq. (8.9), K is equal to the volume per mole of gas and is called **molar volume**. The molar volumes of all gases for given values of T and p are approximately equal. The conditions of temperature of 273.15 K and a pressure of 10^5 Pa (1 bar) respectively are called standard temperature and pressure, often abbreviated as STP. The molar volume of a gas is approximately 22.71 L at STP.

It is important to know the difference between STP and NTP.

STP: Standard Temperature and Pressure and 273.15 K and 10^5 Pa respectively.

NTP: Normal Temperature Pressure are 293.15 K and 1 atm (101.325 kPa) respectively.

It is important to know the difference between STP and the earlier term NTP. The Normal Temperature and Pressure (NTP) are 293.15 K (i.e., 20°C) and 1 atm (101.325 *k*Pa). The molar volume of a gas is approximately 22.41 L at NTP. IUPAC recommends the unit of pressure to be Pa and recommends to use standard pressure of 1 bar (10^5 Pa) rather than earlier term atm (101.325 *k*Pa).

Using the above gas laws, we can arrive at the ideal gas equation. Let us see how?

8.3 EQUATION OF STATE FOR IDEAL GASES

The three gas laws explained above can be summarised as

Boyle's law: $V \propto \frac{1}{p}$ $(T, n = \text{constant})$ …(8.1)

Charles law: $V \propto T$ $(p, n = \text{constant})$ …(8.4)

Avogadro's law: $V \propto n$ $(p, T = \text{constant})$ …(8.7)

These laws can be combined to give the combined gas law i.e.,

$$V \propto \frac{nT}{p} \quad \text{…(8.10)}$$

This can be rearranged to

$$pV = nRT \quad \text{…(8.11)}$$

Where, R is the gas constant. Eq. 8.11 is known as the **equation of state** for an ideal gas. The state of the gas is its condition at a given instance i.e., under given set of conditions. A particular state of a gas is described by its pressure, volume, temperature and the amount. An **ideal** or a **perfect gas** is a hypothetical gas whose pressure-volume-temperature behavior can be completely accounted for by the ideal gas equation. Knowledge of any three of its properties is enough to define the state of the gas completely, since the fourth property can then be determined using Eq. 8.11. However, if in some case, there are changes in pressure, volume, and temperature, or even in the amount of gas then we must use a modified form of the ideal gas equation involving the initial and final conditions. We can write,

$$R = \frac{p_1 V_1}{n_1 T_1} \text{(before change)} \quad \text{and} \quad R = \frac{p_2 V_2}{n_2 T_2} \text{(after change)} \quad \text{… (8.12)}$$

Equating the two, we get

$$\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2} \quad \text{… (8.13)}$$

For fixed amount of a gas, it becomes

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \quad (n = \text{constant}) \quad \text{… (8.14)}$$

Let us now discuss the units of the **gas constant**, R.

From Eq. 8.11 we can write,

$$R = \frac{pV}{nT}$$

Substituting the values of p, V, n and T for one mole of a gas at STP, we get

$$= \frac{(1\,\text{bar})(22.71\,\text{L})}{(1\,\text{mol})(273.15\,\text{K})}$$

Simplifying, we get

$$= 0.08314 \frac{\text{L. bar}}{\text{K.mol}} = 0.08314 \text{ L.bar K}^{-1}\text{ mol}^{-1}$$

$$= 0.08314 \text{ L bar K}^{-1}\text{ mol}^{-1}.$$

The gas constant, R has the dimension of (energy) (amount of substance)$^{-1}$ (temperature)$^{-1}$.The values of R in other units are given below:

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

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

= 1.987 cal K^{-1}mol^{-1}

In SI units, the value of R is 8.314 J K^{-1}mol^{-1}, we will be using this value throughout this course.

Calculations Using Ideal Gas Equation

The ideal gas equation (Eq. 8.11) is useful in calculating any of the unknowns amongst pressure, volume, temperature or the amount of gases from three of the other known quantities. Let us illustrate this by taking some examples.

Example 8.1: Calculate the volume occupied by 0.0660 kg of carbon dioxide gas at a temperature of 300.2 K and a pressure of 9.41 $\times$ 10^{4} Pa assuming ideal behavior for the gas.

Solution: From Eq. (8.11) we have $pV = nRT$

This can be rearranged as: $V = \dfrac{nRT}{p}$

We are given the values of pressure and temperature; R is a constant so we need to know the number of moles of given sample of carbon dioxide to calculate the volume.

$$\text{Number of moles of carbon dioxide}(n) = \frac{\text{Mass of carbon dioxide}}{\text{Molar mass of carbon dioxide}}$$

$$= \frac{0.0660\ \text{kg}}{0.044\ \text{kg mol}^{-1}} = 1.5\ \text{mol}$$

Substituting the values of different quantities in the rearranged gas equation, we get

$$V = \frac{(1.5\ \text{mol}) \times (8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (300.2\ \text{K})}{9.41 \times 10^{4}\ \text{Pa}} = 0.0398\ \text{m}^3$$

Thus, carbon dioxide under given set of conditions would occupy a volume of 0.0398 m^3.

$$\frac{1\text{J}}{1\text{Pa}} = \frac{1\text{kg m}^2\text{ s}^{-2}}{1\text{kg m}^{-1}\text{ s}^{-2}}$$

$$= 1\text{m}^3$$

Also $\dfrac{1\text{J}}{1\text{m}^3} = 1\,\text{Pa}$

Example 8.2: If one mole of nitrogen gas occupied a volume of 25 dm^3 at a temperature of 300 K, calculate its pressure assuming ideal behavior for the gas.

Solution: From Eq. (8.11) we have $pV = nRT$

This can be rearranged as: $p = \dfrac{nRT}{V}$

We are given the values of n , V and T; R is a constant so we can substitutes these values and get the value of pressure.

$$p = \frac{(1.0\ \text{mol}) \times (8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (300\ \text{K})}{25\ \text{dm}^3 \times 10^{-3}\ \text{m}^3\text{dm}^{-3}} \Rightarrow p = 9.977 \times 10^{4}\ \text{Pa}$$

Thus, the pressure of nitrgen gas would be 9.977×10^{4} Pa

Using the ideas developed above; attempt the following simple questions to assess your learning.

SAQ 1

Calculate the density of oxygen gas at 273.2 K and 1.013 $\times 10^5$Pa, assuming ideal behavior. (Given: M_m (O_2) = 0.032 kg mol^{-1})

(Hints: (i) Number of moles = Mass/Molar mass
(ii) Density = Mass/Volume

SAQ 2

How many molecules of oxygen are present in 0.0032 kg of the gas?

8.4 DALTON'S LAW OF PARTIAL PRESSURES

We have so far discussed about the behavior of pure gases. However, many a times we deal with mixtures of gases e.g., air. How can we explain the pressure-volume-temperature relationship of a sample of air or any other mixture containing several gases? In such cases, the total gas pressure is related to partial pressures, that is, the pressures of individual gas components in the mixture. This law is known as Dalton's law of partial pressures. It states that *at constant temperature, the total pressure exerted by a mixture of non-reactive gases behaving ideally, is the sum of the pressures exerted by the individual gases occupying the same volume alone*. The individual pressure of a gas in a mixture of gases is called its *partial pressure*. The essential condition is that the gases should not react chemically.

Mathematical form of Dalton's law

Let us consider three ideal gases, A, B and C. Let the pressure of the gases be p_A, p_B and p_C, respectively when each of them is kept individually at a temperature T and volume V. Let us now force these gases into a vessel of volume V at the same temperature. According to Dalton's law of partial pressures, the total pressure (p_t) of the mixture of gases is given by

$$p_t = p_A + p_B + p_C \qquad \ldots(8.15)$$

Using Eq. 8.11 for each of the gases, we can write

$$p_A = \frac{n_A RT}{V} \qquad \ldots(8.16)$$

$$p_B = \frac{n_B RT}{V} \qquad \ldots(8.17)$$

and $$p_C = \frac{n_C RT}{V} \qquad \ldots(8.18)$$

Substituting Eq. 8.16 to 8.18, in Eq. 8.15, we get,

$$p_t = (n_A + n_B + n_C)\frac{RT}{V} \qquad \ldots(8.19)$$

Since the total number of moles of the gases is equal to the sum of the number of moles of each component, i.e. $n_t = n_A + n_B + n_C$, we can write,

$$p_t = \frac{n_t RT}{V} \quad \ldots(8.20)$$

Dividing Eq. 8.16 to Eq. 8.18 by Eq. 8.20 and rearranging we get,

$$p_A = \frac{n_A}{n_t} p_t \quad \ldots(8.21)$$

$$p_B = \frac{n_B}{n_t} p_t \quad \ldots(8.22)$$

and $$p_C = \frac{n_C}{n_t} p_t \quad \ldots(8.23)$$

$$\frac{p_A}{p_t} = n_A \times \frac{RT}{V} \times \frac{V}{RTn_t}$$

$$p_A = \frac{n_A}{n_t} \times p_t$$

The terms $\frac{n_A}{n_t}, \frac{n_B}{n_t}$ and $\frac{n_C}{n_t}$ are called the mole fractions of gases A, B and C, respectively in the mixture and are represented as x_A, x_B and x_C respectively.

The mole fraction is a dimensionless quantity that expresses the ratio of the number of moles of one component to the number of moles of all components present.

Thus, the Eq. 8.21 to 8.23 can be rewritten as,

$$p_A = x_A p_t \quad \ldots(8.24)$$

$$p_B = x_B p_t \quad \ldots(8.25)$$

$$p_A = x_C p_t \quad \ldots(8.26)$$

In other words, the **partial pressure of a gas in a gaseous mixture is given by the product of its mole fraction in the mixture and total pressure**.

You may remember that in a mixture of gases, the sum of partial pressures of different gases must equal the total pressure of the gas and the sum of mole fractions of all the gases must be equal to 1. Let us take an example to see the application of Dalton's law of partial pressures.

Example 3: At 298 K, 0.002 m^3 of helium gas at a pressure of 10^5 Pa is mixed with 0.003 m^3 of neon gas at a pressure of 1.5×10^5 Pa. Calculate the following

i) the mole fractions of the gases

ii) total pressure, and

iii) partial pressures of the two gases

Solution: i) In order to compute the mole fractions we need to first know about the number of moles of the two gases.

From Eq. (8.11) we have $pV = nRT$

This can be rearranged as: $n = \frac{pV}{RT}$

We are given the values of p , V and T; R is a constant so we can substitutes these values and get the value of number of moles as follows

$$n(\text{He}) = \frac{(1.5 \times 10^5 \text{ Pa}) \times (0.002 \text{ m}^3)}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} = 0.0802 \text{ mol}$$

1 Pa = 1 Jm^{-3}

$$n(\text{Ne}) = \frac{(1.5\times10^5\ \text{Pa})\times(0.003\ \text{m}^3)}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\times(300\ \text{K})} = 0.1804\ \text{mol}$$

Total number of moles = n_t = 0.0802 + 0.1804 = 0.2606

The mole fractions can be calculated as follows

$$x(\text{He}) = \frac{n_{\text{He}}}{n_t} = \frac{0.0802}{0.2606} = 0.3077$$

$$x(\text{Ne}) = \frac{n_{\text{Ne}}}{n_t} = \frac{0.1804}{0.2606} = 0.6923$$

ii) According to Eq. (8.20) $p_t = \frac{n_t RT}{V}$

Substituting the values we get,

$$p_t = \frac{(0.2606\ \text{mol})\times(8.314\ \text{J mol}^{-1}\text{K}^{-1})\times(298\ \text{K})}{0.005\ \text{m}^3} = 1.29\times10^5\ \text{Pa}$$

iii) According to Eq. (8.21), the partial pressure is given as $p_A = \frac{n_A}{n_t} p_t$

Substituting the values,

$$p_{He} = \frac{0.0802}{0.2606}\times(1.29\times10^5\ \text{Pa}) = 3.96\times10^4\ \text{Pa}$$

$$p_{Ne} = \frac{0.1804}{0.2606}\times(1.29\times10^5\ \text{Pa}) = 8.93\times10^4\ \text{Pa}$$

Using the above principles, attempt the following simple questions to assess your learning

SAQ 3

2.00 mol of nitrogen, 1.00 mol of oxygen and 2.00 mol of methane are kept in a vessel of volume 0.0600 m^3 at 250.2 K. calculate the total pressure of the mixture of gases and the partial pressure of the individual gases using Dalton's law of partial pressures.

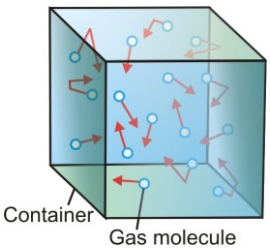
SAQ 4

State the name of the gas present in air which has the highest partial pressure.

8.5 KINETIC THEORY OF GASES

The gas laws discussed so far were arrived at on the basis of experimental work. The kinetic theory of gases put forward by Maxwell (1860) and Boltzmann (1867) provided a theoretical explanation for the properties of gases. Let us first go through the following basic assumptions of the kinetic theory of gases.

1) A gas is composed of a very large number of tiny molecules. The gas molecules are far apart from one another in comparison with their own dimensions. The gas molecules are considered as small hard spheres. Their volume is negligible compared to the total volume occupied by the gas. The molecules can be considered to be “point masses”; that is, they possess mass but have negligible volume



2) The gas molecules are in a state of constant random and rectilinear motion, i.e., they move in all possible directions with different speeds.

3) During their motion they collide frequently with each other and with the walls of the container. These collisions are perfectly elastic, which means that the total kinetic energy of the molecules before and after the collision is the same. In other words, we can say that the energy can be transferred from one molecule to another as a result of a collision but, the total energy of all the molecules in a system remains the same.

4) There are no intermolecular forces between the molecules, i.e., there are no forces of attraction or repulsion between them.

5) The pressure exerted by the gas is due to the force exerted on the walls of the container due to non-stop bombardment of the molecules.

6) The absolute temperature of a gas is proportional to the mean kinetic energy of the molecules present in it.

We shall use these assumptions in the next section. Let us first discuss some of the features regarding molecular velocities which will be required for deriving the equation of state for the gases.

8.5.1 Resolution of Molecular Velocities

Velocity (***u***) is a vector quantity. The components of ***u*** in the *x*, *y* and *z* directions are $\boldsymbol{u_x}$, $\boldsymbol{u_y}$ and $\boldsymbol{u_z}$. The speed *u* is the magnitude of the vector ***u*** and the latter is represented by the distance OC (Fig. 8.3).

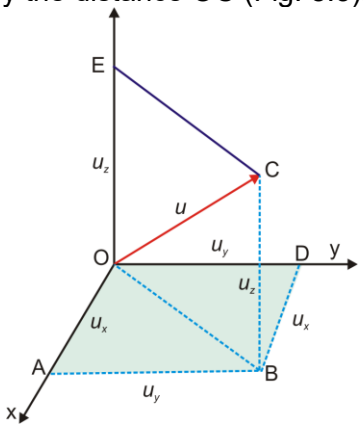


Fig. 8.3: Components of velocity, *u* in *x*, *y* and *z* directions.

The lengths OA, OD and OE represent the x, y and z components of the velocity vector i.e., $\boldsymbol{u_x}$, $\boldsymbol{u_y}$ and $\boldsymbol{u_z}$. Hence, note that OC = *u*

OA = DB = $\boldsymbol{u_x}$

OD = AB = $\boldsymbol{u_y}$

OE = BC = $\boldsymbol{u_z}$

CB is perpendicular to *xy* plane (shaded). Since OB is in *xy* plane, BC is perpendicular to OB. Hence, ∠OBC = 90°

From the right angled triangle OBC, $u^2 = OC^2 = OB^2 + BC^2 = OB^2 + u_z^2$

You can see from the diagram that OD is on *y* axis. Since DB is parallel to *x* axis, DB is perpendicular to OD, i.e., ∠ODB = 90°

In the right angled triangle ODB, $OB^2 = OD^2 + DB^2 = u_y^2 + u_x^2$

$$\therefore \quad u^2 = OB^2 + u_z^2 = u_x^2 + u_y^2 + u_z^2 \qquad \ldots(8.27)$$

The velocity component like $\boldsymbol{u}_x$ can be positive, negative or zero (corresponding to motion in the positive *x*-direction, motion in the negative *x*-direction or no motion in the *x*-direction), but the speed, *u* by definition must be positive or zero.

8.5.2 Mean Square Speed

All the molecules of the gas do not move at the same speed. As a result, *x* components of the velocities of different molecules are different. This is also true of *y* components and *z* components of the velocities. If $u_{1x}^2, u_{2x}^2, u_{3x}^2, \ldots u_{Nx}^2$, are the square of the *x* components of the velocities for the molecules, 1, 2, 3, ... *N*, then the average of these values, $\overline{u}_x^2$, is given by,

The bar in $\overline{u}^2$ represents the average of the u^2 values.

$$\overline{u}_x^2 = \frac{(u_{1x}^2 + u_{2x}^2 + u_{3x}^2 + \ldots u_{Nx}^2)}{N} \qquad \ldots(8.28)$$

For $\overline{u}_y^2$ and $\overline{u}_z^2$ also, the expressions similar to Eq. 8.28 can be written. Further, similar to Eq. 8.27, the average of the square of the molecular speeds, $\overline{u}^2$, is related to $\overline{u}_x^2, \overline{u}_y^2$ and $\overline{u}_z^2$ as

$$\overline{u}^2 = \overline{u}_x^2 + \overline{u}_y^2 + \overline{u}_z^2 \qquad \ldots(8.29)$$

The quantity $\overline{u}^2$ is called the **mean square speed**. Since the gas molecules are in random motion, no particular direction is preferred. Secondly, since the quantities $\overline{u}_x^2, \overline{u}_y^2$ and $\overline{u}_z^2$ are equal. Hence, we can write

$$\overline{u}_x^2 = \overline{u}_y^2 = \overline{u}_z^2 = \overline{u}^2/3 \qquad \ldots(8.30)$$

The above equations will be helpful to you in understanding the derivation described in the next section.

8.6 DERIVATION OF THE EXPRESSION FOR PRESSURE OF A GAS

Let us consider a cubical container with side '*l*' filled with *N* gas molecules, each with mass '*m*'. Let us assume that one of the molecules moves in the *x* direction with velocity component u_{1x} (Fig. 8.4). It will strike the wall at the *yz*

plane (shaded face) with momentum mu_{1x} and will suffer an elastic collision so that it bounces back with a momentum $-mu_{1x}$.

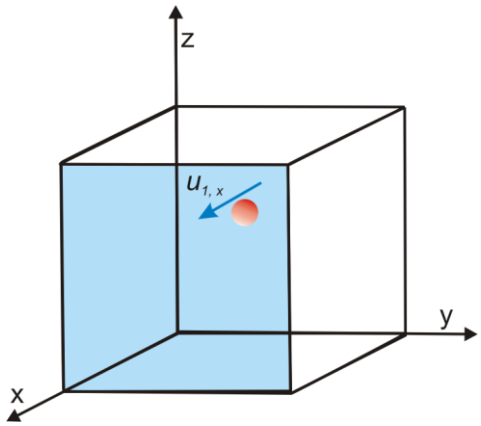


Fig. 8.4: Schematic representation of the motion of a gas molecule in a cubical box.

The change in momentum of the molecule in one collision is, $mu_{1x} - (-mu_{1x}) = 2\,mu_{1x}$. The molecule will travel back towards the opposite face and strike it. After bouncing back from there it will again travel towards the shaded face and strike it again. Thus, this molecule has to travel a distance of $2l$ before it collides with the shaded face again. Therefore, the time required for the next collision can be calculated as follows:

We consider the momentum change along x axis only.

The molecule travels a distance of u_{1x} in one second. Hence, to travel a distance of $2l$, the time required $= \frac{2l}{u_{1x}}$ second. That is, the time interval required for each successive collision with the shaded face is $\frac{2l}{u_{1x}}$ second.

Hence the number of collisions between the molecule and the shaded face taking place in unit time will be the inverse of the above expression, i.e. $\frac{u_{1x}}{2l}$.

The change of momentum in one second (or rate of change of momentum) per molecule = Change of momentum per molecule per collision × number of collisions a molecule undergoes with the shaded face in one second

$$= 2mu_{1x} \times \frac{u_{1x}}{2l}$$

$$= \frac{mu_{1x}^2}{l}$$

As per Newton's second law of motion, we know that force = rate of change of momentum

Hence force due to collisions by one molecule $= \frac{mu_{1x}^2}{l}$ …(8.31)

Similarly we can derive expressions for the force exerted by second, third ….. N^{th} molecule over the shaded face. The total force (F) exerted by N molecules over the shaded face can be calculated as follows:

$$F = \frac{m}{l}[u_{1x}^2 + u_{2y}^2 + u_{3z}^2 + ... + u_{Nx}^2] \quad \ldots(8.32)$$

From Eq. (8.28), the term in the bracket is equal to $N\bar{u}_x^2$.

Substituting it in Eq. (8.32), we get

$$= \frac{m}{l} N\bar{u}_x^2 \quad \ldots(8.33)$$

Using Eq. 8.32, we can write $\bar{u}_x^2 = \bar{u}^2 / 3$

Substituting it in Eq. (8.32), we get $F = \frac{mN\bar{u}^2}{3l}$ … (8.34)

Now, we know that pressure (p) is force per unit area (A). The area of the shaded face is l^2. Therefore, we get

$$\therefore \quad p = \frac{F}{A} = \frac{F}{l^2} = \frac{mN\bar{u}^2}{3l \,.\, l^2} = \frac{mN\bar{u}^2}{3l^3} \quad \ldots(8.35)$$

Since for a cube, volume (V) = l^3, we can write that

$$p = \frac{mN\bar{u}^2}{3V} \quad \ldots(8.36)$$

$$\therefore \quad pV = \frac{1}{3} mN\bar{u}^2 \quad \ldots(8.37)$$

We shall use this equation in the next section for calculating the average kinetic energy, number density, and concentration etc. of the gas molecules.

8.7 IDEAL GAS EQUATION

Although all the gas laws could be derived from Eq. 8.35, we shall derive the ideal gas equation only and then proceed to calculate different molecular parameters. Eq. 8.37 can be rewritten as,

$$pV = \frac{2}{3} N\left(\frac{1}{2} m\bar{u}^2\right) \quad \ldots(8.38)$$

From the kinetic theory of gases (postulate 6) it is known that the absolute temperature of a gas sample is directly proportional to the mean kinetic energy of the molecules, i.e.,

$$T \propto \frac{1}{2} m\bar{u}^2$$

or $$\frac{1}{2} m\bar{u}^2 = K_1 T \quad \ldots(8.39)$$

Where, K_1 is a constant.

Substituting this in Eq. 8.38, we obtain,

$$pV = \frac{2}{3} NK_1 T \quad \ldots(8.40)$$

This can be written as $pV = Nk_B T$ …(8.41)

Where, k_B is known as Boltzmann constant, and is equal to $2/3K_1$. The value of k_B is 1.38×10^{-23} JK^{-1}. Eq. 8.41 is the ideal gas equation for N molecules. For a gas having n moles, the number of molecules N is given by,

R is the gas constant for one mole and k_B is the gas constant for one molecule.

$$N = n\,N_A \qquad \ldots(8.42)$$

where N_A is Avogadro constant, and it is equal to the number of molecules (or species) in one mole of a substance. It is equal to 6.022×10^{23} mol^{-1}. Hence the equation for n moles of the gas can be written by substituting Eq. 8.42 in Eq. 8.41.

$$pV = nN_Ak_BT = nRT \qquad \ldots(8.43)$$

where R is equal to N_Ak_B. Eq. 8.43 is the same as Eq. 8.11 which has been derived in Sec. 8.3. Let us now calculate some parameters of the gas molecules by the combined use of Eq. 8.37, 8.39, 8.41 and 8.43.

8.7.1 Calculation of Average Kinetic Energy

According to Eq. 8.39 we know that the average kinetic energy ($\frac{1}{2}m\bar{u}^2$) is given as

$$\frac{1}{2}m\bar{u}^2 = K_1T \qquad \ldots(8.39)$$

We also know that $K_1 = \frac{3}{2}k_B$. Substituting it in Eq. 8.39 we get

$$\text{Average kinetic energy per molecule} = \frac{1}{2}m\bar{u}^2 = \frac{3}{2}k_BT \qquad \ldots(8.44)$$

Similarly, average kinetic energy per mole can be obtained by multiplying the expression with Avogadro's constant, N_A and simplifying as given below

$$= (N_A)\left(\frac{1}{2}m\bar{u}^2\right) = (N_A)\left(\frac{3}{2}k_BT\right)$$

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

$$= \frac{3}{2}RT\,(\because R = N_Ak_B) \qquad \ldots(8.45)$$

The energy calculated using this expression is also called the **translational energy**; this energy is due to the motion of the molecules in space.

Let us take an example to understand the use of Eq. 8.44 and Eq. 8.45

Example8.4: Calculate the average translational energy i) per molecule and ii) per mole of a gas at 300 K.

Solution: According to Eq. 8.44, the translational energy per molecule is given as

Translational energy per molecule $= \frac{1}{2} m \bar{u}^2 = \frac{3}{2} k_B T$

Substituting the value of Boltzmann's constant and temperature we get

$$= \frac{3}{2} \times 1.38 \times 10^{-23} \text{ JK}^{-1} \times 300\text{K}$$

The kinetic energy of a gas is due to random motion of the gas molecules. This is also called thermal energy. Temperature is a measure of kinetic (or thermal) energy.

Simplifying we get Translational energy per molecule $= 6.21 \times 10^{-21}$ J mol^{-1}

ii) Similarly, the translational energy per mole of gas can be obtained by using Eq. (8.45). Substituting the value of Boltzmann's constant and temperature we get

Translational energy per mole $= \frac{3}{2} \times 8.314$ J K^{-1}mol^{-1} $\times 300$K

Simplifying we get Translational energy per mole $= 3.74 \times 10^3$ J mol^{-1}

8.7.2 Calculation of Number Density and Concentration

Number density (n_o) is defined as the number of molecules of a gas in unit volume. It can be calculated by rearranging Eq. 8.41 as follows.

Number density of a gas (n_o) $= \frac{N}{V} = \frac{p}{k_B T}$ …(8.46)

Similarly, concentration (c), defined as the number of moles of a gas in unit volume, can be calculated by rearranging Eq. 8.43.

Concentration of a gas (c) $= \frac{n}{V} = \frac{p}{RT}$ …(8.47)

Thus, we note that the number density and the concentration of a gas depend on its pressure and the temperature. It is directly proportional to the pressure and inversely proportional to the temperature. Let us apply Eq. (8.46) and Eq. (8.47) to calculate the number density and concentration of a gas at a temperature of 298.2 K and pressure of 1.013×10^5 Pa.

Number density (n_o) of gas molecules at given temperature and pressure can be obtained by substituting the values of different terms in Eq. 8.46.

$$n_0 = \frac{p}{k_B T} = \frac{1.013 \times 10^5 \text{ Pa}}{1.38 \times 10^{-23} \text{ JK}^{-1} \times 298.2\text{K}}$$

$$= 2.462 \times 10^{25} \text{m}^{-3}$$

Similarly, the concentration (c) of gas molecules at given temperature and pressure can be obtained by substituting the values of different terms in Eq. (8.47)

$$= \frac{p}{RT} = \frac{1.013 \times 10^5 \text{ Pa}}{8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.2\text{K}} = 40.86 \text{mol m}^{-3}$$

Let us take up the calculation of mean square speed and root mean square speed

8.7.3 Calculation of Mean Square Speed and Root Mean Square Speed

In Subsec 8.6.2, we have defined mean square speed $(\bar{u}^2)$. The square root of its value is called root mean square speed and is represented as u_{rms}. For one mole of the gas, we can write by combining Eq. (8.37) and Eq. (8.43),

$$pV = RT = \frac{M_m \bar{u}^2}{3} \left\{ \begin{array}{l} \because\ n = 1 \text{ and} \\ M_m = mN = \text{Molar mass} \end{array} \right\}$$

For 1 mol, n =1

$N = N_A$

m $N_A = M_m$

i.e., mean square speed $(\bar{u}^2) = \frac{3RT}{M_m}$ …(8.48)

Root mean square speed $\left(\sqrt{\bar{u}^2}\right) = u_{rms} = \sqrt{\frac{3RT}{M_m}}$ …(8.49)

Let us take an example to see the application of Eq. (8.49)

Example 8.5: Calculate the root mean square speed (u_{rms}) of methane molecules at 515 K. (Given M_m (CH_4) = 0.016 kg mol^{-1}).

Solution: Substituting the values of different terms in Eq. 8.49 we get

$$u_{rms} = \sqrt{\frac{3RT}{M_m}} = \sqrt{\frac{3 \times 8.314\,\text{J K}^{-1}\text{mol}^{-1} \times 515\text{K}}{0.016\ \text{kg mol}^{-1}}}$$

$$= 8.96 \times 10^2\ \text{m s}^{-1}$$

$$\sqrt{\frac{1\,\text{J}}{1\,\text{kg}}} = \sqrt{\frac{1\,\text{kg m}^2\,\text{s}^{-2}}{1\,\text{kg}}}$$

$$= \sqrt{1\ \text{m}^2\,\text{s}^{-2}} = 1\,\text{m s}^{-1}$$

Thus, the root mean square speed of methane molecules at 515 K would be

$$= 8.96 \times 10^2\,\text{m s}^{-1}$$

Using the above example answer the following simple question.

SAQ 5

Calculate the root mean square speed of hydrogen molecules at 500 K. (Molar mass of hydrogen = 0.002 kg mol^{-1})

Air has average molar mass of 0.029 kg mol^{-1}. At room temperature (300 K), u_{rms} of air molecules is 510 ms^{-1}.

8.8 DISTRIBUTION OF MOLECULAR SPEEDS

A fundamental assumption of the kinetic theory of gases is that the molecules of the gas are in random and continuous motion. The molecules, however, do not move with constant velocity throughout. They travel with changing velocities due to the large number of collisions. Since velocity is a vector quantity and the molecules are in random motion, the average velocity is zero. But the speed of the molecules is not a vector quantity and hence the average speed is a finite quantity. Since there are a large number of molecules in any

sample of a gas, there will be different numbers of molecules having different speeds.

A typical distribution of the speeds of the molecules of nitrogen gas at 273 K is shown in Fig. 8.5.

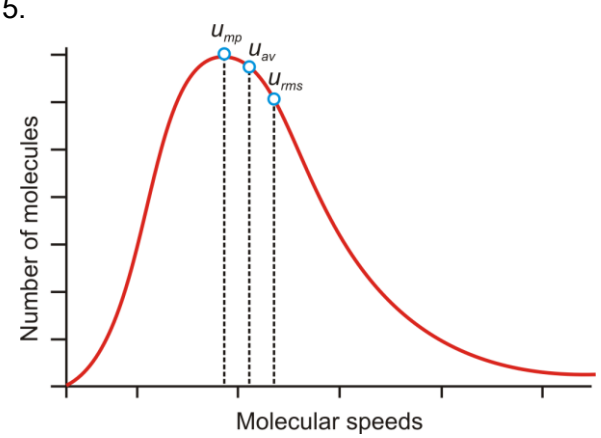


Fig. 8.5: Distribution of speeds of nitrogen molecules at 273 K.

Sound waves are caused by the oscillations of the air molecules. Hence, speed of the sound waves cannot be more than the u_{rms} of the air molecules. The speed of sound in air is 340 ms^{-1} (i.e., around two thirds of u_{rms} of air molecules).

Here the number of molecules having a particular speed is plotted against speed. The curve is not symmetrical and shows that there are more molecules with higher speeds than the ones with the lower speeds. Very few molecules have extremely small or extremely high speeds. The distribution is characterised by most probable, average and root mean square speeds. These are defined below:

i) The most probable speed, u_{mp}, is that which the largest fraction of molecules possesses. It corresponds to the maximum in the distribution curve for speeds (Fig. 8.5).

ii) The average speed $\bar{u}$, (also called the mean speed) is defined by the equation:

$$\bar{u} = \frac{1}{N}(u_1 + u_2 + u_3 + ... + u_N) \qquad ...(8.50)$$

Here, $\bar{u}$ is the average speed of N molecules.

iii) The root mean square speed, u_{rms}, is defined by the equation:

$$u_{rms} = \sqrt{\bar{u}^2} = \sqrt{\frac{1}{N}(u_1^2 + u_2^2 + u_3^2 + ... + u_N^2)} \qquad ...(8.51)$$

Maxwell and Boltzmann derived an expression for the distribution of molecular speeds. Using this expression, it is possible to derive the following relationships between molar mass and the three types of speeds:

$$u_{mp} = \sqrt{\frac{2RT}{M_m}} \qquad ...(8.52)$$

$$\bar{u} = \sqrt{\frac{8RT}{\pi M_m}} \qquad ...(8.53)$$

$$u_{rms} = \sqrt{\frac{3RT}{M_m}} \qquad ...(8.54)$$

Let us calculate the average speed of nitrogen molecules at 298.2 K using Eq. (8.53). Average speed $(\bar{u})$ of nitrogen molecules at 298.2 can be obtained by substituting the values of *R, T,* π and M_m, in Eq. (8.53).

$$= \sqrt{\frac{8RT}{\pi M_m}} = \sqrt{\frac{8 \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.2K}{3.142 \times 0.028 \text{ kg mol}^{-1}}}$$

$$\bar{u} = 474.8 \text{ms}^{-1}$$

A change in temperature affects the molecular speed distribution curve. The distribution curves for nitrogen gas at temperatures of 100, 300 and 700 K are shown in Fig. 8.6.

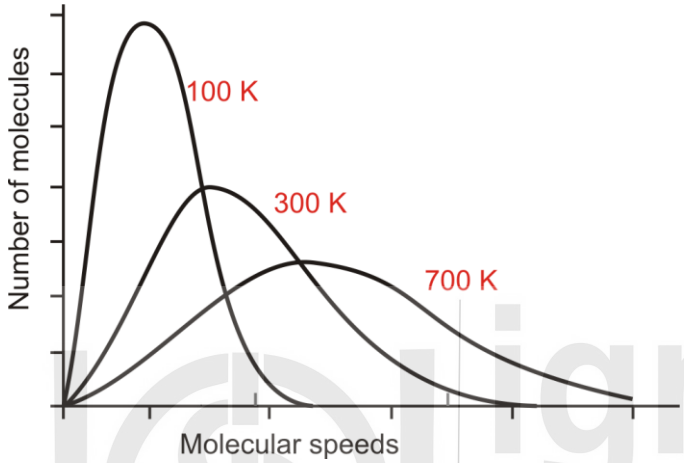


Fig. 8.6: Distribution of speeds of nitrogen molecules at three different temperatures.

From the above curves, it can be seen that at higher temperatures (i) the most probable speed is higher (ii) the fraction of the molecules possessing the most probable speed decreases and (iii) the distribution of the molecular speeds changes such that the spread is broader, compared to the distribution at lower temperatures. Using the principles discussed above, answer the following simple question.

SAQ 6

Calculate the ratio $u_{mp} : \bar{u} : u_{rms}$ for a gas of molar mass M_m. Does the value of this ratio depend on temperature?

8.9 PRINCIPLE OF EQUIPARTITION OF ENERGY

In Subsec 8.8.1, we showed that the translational kinetic energy per mole is $\frac{3}{2}RT$. Likewise we can calculate the contribution to energy arising out of rotation and vibration of molecules. Each mode of motion is called a degree of freedom. All gaseous molecules have three translational degrees of freedom. This is so since the translational motion is described by three independent coordinates.

Apart from the translational degrees of freedom a linear molecule has two rotational degrees of freedom since rotation is possible only around the two axes perpendicular to its molecular axis. A non-linear molecule can rotate around all the three mutually perpendicular axes and hence has three rotational degrees of freedom.

A molecule having F atoms (i.e., atomicity is F) has totally $3F$ degrees of freedom because $3F$ coordinates are required to locate their nuclei in space. That is, the sum of translational, rotational and vibrational degrees of freedom for a molecule is $3F$. The vibrational degrees of freedom for linear and non-linear molecules can be calculated using the following expression:

$$\left.\begin{array}{l}\text{Vibrational degrees of freedom}\\ \text{of a molecule having } F \text{ atoms}\end{array}\right\} = 3F - (\text{sum of translational and rotational degrees of freedom})$$

Hence, a linear molecule has $3F - (3 + 2) = 3F - 5$ vibrational degrees of freedom. But a non-linear molecule has $3F - (3 + 3) = 3F - 6$ vibrational degrees of freedom. For example, carbon dioxide (F = 3, a linear molecule) has $[(3 \times 3) - 5] = 4$ vibrational degrees of freedom and water (F = 3, a non-linear molecule) has $[(3 \times 3) - 6 = 3]$ vibrational degrees of freedom.

So far, we have calculated the degrees of freedom for each kind of motion. We can calculate the energy of molecules due to each kind of motion using the *equipartition theorem* of classical physics. This theorem can be stated as follows:

"The average energy of each different mode of motion of one mole of molecules is $\frac{1}{2}RT$."

Thus each translational and rotational degree of freedom contributes energy equivalent to $\frac{1}{2}RT$ to the energy of one mole of molecules. But each vibrational degree of freedom must contribute RT to the energy. This is because vibrational motion has both potential and kinetic energy associated with it and each contributes $\frac{1}{2}RT$ to energy.

Molar heat capacity is the quantity of heat required to raise the temperature of one mole of a substance through one degree kelvin

Molar heat capacity = Molar mass × specific heat

$\overline{C}_p, \overline{C}_V$ and R have the same units, viz., J K^{-1} mol^{-1}.

Using this principle, the total energy (U) of the gaseous molecules can be calculated. From the values of U at different temperatures, molar heat capacity values at constant volume $(\overline{C}_V)$ and at constant pressure $(\overline{C}_p)$ can be calculated using the following expressions.

$$\overline{C}_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \ldots (8.55)$$

$$\overline{C}_p = \overline{C}_V + R \quad \ldots (8.56)$$

The contribution RT to energy due to each vibrational degree of freedom is significant only at high temperatures. At room temperature we need to consider the contributions due to translational and rotational degrees of

freedom only. This is evident from the molar heat capacity values and $\overline{C}_p / \overline{C}_v$ ratios of some gases at 298 K given in Table 8.1. Classical physics cannot explain as to why contributions of vibrational degrees of freedom to heat capacity values is significant only at high temperatures

This can be explained this using the principles of quantum mechanics, which you have learnt in BCHCT-131 course. However, this is beyond the scope of this course.

Table 8.1: $\overline{C}_p$ and $\overline{C}_v$ values and their ratio at 298 K

Type of the molecule	Example	Degrees of freedom	$\frac{U^*}{\text{J mol}^{-1}}$	$\frac{\overline{C}_v}{\text{J mol}^{-1}\text{K}^{-1}}$	$\frac{\overline{C}_p}{\text{J mol}^{-1}\text{K}^{-1}}$	$\frac{\overline{C}_p}{\overline{C}_V}$
Monoatomic gas	Helium	3 (translational)	$\frac{3}{2}RT$	$\frac{3}{2}R$	$\frac{5}{2}R$	1.66
Diatomic gas	Carbon monoxide	3 (translational)	$\frac{3}{2}RT$	$\frac{5}{2}RT$	$\frac{7}{2}RT$	1.40
		2 (rotational)	$2\times\frac{1}{2}RT$ ($\frac{5}{2}RT$)			
		1 (vibrational not active at 298 K)	-----			
Non-linear triatomic molecule	Water	3 (translational)	$\frac{3}{2}RT$	$3R$	$4R$	1.33
		3 (rotational)	$3\times\frac{1}{2}RT$ ($3RT$)			
		3 (vibrational not active at 298 K)	----			

Using the ideas given above, answer the following SAQ.

SAQ 7

The specific heat capacity of a gas at constant volume at 298 K is 692 J kg^{-1} K^{-1} and its molar mass is 0.018 kg mol^{-1}. What is the value for $\overline{C}_p / \overline{C}_v$ ratio for the gas? (Hint: $\overline{C}_v$ = specific heat at constant volume $\times$ molar mass)

8.10 INTERMOLECULAR COLLISIONS

A cubic meter of nitrogen gas at room temperature and pressure contains about 2.462×10^{25} molecules (Subsec. 8.7.2) moving with an average speed of 474.8 m s^{-1} (Sec. 8.8). In a gas, the molecules are not only in continuous motion, but also are constantly colliding with one another. Because of collisions, a molecule changes its direction often and moves in a zigzag way. The path of such a molecule can be imagined (as shown in Fig. 8.7) to be within a cylinder. An estimate of the number of collisions taking place in one

second in unit volume (known as total collision frequency) can be made by introducing the concept of molecular size. For the sake of simplicity, the gas molecules are considered to be hard spheres with diameter σ. Thus, two molecules will collide with each other ('hit') if they are within a distance σ. If the distance is more than σ, the two molecules do not collide('miss') Fig. 8.7 depicts the motion of a molecule and indicates the condition under which it hits or misses another molecule.

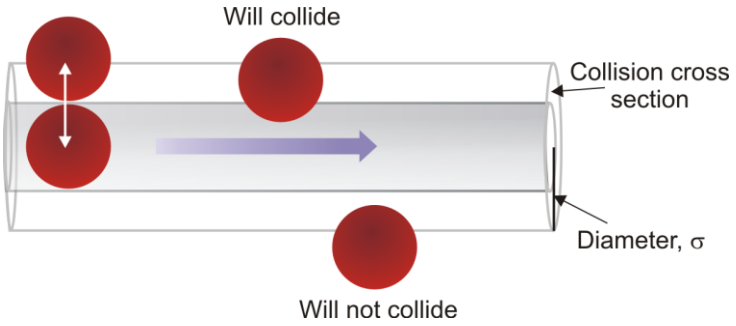


Fig. 8.7: The motion of molecule in a cylinder.

Since the average speed of a molecule is $\bar{u}$, it covers a distance equal to $\bar{u}$ in one second. Due to its zigzag motion, all molecules present in the cylinder with base equal to $\pi\sigma^2$ collide with the moving molecule. The volume covered by the molecule in one second is given by Eq. 8.51.

Collision density is an important parameter in deciding the reaction rate. We shall study this in the unit on chemical kinetics.

Volume covered by the molecule in one second = base of the cylinder × height

$$= \pi\sigma^2\bar{u} \qquad \ldots(8.57)$$

We know that the number of molecules present per unit volume (number density) is n_o. The collision frequency for a single molecule ($z_1(1)$) is equal to the number of collisions a molecule undergoes in one second. It is given by the product of the volume covered by the molecule in one second and the number density.

$$z_1(1) = \pi\sigma^2\bar{u}n_o \qquad \ldots(8.58)$$

In the derivation of Eq. 8.58, we have assumed that only one molecule moves and the others are static. In reality, all the molecules are moving. To account for this fact, the relative average speed $\bar{u}\sqrt{2}$ should be used instead of $\bar{u}$ in Eq. 8.58. Hence the collision frequency for a single molecule, becomes

$$z_1(1) = \sqrt{2}\,\pi\sigma^2\bar{u}n_o \qquad \ldots(8.59)$$

Eq. 8.59 gives the number of collisions experienced by one molecule in unit time. The number of collisions experienced by all the molecules in unit time in unit volume (i.e., total collision frequency, or collision density, Z_{11}) is given by

$$Z_{11} = \frac{1}{2}z_1(1)n_o = \frac{1}{\sqrt{2}}\pi\sigma^2\bar{u}n_o^2 \qquad \ldots(8.60)$$

The factor $\frac{1}{2}$ has been introduced so that collision between any two molecules is not counted twice. Let us take an example to learn the calculation of collision density

Example 8.6: Calculate the collision density of nitrogen gas at 298.2 K and 1.013×10^5 Pa. The collision diameter of nitrogen gas is given as 3.740×10^{-10} m.

Solution: According to Eq. (8.60), to calculate the collision density we need to know the number density, average speed and collision diameter. We are given the value of collision diameter and the other two terms have been already calculated in Subsec. 8.7.2 and Section 8.8 respectively. Let us recall them

Number density $n_o = 2.462 \times 10^{25}\ \text{m}^{-3}$

Average speed, $\bar{u} = 474.8\,\text{m s}^{-1}$

According to Eq. (8.60) the collision density $Z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{u} n_o^2$

Substituting the values of different terms, we get

$$= \frac{1}{\sqrt{2}} \times 3.142 \times (3.740 \times 10^{-10}\,\text{m})^2 \times 474.8\,\text{m s}^{-1} \times (2.462 \times 10^{25}\,\text{m}^{-3})^2$$

$$\therefore Z_{11} = 8.945 \times 10^{34}\ \text{m}^{-3}\text{s}^{-1}$$

8.11 MEAN FREE PATH

An important quantity in the kinetic theory of gases is the mean free path, λ. This is defined as the mean distance travelled by a gas molecule between two consecutive collisions. An equation useful in calculating the mean free path can be derived as follows:

Average distance travelled by a molecule in one second = $\bar{u}$

The number of collisions per molecule per second = $z_1(1)$

Mean free path (λ) = Average distance travelled between two consecutive collisions

$$\frac{\bar{u}}{z_1(1)} \qquad \ldots(8.61)$$

Substituting the value of $z_1(1)$ from Eq. (8.59) we get

$$= \frac{\bar{u}}{\sqrt{2} \pi \sigma^2 \bar{u} n_o}$$

i.e., $$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 n_o} \qquad \ldots(8.62)$$

It can be seen that the value of λ Is inversely proportional to n_o and hence it should be inversely proportional to pressure (Subsec. 8. 7. 2).

The lower value of λ at higher pressure is understandable since at higher pressure, a molecule will undergo larger number of collisions. It may also be

noted that the mean free path is inversely proportional to σ^2. This means that a larger molecule will have greater chance of collisions. As a matter of fact, quantity $\pi\sigma^2$ is called the collision cross section of the molecule in the hard sphere model proposed for gas molecules.

Using the above principles, work out the following SAQ.

SAQ 8

Calculate the mean free path of nitrogen molecule at 298.2 K and 1.013×10^5 Pa. The collision diameter for the molecule is 3.740×10^{-10} m.

8.12 SUMMARY

In this unit, we have discussed some characteristic features of gases. Laws governing the behavior of gases at low pressures and high temperatures are stated and explained. It has been shown how a simple kinetic molecular model of the gas can he used to derive an equation to calculate the pressure exerted by a gas. This equation can be used further to derive the ideal gas equation. This model is useful in showing how the constant collisions between molecules are responsible for a distribution of the speed of molecules. Further, this model helps us in deriving expressions for various kinds of speeds. We have also evolved a method of calculating the collision density and the mean free path assuming hard sphere model for the molecules.

8.13 TERMINAL QUESTIONS

1. Calculate the molar mass of a gas for which density is 1.25×10^3 kg m^{-3} at 273.2 K and 1.013×10^5 Pa.

2. A mixture of 2.00×10^{-3}kg of H_2 and 2.00×10^{-3}kg of He exerts a pressure of 1.50×10^5 Pa. What are the partial pressures of H_2 and He?

3. Calculate the ratio of mean square speeds of oxygen to nitrogen molecules at 300 K.

4. Calculate the number density and concentration of oxygen at 1.013×10^5Pa and 300 K.

5. What is the $\overline{C}_p / \overline{C}_v$ value of non-rigid diatomic gas?

   [Hint: A non-rigid molecule has vibrational degree of freedom too.]

8.14 ANSWERS

Self-Assessment Questions

1. $pV = nRT = \frac{w}{M_m} RT$

$$\text{Density} = w/V = \frac{pM_m}{RT}$$

Substituting the values,

$$= \frac{1.013\times10^5\ \text{Pa}\times0.032\ \text{kg mol}^{-1}}{8.314\ \text{J K}^{-1}\text{mol}^{-1}\times273.2\ \text{K}}$$

$$= 1.472\ \text{kg m}^{-3}.$$

$$\frac{1\ \text{Pa kg}}{1\ \text{J}} = \frac{1\ \text{kg m}^{-1}\ \text{s}^{-2}\ \text{kg}}{1\ \text{kg m}^2\ \text{s}^{-2}} = 1\ \text{kg m}^{-3}$$

2. 6.022×10^{22} molecules.

3. Total number of moles $(n_t) = n_{N_2} + n_{o_2} + n_{CH_4} = 5.00\,\text{mol}.$

$$\text{Total pressure } (p_t) = \frac{n_t RT}{V}$$

$$= \frac{5.00\,\text{mol}\times8.314\,\text{JK}^{-1}\,\text{mol}^{-1}\times250.2\,\text{K}}{0.0600\,\text{m}^3} = 1.73\times10^5\,\text{Pa}$$

$$p_{N_2} = \frac{n_{N_2}}{n_t}p_t = \frac{2.00}{5.00}\times1.73\times10^5\,\text{Pa} = 6.92\times10^4\,\text{Pa}$$

Similarly $p_{o_2} = 3.46\times10^4\ \text{Pa}$

$$p_{CH_4} = 6.92\times10^4\ \text{Pa}$$

4. Nitrogen

5. Root mean square speed of hydrogen at 500 K

$$= \sqrt{\frac{3RT}{M_m}} = \sqrt{\frac{3\times8.314\,\text{J K}^{-1}\text{mol}^{-1}\times500\,\text{K}}{0.002\ \text{kg mol}^{-1}}}$$

$$= 2.50\times10^3\ \text{ms}^{-1}$$

6. $u_{mp} : \bar{u} : u_{rms}$

$$= \sqrt{\frac{2RT}{M_m}} : \sqrt{\frac{8RT}{\pi M_m}} : \sqrt{\frac{3RT}{M_m}}$$

Dividing by $\sqrt{\frac{RT}{M_m}}$ we get

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

Dividing by $\sqrt{2}$

$$= 1.000 : 1.128 : 1.225$$

The above ratios do not vary with temperature since temperature term does not appear in it.

7. $\overline{C}_v = 692\,\text{J kg}^{-1}\,\text{K}^{-1} \times 0.018\,\text{kg mol}^{-1}$

$= 12.5\ \text{J K}^{-1}\text{mol}^{-1}$

Since $\overline{C}_p = \overline{C}_v + R$

$\overline{C}_p = (12.5 + 8.314) = 20.8\,\text{J K}^{-1}\text{mol}^{-1}$

$\frac{\overline{C}_p}{\overline{C}_v} = 1.66$

8. $\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n_o}$

Using n_o calculated in Subsec. 8.7.2,

$\lambda = \frac{1}{1.414 \times 3.142 \times (3.740 \times 10^{-10}\,\text{m})^2 \times 2.462 \times 10^{25}\,\text{m}^{-3}}$

$= 6.536 \times 10^{-8}\,\text{m}$

Terminal Questions

1. Molar mass of the gas = 28.02 kg mol^{-1}.

2. $p_{H_2} = 1.00 \times 10^5$ Pa; $p_{He} = 5.00 \times 10^4$ Pa

3. $\frac{\overline{u}^2_{\text{Oxygen}}}{\overline{u}^2_{\text{Nitrogen}}} = \frac{7}{8}$

4. Number density = 2.447×10^{25} m^{-3};

Concentration = 40.61 mol m^{-3}.

5. $U = (3 \times RT / 2) + (2 \times RT / 2) + (1 \times RT)$

$= 7 / 2\ RT$

$\overline{C}_v = 7/2R$ and $\overline{C}_p = \frac{9}{2}R$

Hence, $\overline{C}_p / \overline{C}_v = \frac{9}{7}$

UNIT 9

REAL GASES AND THEIR LIQUEFACTION

Structure

9.1 INTRODUCTION

In the previous unit you have learnt about the gas laws based on experimental observations, ideal gas equation, kinetic theory of gases and different molecular parameters characteristic of gaseous state. Though the ideal gas equation explains the behaviour of gases fairly well, but it is not valid for all conditions. It is observed that the real gases obey ideal gas laws only at low pressures and high temperatures.

In this unit we wish to take up the behaviour of real gases and to start with we would discuss the deviation of the real gases from ideal gas behaviour. The ideal gas equation will be suitably modified to accommodate these deviations and van der Waals Equation that is valid for real gases would be derived. This will be followed by a discussion on critical phenomena and critical constants. The relationships between critical constants and van der Waals constants and the principle of corresponding states will be explained. Then we will discuss about the liquefaction of gases and describe two methods for the same.

Finally, we would explain the concept of viscosity of gases and discuss the effects of pressure and temperature on it.

In the next unit we would take up the behavior of liquids.

Expected Learning Outcomes

After studying this unit, you should be able to:

- state the difference in behaviour of real and ideal gases;
- explain the pressure and volume correction terms to the ideal gas equation; and deduce van der Waals equation;
- define the terms: critical temperature, critical pressure and critical volume;
- derive the relationships between the critical constants and van der Waals constants;
- state and discuss the principle of corresponding states;
- state the principles of methods of liquefaction of gases;
- explain the concept of viscosity and define the term: coefficient of viscosity;
- derive the relation between the coefficient of viscosity of gases and mean free path of a gas; and
- discuss the effect of temperature and pressure on the viscosity of gases.

9.2 DEVIATION FROM IDEAL GAS BEHAVIOUR

You would recall from the previous unit that we defined an ideal gas to be the one that follows the ideal gas equation, viz.,

$$pV = nRT \qquad \ldots(9.1)$$

In fact, an ideal gas is a hypothetical concept; real gases behave differently. These deviate from the ideal behaviour under certain conditions. Let us study the behaviour of real gases at different pressures and temperatures to ascertain the conditions under which these deviate from ideal behaviour. Then we will take up the reasons for these deviations.

Behaviour of Real Gases

For real gases, the value of Z is greater than or less than unity.

Experimentally, the behaviour of a gas can be studied by measuring its pressure, volume, temperature and the number of moles. If it behaves ideally, its compressibility factor, Z which is defined by Eq. 9.2 must be equal to 1.

$$Z = \frac{pV}{nRT} \qquad \ldots(9.2)$$

If the value of Z deviates from unity the gas is said to deviate from ideal behaviour.

In order to understand the effect of pressure the value of Z is plotted against pressure for a few gases, Fig. 9.1.

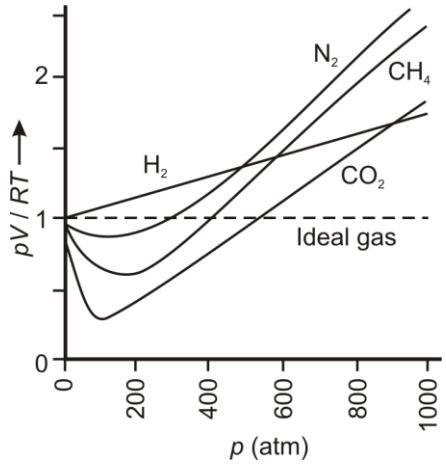


Fig. 9.1: Plots of compressibility factor, Z against pressure, *p* for a few gases.

We notice that all gases approach ideal behaviour at low pressures. This is inferred from the fact that Z approaches unity at low pressure for all gases. To illustrate the effect of temperature, as an example, the value of Z is plotted against pressure for nitrogen gas at three different temperatures in Fig. 9.2.

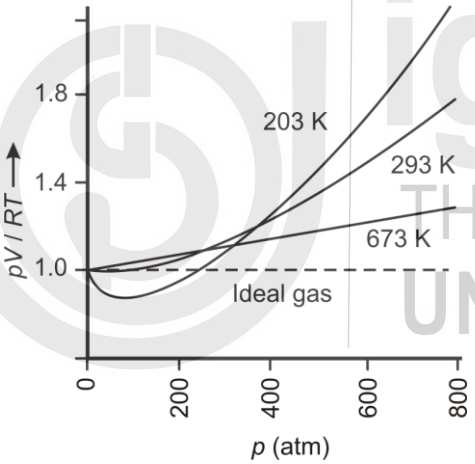


Fig. 9.2: Plots of compressibility factor, Z against pressure, *p* for nitrogen gas at three different temperatures.

Note that the curve at high temperature (673 K) approaches ideal gas behaviour much more than the curves at lower temperatures (203 K and 293 K). This is true of all the gases. Thus, we can conclude that ***the real gases behave ideally at low pressures and at high temperatures***. van der Waals derived an equation of state for explaining the experimental facts of the behaviour of real gases. We shall study this in the next section.

9.3 van der WAALS EQUATION

The origin of the deviations of real gases from ideal gas behaviour lies in two faulty assumptions of the kinetic theory of gases (discussed in Unit 8). Firstly, you would recall that the kinetic theory of gases assumes that the gas molecules to be “point masses”; that is, they possess mass but have negligible volume. That is, their volume is negligible compared to the total volume occupied by the gas. However, in reality the volume of a molecule is by no

means negligible and cannot be ignored under all conditions. Secondly, the kinetic theory assumes that there are no forces of attraction or repulsion between the molecules. Here again, it is observed that intermolecular interactions do exist between molecules especially at close distances. van der Waals modified the ideal gas equation by taking into account these two shortcomings of the kinetic theory of gases. These modifications are in terms of volume and pressure corrections to the ideal gas equation. Let us learn about them.

The van der Waals constant '*b*' is equal to the excluded volume of one mole of a gas. It can be shown that '*b*' is equal to four times the actual volume of the molecules. The constant '*b*' has the units, $m^3\ mol^{-1}$.

Volume Correction: van der Waals realised that the molecules of a real gas have finite volume and also, we know that they are in constant motion. Therefore, the entire volume (V) of the container is not available for the free movement of the gas molecules. The volume available for the motion of the molecules can be given by ($V - nb$), where n is the number of moles of the gas and 'b' the correction in volume for one mole of the gas. The quantity 'b' is known as co-volume or excluded volume. The excluded volume due to the motion of the molecules can be shown to be equal to four times the actual volume of the molecules at rest.

Hence, corrected volume = $V_{corr} = V - nb$ …(9.3)

Pressure Correction: van der Waals applied pressure correction by taking into account the intermolecular forces. The pressure of a gas is due to the collision of the gas molecules on the walls of its container. Consider two identical molecules in a gas such that one is somewhere in the middle of the container and the other just strikes the wall (Fig. 9.3).

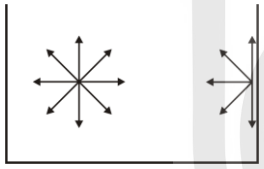


Fig. 9.3: The attraction experienced by the molecules of a gas.

It can be seen that a molecule in the middle of the container is attracted on all sides by the other molecules surrounding it. However, in case of a molecule which just strikes the wall, there is a net backward drag on the molecule and it will strike the wall with a somewhat weakened impact. Hence, the observed pressure (p) of a gas will be less than the pressure exerted by an ideal gas. A pressure correction is, therefore, to be applied. The correction term in pressure (Δp) is proportional to two factors. viz.,

- the number of molecules striking the wall per unit area and
- the number of molecules attracting a molecule from behind.

Liquefaction of gases (Sec. 9.7) clearly indicates the presence of forces of attraction among gaseous molecules.

Each of the above factors is proportional to the concentration of the gas.

i.e., $\Delta p \propto (\text{concentration})^2$

But the concentration of the gas = $\dfrac{\text{Number of moles}\,(n)}{\text{Volume of the container}\,(V)}$

Hence, it can be written that,

$$\Delta p \propto \frac{n^2}{V^2} \quad \text{i.e.,} \quad \Delta p = \frac{n^2 a}{V^2} \qquad \ldots(9.4)$$

The constant 'a' has the units, Pa m^6 mol^{-2}.

Where, the proportionality constant 'a' is a parameter characteristic of a gas. Hence the corrected pressure (p_{corr}) is given by,

$$p_{corr} = p + \frac{n^2 a}{V^2} \qquad \ldots(9.5)$$

If the corrected pressure and the corrected volume of the gas are substituted in the ideal gas equation (Eq. (9.1)), we obtain

$$(p + \frac{n^2 a}{V^2})(V - nb) = nRT \qquad \ldots(9.6)$$

The equation is known as **van der Waals equation**. Since for one mole of a gas, $V = V_m$ (i.e., molar volume) and $n = 1$, hence, Eq. (9.6) becomes

$$(p + \frac{a}{V_m^2})(V_m - b) = RT \qquad \ldots(9.7)$$

van der Waals equation (Eq. 9.6 or 9.7) is quite important and is applicable over a much wider range of p–V–T data for the real gases than the ideal gas equation. The quantities 'a' and 'b' are called the van der Waals constants (or parameters). The values of 'a' and 'b' are obtained empirically by fitting in experimental p–V–T data to Eq. 9.6. It may be pointed that 'b' is a measure of the molecular size and 'a' is related to the intermolecular interactions. Table 9.1 gives the values of the parameters 'a' and 'b' of some selected gases. It can be seen that 'b' increases as the size of the molecule increases whereas 'a' has large value for an easily liquefiable gas. The values of the critical constants p_c, V_c and T_c are also given in Table 9.1. Their significance will be dealt with later.

Table 9.1: van der Waals Parameters and Critical Constants of Some Gases.

Gas	'a'/Pa m^6 mol^{-2}	$10^6\times$ 'b'/m^{3}mol^{-1}	$10^{-5}\times p_c\times$ Pa	$10^6\times V_c$ /m^{3}mol^{-1}	T_c / K
He	0.003457	23.70	2.20	57.8	5.21
Ar	0.1373	32.19	48.64	73.3	150.7
H_2	0.02476	26.61	12.97	65.0	33.2
O_2	0.1378	31.83	50.76	78.0	154.8
N_2	0.1408	39.13	33.94	90.1	126.3
CO_2	0.3639	42.67	73.66	94.0	304.2
H_2O	0.5536	30.49	220.89	55.3	647.4
NH_3	0.4225	37.07	112.5	72.5	405.5
CH_4	0.2283	42.78	46.41	99.0	191.1

To help you to use Table 9.1, the actual values of the parameters for methane are given below:

a = 0.2283 Pa m^6 mol^{-2}

b = 42.78 $\times 10^{-6}$ m^{3}mol^{-1}

p_c= 46.41 $\times 10^5$ Pa

V_c= 99.0 $\times 10^{-6}$ m^{3}mol^{-1}

T_c= 191.1 K

Explanation of the behaviour of gases using van der Waals equation:

Many a times, either one or both the correction terms could become negligible. Let us study these cases.

When 'b' is very small,

The Eq. 9.7 becomes, $(p + \frac{a}{V_m^2})V_m = RT$ …(9.8)

On simplification and rearrangement, we get

$$pV_m = RT - \frac{a}{V_m} \quad \ldots(9.9)$$

Dividing throughout by RT

$$Z = \frac{pV_m}{RT} = 1 - \frac{a}{RTV_m} \quad \ldots(9.10)$$

This shows that under these conditions, pV_m will be less than RT or Z will be less than unity. Eq. 9.10 will be valid for substances like water vapour for which 'a' is large and 'b' is comparatively small (see Table 9.1). Also, for gases such as N_2, CH_4 and CO_2 at moderately low pressures, V_m is large such that $(V_m - b)$ is nearly equal to V_m. Hence, Eq. 9.10 is applicable for such gases at moderately low pressure.

When 'a' is negligible

If 'a' is negligible, we have

$$p(V_m - b) = RT \quad \ldots(9.11)$$

i.e., $$pV_m = RT + pb \quad \ldots(9.12)$$

Dividing throughout by RT

$$Z = \frac{pV_m}{RT} = 1 + \frac{pb}{RT} \quad \ldots(9.13)$$

Hence, pV_m will be greater than RT or Z will be greater than unity. Particularly this is true for hydrogen and noble gases for which the value of 'a' is small. At high pressure this is true for all the gases; since then $\frac{a}{V_m^2}$ term is negligible in comparison to p.

When a and b both are negligible

When pressure is very low or the temperature is very high, p *is* small but V_m is very large. In this case, the correction terms, $\frac{a}{V_m^2}$ and b both are negligible in comparison to p and V_m.

Hence, at very low pressure or high temperatures, the real gases obey ideal gas equation, and their Z value is nearly equal to unity.

Let us take an example to illustrate the use of Eq. 9.6

Example 9.1: Calculate the pressure of 2.000 mol of methane at temperature of 1.000×10^3 K and occupying a volume of 5.000×10^{-2} m^3 using van der Waals equation. Compare it with the pressure of methane gas assuming ideal behaviour under these conditions. [use Table 9.1 for the values of a and b].

Solution: Rearranging Eq. 9.6 we can write,

$$p = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

From Table 9.1, for methane a = 0.2283 Pa m^6 mol^{-2}

And $b = 42.78 \times 10^{-6}$ m^3 mol^{-1}

substituting the values of the parameters we get,

$$p = \frac{2.000\ \text{mol} \times 8.314\ \text{J K}^{-1}\text{mol}^{-1} \times 1.000 \times 10^3\ \text{K}}{(5.000 \times 10^{-2}\ \text{m}^3 - 2.000\ \text{mol} \times 42.78 \times 10^{-6}\ \text{m}^3\text{mol}^{-1})}$$

$$- \frac{(2.000\ \text{mol})^2 \times (0.2283\ \text{Pa m}^6\text{mol}^{-2})}{(5.000 \times 10^{-2}\ \text{m}^3)^2}$$

$$p = 3.328 \times 10^5\ \text{Pa}$$

Thus, by applying van der Waals equation to methane at 1.000×10^3 K, the pressure calculated is 3.328×10^5 Pa. Let us also calculate the pressure of methane using the same values of n, T and V but assuming ideal behavior.

$$p = \frac{nRT}{V} = \frac{2.000\ \text{mol} \times 8.314\ \text{J K}^{-1}\text{mol}^{-1} \times 1.000 \times 10^3\ \text{K}}{5.000 \times 10^{-2}\ \text{m}^3}$$

$$p = 3.326 \times 10^5\ \text{Pa}$$

It is interesting to see that the pressure values of methane obtained by van der Waals equation and ideal gas equation at 1.000×10^3 K are more or less same. This indicates that the methane behaves ideally at 1.000×10^3 K.

Virial Equation of State

In addition to the van der Waal's equation, a number of other attempts have also been made to propose equation of state for real gases. These are supposed to represent the p–V–T data over as wide a range as possible. However, from practical consideration, it is desirable that the equation of state should have only a few adjustable parameters and it should be simple from mathematical point of view.

The most general equation of state was proposed by Kammerlingh-Onnes and is known as **virial equation of state**. In this equation, the pressure is represented as power series of $\frac{1}{V_m}$ as under:

$$p = \frac{RT}{V_m} + \frac{B(T)}{V_m^2} + \frac{C(T)}{V_m^3} + \ldots \qquad \ldots(9.14)$$

The coefficients B(T), C(T) are known as virial coefficients. It may be noted that these coefficients depend on temperature. By having sufficient number of terms in this equation, experimental p–V–T data can be represented to desired accuracy. In the next section, we will introduce the critical phenomena and then study the relationship between van der Waals constants and critical constants.

Before that, solve the following simple question to assess your understanding.

SAQ 1

Calculate the pressure of 2.000 mol of methane at 298.2 K using the other data from the above illustration and assuming that it obeys van der Waals equation. Also calculate its value, if methane were to behave ideally at 298.2 K.

9.4 CRITICAL PHENOMENA

Andrew performed a series of experiments and obtained isotherms (p versus V plots at constant temperature) for carbon dioxide. The results obtained by him are shown in Fig. 9.4.

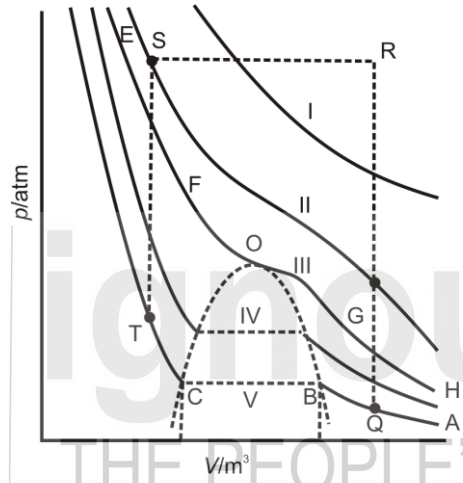


Fig. 9.4: Andrew's isotherms of carbon dioxide.

The point O where two falling curves. EFO and OGH, meet is mathematically known as inflection point. Around this point, the curve remains horizontal. That is, around this point, volume change does not produce pressure change.

At high temperature, the isotherm is a hyperbola (curve I) in accordance with Boyle's law (Unit 8). At low temperatures, the isotherms (the curves III, IV and V) show considerable deviation from ideal gas behaviour. The isotherm at 304.2 K (curve III) remains horizontal for a certain value of pressure. The two falling portions of the curve III, EFO and OGH, meet at O. The point O is known as the critical point; the temperature and pressure at this point are known as critical temperature, T_c. and critical pressure, p_c.

Along OFE (i.e., at pressures above that of point O), the curve represents the liquid state while along OGH (at pressures lower than that at O) the curve represents the vapour phase. Note that the substances in the gaseous state below the critical temperature are said to be in the vapour state. Below the critical temperature (in this case 304.2 K), the isotherms (such as curves III and IV) take a general form consisting of (i) a low-pressure region (AB) where there is only vapour, (ii) a flat constant pressure portion (BC) representing the liquid-vapour equilibrium and (iii) a high-pressure portion (CD) which is the isotherm of liquid carbon dioxide. At point B. the first drop of liquid appears and along BC, both the vapour and liquid forms of carbon dioxide are present. The pressure along BC is constant and is called the vapour pressure curve of carbon dioxide at the temperature of the isotherm. At C, the last drop of liquid is formed from the vapour. It can be seen that on changing from B to C, the volume has decreased due to conversion of vapour into liquid (without change

in pressure). It may be noted that the curve CD is much steeper than AB. This is because of the fact that liquids are much less compressible than gases and so a small change in volume requires a large change in pressure.

An interesting observation is that if the extremities of the horizontal portions like BC of different isotherms (like curves III, IV and V) are joined, a bell-shaped curve is obtained with crest at O. This is the area of discontinuity in which liquid and vapour phase coexist. Outside this area, there is either only vapour) or only liquid carbon dioxide.

Now the question arises, whether it is necessary to cross this area of discontinuity when the gas is converted into liquid or *vice versa*. The answer is no. For example, assume that there is a certain amount of vapour with pressure and volume corresponding to the point Q. It is desired to convert this into liquid directly without the simultaneous presence of both liquid and vapour. For this, we have to avoid passing through the area of discontinuity (bell-shaped area, BOC). First, we can heat the vapour at constant volume until it reaches a point R which lies above the critical pressure and temperature. The gas is then cooled at constant pressure which results in decrease of volume up to the point S. Now the volume is kept constant, and the gas is again cooled until the point T is reached, which results in the decrease of pressure. We see that as a result of these changes, the gas changes over to the liquid state without any discontinuity.

Thus, it can be seen that along the path QRST, the substance remains wholly in the gaseous state or in the liquid state. There is a smooth transition without any sudden change in any of the properties like p, or V along this path. This is called the continuation of state. That is, the gas and the liquid are the combination of the same state and it is not necessary to pass through a stage where both the states exist simultaneously during their inter conversion. The gaseous and liquid states are collectively known as **fluids**.

9.5 CRITICAL POINT AND CRITICAL CONSTANTS

Without going into the process of continuity of state, one gets the feeling that if we apply enough of pressure on a gas, we should be able to liquefy it. However, it is an experimental observation that a gas does not liquefy above a certain temperature, however, high may be the pressure. The characteristic temperature above which a gas does not liquefy is called the critical temperature (T_c). The vapour pressure of a liquid at its critical temperature is called its critical pressure (p_c). It is the minimum pressure required to produce liquefaction of a vapour at its critical temperature. The volume occupied by one mole of a fluid at its critical temperature and pressure is called critical volume (V_c). Let us now see how T_c, p_c and V_c are related to van der Waals constants.

9.5.1 Critical Constants and van der Waals Constants

The van der Waals equation (Eq. 9.7) can be made the basis of a theoretical consideration. The curves in Fig. 9.5, known as van der Waals isotherms, show the isotherms calculated on the basis of this equation.

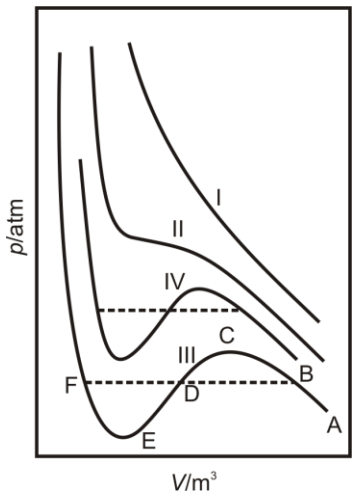


Fig. 9.5: van der Waals isotherms.

$$(p + \frac{a}{V_m^2})(V_m - b) = RT \quad \ldots(9.7)$$

Expanding Eq. 9.7 we get,

$$pV_m - pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT \quad \ldots(9.15)$$

Multiplying the equation throughout by $\frac{V_m^2}{p}$, we obtain,

$$V_m^3 - bV_m^2 + \frac{aV_m}{p} - \frac{ab}{p} = \frac{RTV_m^2}{p} \quad \ldots(9.16)$$

i.e., $V_m^3 - V_m^2(b + \frac{RT}{p}) + \frac{a}{p}V_m - \frac{ab}{p} = 0$ …(9.17)

This cubic equation will yield three values for V_m corresponding to a given pressure and temperature. All the three values of V_m may be real or one may be real and the other two may be imaginary (complex conjugates). van der Waals sotherms III and IV do yield three values of V_m in certain ranges of p and V. This is true in general for all isotherms below the critical temperature.

Curve II corresponds to critical temperature and curves at higher temperature (such as curve I) approach the isotherm representing the Boyle's law. These theoretical curves are similar to those obtained by Andrews for CO_2, but a major difference is the wave like portion BCDEF in the theoretical curves. If experiments are performed without perturbance, then portions BC and EF are realisable; these portions represent the supersaturated vapour and superheated liquid, respectively.

The wave like portions decreases as temperature increases. At the critical temperature, it is reduced to a point which means that all the three roots of Eq. 9.13 are identical and equal to the critical volume, V_c,

i.e., $V_m = V_c$ or $V_m - V_c = 0$ …(9.18)

We can obtain a cubic equation by raising it to power three, i.e.,

$$(V_m - V_c)^3 = 0 \quad \ldots(9.19)$$

or $V_m^3 - 3V_c V_m^2 + 3V_c^2 V_m - V_c^3 = 0$ …(9.20)

This equation should be identical with the expanded from of van der Waals equation (Eq. 9.17) at critical temperature and pressure i.e.,

$$V_m^3 - V_m^2(b + \frac{RT_c}{p_c}) + \frac{a}{p_c}V_m - \frac{ab}{p_c} = 0 \quad \ldots(9.21)$$

Now comparing equal powers of V_m in Eqs. 9.20 and 9.21 we obtain

$$-3V_c = -(b + \frac{RT_c}{p_c}) \quad \text{or} \quad 3V_c = b + \frac{RT_c}{p_c} \quad \ldots(9.22)$$

$$3V_c^2 = \frac{a}{p_c} \quad \ldots(9.23)$$

and $-V_c^3 = -\frac{ab}{p_c}$ or $V_c^3 = \frac{ab}{p_c}$ …(9.24)

Dividing Eq. 9.24 by Eq. 9.23, we obtain

$$\frac{V_c}{3} = b \quad \text{or} \quad V_c = 3b \quad \ldots(9.25)$$

Substituting the value of V_c in Eq. 9.23,

$$p_c = \frac{a}{27b^2} \quad \ldots(9.26)$$

From Eq. 9.22 and 9.25, we get

$$\frac{RT_c}{p_c} = (3V_c - b) = 8b$$

Which on simplification gives

$$T_c = 8b.\frac{p_c}{R} \quad \ldots(9.27)$$

$$= 8b \cdot \frac{a}{27b^2} \cdot \frac{1}{R} \text{ (using Eq. 9.26)}$$

$$T_c = \frac{8a}{27Rb} \quad \ldots(9.28)$$

Hence, the values of p_c, V_c and T_c can be calculated in terms of van der Waals constants.

9.5.2 Test for van der Waals Equation

At the critical point the calculation of the compressibility factor (Z_c) based on experimental p_c, V_c and T_c values can be a test for van der Waals equation. Theoretically the value of Z_c can be derived as follows:

$$Z_c = \frac{p_c V_c}{RT_c} \quad \ldots(9.29)$$

Substituting the values pf p_c, V_c and T_c in terms of van der Waals constants we get

$$Z_c = \left(\frac{a}{27b^2}\right).(3b).\frac{1}{R}.\frac{1}{8a/27Rb} \quad \ldots(9.30)$$

On simplification,

$$Z_c = \frac{3}{8} = 0.375 \quad \ldots(9.31)$$

For most gases, the value of Z_c obtained from the experimental values of the critical constants lies between 0.2-0.4. This variation from the theoretical value of 0.375 indicates the approximate nature of van der Waals equation. Why don't you apply these principles in solving the following simple questions?

SAQ 2

Liquefied Petroleum Gas (LPG) supplied for household use is mostly a mixture of propane and butane. Are the critical temperatures of these two gases higher than 298 K?

SAQ 3

Using p_c, V_c and T_c values of methane from Table 9.1, calculate the value of Z_c. Does methane obey van der Waals equation at the critical point?

9.6 LAW OF CORRSEPONDING STATES

The pressure, volume and temperature of a gas when expressed in terms of the critical constants are called reduced quantities. Mathematically, the reduced quantities are defined as follows:

Reduced pressure $= \pi = \frac{p}{p_c}$ or $p = \pi p_c$ …(9.32)

Reduced volume $= \phi = \frac{V_m}{V_c}$ or $V_m = \phi V_c$ …(9.33)

Reduced temperature $= \theta = \frac{T}{T_c}$ or $T = \theta T_c$ …(9.34)

These quantities were introduced by van der Waals in the hope that one single equation could be obtained which is valid for all substances. Using Eqs. 9.7, 9.32, 9.33 and 9.34 we obtain,

$$\left(\pi p_c + \frac{a}{\varphi^2 V_c^2}\right)(\varphi V_c - b) = R\theta T_c \quad \ldots(9.35)$$

Now substituting the values of p_c, V_c and T_c from Eqs. 9.25, 9.26 and 9.28,

$$\left(\pi \,.\, \frac{a}{27b^2} + \frac{a}{\varphi^2 9b^2}\right)(3\varphi b - b) = R\theta \frac{8a}{27Rb} \quad \ldots(9.36)$$

$$\frac{a}{27b^2}\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1)b = \frac{8\theta a}{27b} \quad \ldots(9.37)$$

Dividing both sides by $\frac{a}{27b}$,

$$\left(\pi + \frac{3}{\varphi^2}\right)(3\varphi - 1) = 8\theta \quad \ldots(9.38)$$

This is known as the **law of the corresponding states** or **the reduced equation of state**. It should be valid for all gases. In general, if any two gases have the same values for any two of the reduced quantities (π, ϕ and θ), then the values of the third quantity will also be equal and the two substances are said to be in the corresponding states. This is also called the **principle of corresponding states**. It tells us that if the isotherms are plotted in terms of reduced quantities (π and ϕ at constant θ), the same curves should be obtained for all gases. Using Eq. 9.38, work out the following simple question.

SAQ 4

Using the values of p_c and V_c for methane from Table 9.1, calculate its reduced temperature if it occupies 5.000×10^{-2} m^3 volume at 3.328×10^5 Pa. [Hint: First find out π and ϕ and then evaluate θ using Eq. 9.38]

9.7 LIQUEFACTION OF GASES

The critical phenomena and the knowledge of the critical constants have a practical use in the liquefaction of gases. The liquefaction of air is important in the manufacture of liquid nitrogen and oxygen which are both important industrial chemicals. The liquefied petroleum gas (mixture of propane and butane) is used as a domestic fuel. Liquid helium and nitrogen are particularly important for making the materials superconducting. Easily liquefiable gases such as ammonia and dichlorodifluoromethane (Freon) are used in refrigeration and air conditioning.

The superconducting materials conduct electricity without offering any resistance. There is no energy loss as heat during such electric conduction. The superconducting materials are extremely useful in power transmission, computers, the development of nuclear fusion power and superfast trains, disease diagnosis and so on.

Let us now study some methods of liquefaction of gases. It has already been clarified that a gas cannot be liquefied above its critical temperature. Many substances like water, ethyl alcohol etc., have high critical temperatures and hence exist as liquids even at room temperature. Others like ammonia, sulphur dioxide etc., under ordinary conditions are above their critical temperature but can be easily liquefied by cooling using freezing mixtures under moderate pressure. This implies that the freezing mixture lowers the temperature of a substance below its critical temperature and the moderate pressure is then sufficient to liquefy the gas. On the other hand, there are many gases like oxygen, nitrogen, hydrogen and helium whose critical temperatures are much lower. Special methods are adopted to cool these gases below their critical temperature. Let us study the principles of two of the common methods of liquefaction.

9.7.1 Linde's Method

This method is based on the principle known as Joule-Thomson effect. According to this principle, when a gas under high pressure is allowed to expand into a region of low pressure, its temperature falls. The gas does not do any external work but the kinetic energy and hence, the temperature of the gas is lowered because of the work done in separating the molecules against their attractive intermolecular forces. A precaution is required in this process. To have a cooling effect, a gas is to be brought below a characteristic temperature, known as **inversion temperature**, before allowing it to expand. If the temperature of the gas is above its inversion temperature, Joule-Thomson expansion results in heating. A schematic diagram of the equipment used in Linde's method is shown in Fig. 9.6.

The inversion temperature (T_i) of a gas is related to its van der Waals constants as per the following equation.

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

For hydrogen gas, the inversion temperature calculated as per this equation is 223.8 K.

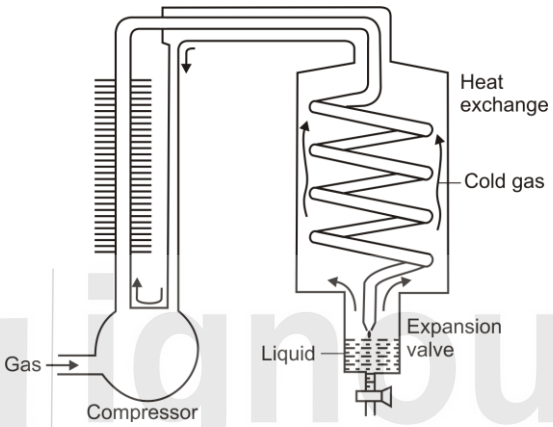


Fig. 9.6: Schematic diagram for the liquefaction of gases using Linde's method.

The gas at a temperature lower than its inversion temperature is compressed using a compressor. This gas is then allowed to expand through a valve which, results in its cooling. The cold gas is used in cooling the high pressure gas in the heat exchanger and is recirculated through the compressor. It gets cooled still further, as it expands. The cycle continues till the liquefied gas drops from the throttle.

9.7.2 Claude's Method

Claude's method (Fig. 9.7), is more efficient than Linde's method. The compressed gas in the insulated vessel (i.e., under adiabatic conditions) is partly used to do work against a piston in a cylinder and partly expanded through a valve.

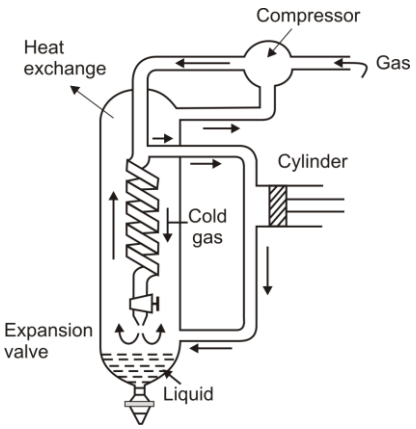


Fig. 9.7: Schematic diagram for the liquefaction of gases using Claude's method.

You would recall from BCHCT-133 course that If the container used in a process does not allow heat transfer with the surroundings, it is called adiabatic. The energy required for adiabatic expansion is supplied by the gas molecules. The energy loss of the gas molecules results in their cooling. The cooled gas obtained by adiabatic expansion is used for cooling the incoming gas in the heat exchanger. The process is repeated till the gas is liquefied.

Using the principles of Linde's method, answer the following SAQ.

SAQ 5

If hydrogen gas is allowed to undergo Joule-Thomson expansion at room temperature, it is heated but not cooled. Explain.

9.8 VISCOSITY OF GASES

Viscosity is a property associated with fluid flow. It refers to the internal friction between layers of fluid as they pass over each other when moving with different velocities. It is exhibited by gases as well as liquids however; it is easier to understand by taking the example of a flowing liquid. Let us consider the laminar flow of a liquid through a horizontal cylindrical pipe as shown in Fig. 9.8.

Laminar flow refers to the smooth flow of a fluid (liquid or gas) in layers such that each layer moves past the adjacent layers smoothly with little or no mixing.

Fig. 9.8: Schematic representation of laminar flow of a liquid through a horizontal cylindrical pipe.

When the flow of the liquid is steady (i.e., streamline) its layer in immediate contact with the wall (fixed surface) is stationary and the velocity of layers increases with the distance from the fixed surface as indicated by the length of arrows. That is, there is **velocity gradient** between the moving layers. If we take any of the layers, the layer immediately above (moving faster) will try to accelerate it. On the other hand, the layer immediately below it will try to retard it. The effects of acceleration and deceleration arise due to the intermolecular interaction between the molecules of the adjacent layers. Thus, there is a tendency to destroy the relative motion as if there is a tangential force dragging backwards. Alternatively, we can say that a tangential force is required to maintain the flow. This force is called the viscous force. Newton showed that this force of internal friction '*f*' is directly proportional to the area of contact 'A' and the velocity gradient, $\frac{du}{dx}$.

Hence, $f = -\eta A \frac{du}{dx}$ … (9.39)

The negative sign is indicative of the fact that the force is opposite to the direction of flow. The proportionality constant η is called the **coefficient of**

viscosity. The equation (9.39) is applicable for gases as well as for liquids, provided the flow is laminar and steady and not turbulent and disorderly.

When, A= 1 and $\frac{du}{dx} = 1$; $\eta = -f$ … (9.40)

Hence, we can define the coefficient of viscosity as the tangential force that is required to maintain unit difference of velocity between two layers unit distance apart and having unit area of contact. Alternatively, we can say that coefficient of viscosity refers to the tangential force that must be applied to maintain a velocity difference of unity between two adjacent layers that are a unit distance apart and have a unit area of contact. The SI unit of coefficient of viscosity is N m^{-2}s.

Viscosity of Gases

When we consider flow of a gas through a cylindrical tube as discussed above, here again the layer next to the wall of the tube will be stationary and the velocity of each subsequent layers would increase. However, since gases are compressible fluids, the mechanism of retardation of adjacent layers is different. Apart from the flow of the gas due to an external pressure, the molecules are all in random thermal motion. As a consequence, an exchange of molecules occurs between the layers.

Here, the molecules of a faster moving layer pass on to the slower layer and transport (transfer) their momentum to it and vice-versa. Now when a molecule passes from a lower layer to the upper layer it will carry to the latter a momentum less than the average momentum possessed by the molecules in the upper layer. On the other hand, if a molecule passes from the upper to the lower layer, the lower layer will obtain a momentum higher than the average momentum possessed by molecules of the lower layer. As a result, the average velocities of the molecules of the upper layer will decrease and those of the lower layer will increase. In other words, we can say that the transport of momentum across different layers counteracts the relative velocities of the flowing gas.

Thus, we see that in cases of gases there is a transfer of momentum amongst the neighbouring layers, and it is this transfer of momentum that is responsible for the viscous drag in gases. You may recall that in case of liquids, the intermolecular interactions between the molecules of neighbouring layers were responsible for the viscous drag.

9.8.1 Relation Between Coefficient of Viscosity of Gas and Mean Free Path

As you have learnt above that the viscosity (viscous drag) of gases is due the transport of momentum across neighbouring layers. Such a transport can be understood by introducing the concept of **flux**. It is defined as the quantity transferred through a given area in a given amount of time divided by the area and the duration of time interval. In other words, it can be seen as the quantity transferred through a unit area in unit time. It occurs when there is a gradient

of the property in the system, and it acts in direction opposite to the gradient. It is denoted as J and is mathematically defined as,

$$J_x = -\alpha \frac{d(property)}{dx} \quad \ldots (9.41)$$

Here, J_x is the flux expressed in units of property; the derivative term gives the gradient of the property of interest and α is the coefficient of proportionality. To derive an expression for coefficient of viscosity of a gas we consider the gas in a laminar flow as shown in Fig. 9.9.

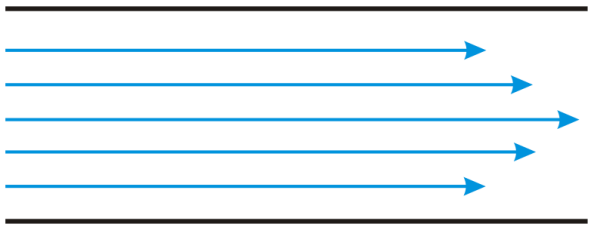


Fig. 9.9: Schematic representation of laminar flow of a gas.

Such a gas can be visualised as a series of layers of varying velocities as indicated by the arrows. This means that there is a velocity gradient. Now since all the molecules of gas have same mass, the velocity gradient can be seen as the gradient of linear momentum (p) along z-direction i.e., $\left(\frac{dp}{dz}\right)$.

Let us consider three parallel layers of gas each separated by mean free path, λ from the neighbouring layer, Fig. 9.10. These layers are located at z = -λ, 0 and λ; the layer I is the slowest whereas the layer III is the fastest as indicated by the length of the vertical arrows. The layer II is called the flux layer.

The mean free path is the distance a particle travels on an average between collisions.

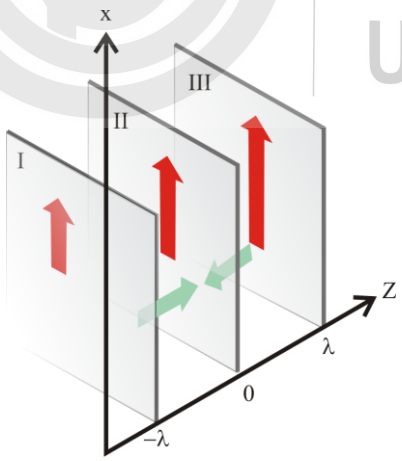


Fig. 9.10: Set up used to calculate flux of linear momentum.

The linear momentum of the three layers would be as

Layer I : $$p(-\lambda) = p(0) - \lambda\left(\frac{dp}{dz}\right)_{z=0} \quad \ldots (9.42)$$

Layer II: $$p(0) = p(0) \quad \ldots (9.43)$$

Layer III: $$p(\lambda) = p(0) + \lambda\left(\frac{dp}{dz}\right)_{z=0} \quad \ldots (9.44)$$

The gas particles will move to the flux plane (layer II) from layer I and III and transfer their momentum to it. The transfer of linear momentum occurs by a particle from one momentum layer colliding with the flux plane and thereby transferring its momentum to the adjacent layer. The particles from layer III will bring larger momentum whereas those from layer I will carry lesser momentum. As a consequence, there will be a net flux of momentum in the direction opposite to that of the gradient i.e., from layer III to layer II. The magnitude of this can be is determined by calculating the flow of particles per unit time through the flux plane located at z =0 and having area *A*.

As we have taken layers that are separated by a distance equal to the mean free path, only those molecules will reach layer II which have made their last collision at a distance λ from it. Flux in momentum from layer III to layer II will be given by the following expression

$$J_{\lambda,0} = -\frac{1}{4}\bar{u}n_0 p(\lambda) = -\frac{1}{4}\bar{u}n_0 \left[p(0) + \lambda\left(\frac{dp}{dz}\right)_{z=0} \right] \quad \ldots(9.45)$$

Where, $\bar{u}$ is the average velocity of the molecules and n_0 is the number density. The flux in momentum from layer I to layer II will be given by the following expression

$$J_{-\lambda,0} = -\frac{1}{4}\bar{u}n_0 (-\lambda) = -\frac{1}{4}\bar{u}n_0 \left[p(0) - \lambda\left(\frac{dp}{dz}\right)_{z=0} \right] \quad \ldots(9.46)$$

Thus, the net flux of momentum to layer II will be

$$J_{Total} = J_{\lambda,0} - J_{-\lambda,0}$$
$$= -\frac{1}{4}\bar{u}n_0 \left[p(0) + \lambda\left(\frac{dp}{dz}\right)_{z=0} \right] + \frac{1}{4}\bar{u}n_0 \left[p(0) - \lambda\left(\frac{dp}{dz}\right)_{z=0} \right] \quad \ldots(9.47)$$

$$J_{Total} = -\frac{1}{4}\bar{u}n_0 \left(2\lambda\left(\frac{dp}{dz}\right)_{z=0} \right) \quad \ldots(9.48)$$

$$J_{Total} = -\frac{1}{2}\bar{u}n_0\lambda\left(\frac{d(mu_x)}{dz}\right)_{z=0} \quad \ldots(9.49)$$

$$J_{Total} = -\frac{1}{2}\bar{u}n_0\lambda m\left(\frac{du_x)}{dz}\right)_{z=0} \quad \ldots(9.50)$$

Applying the correction term (2/3) to account for orientation averaging of the particle trajectories we get the final expression for the total flux of linear momentum as

$$J_{Total} = -\frac{1}{3}\bar{u}n_0\lambda m\left(\frac{(du_x)}{dz}\right)_{z=0} \quad \ldots(9.51)$$

Since, the momentum transferred in unit time is equal to force, we can write

$$f_x = -\frac{1}{3}\bar{u}n_0\lambda m\left(\frac{du_x)}{dz}\right)_{z=0} \quad \ldots(9.52)$$

Let us recall Eq. (9.39)

$$f = -\eta A\frac{du}{dx} \quad \ldots (9.39)$$

For unit area, it becomes

$$f = -\eta\frac{du}{dx} \quad \ldots(9.53)$$

On comparison of Eq. (9.53) with Eq. (9.52) we get

$$\eta = \frac{1}{3}\bar{u}n_0\lambda m = \frac{1}{3}\rho_g\bar{u}\lambda \quad \ldots(9.54)$$

Where,

$n_0 m = \rho_g$

the density of the gas

This is the desired expression for the viscosity coefficient of a gas under laminar flow.

Effect of pressure and temperature on viscosity of gases

We expect that if we increase the pressure on the gas, its resistance to flow and hence the viscosity would increase. However, the viscosity of the gas is independent of the pressure. Let us demonstrate it mathematically. Let us substitute the expressions for average velocity and the mean free path in the Eq. (9.54). we get

$$\eta = \frac{1}{3}mn_0\sqrt{\frac{8kT}{\pi m}}\left(\frac{1}{\sqrt{2}\pi d^2\rho}\right) \quad \ldots(9.55)$$

Simplifying we get,

$$\eta = \frac{2\sqrt{mkT}}{3\pi^{3/2}d^2} = \frac{2\sqrt{MRT}}{3\pi^{3/2}N_A d^2} \quad \ldots(9.56)$$

You may note that there is no pressure term in this expression. Hence, we can say that the viscosity of gas is independent of pressure. This has also been confirmed experimentally. As regards temperature, according to Eq. (9.56), viscosity of gas is directly proportional to $T^{1/2}$. However, experimentally it has been observed that the viscosity of gas depends on slightly higher power (0.7-0.8) of temperature.

Let us sum up what have we discussed in this unit. However, before that answer the following simple question to assess your understanding of viscosity.

SAQ 6

What is the basis of frictional drag or viscosity of i) liquids and, ii) gases?

9.9 SUMMARY

In this unit, we have discussed the behaviour of real gases. In the beginning of the unit we established the deviation of real gases from ideal behaviour in terms of the variation of compressibility factor of gases at different pressures

and temperatures. These deviations from ideal gas behaviour have been explained in terms of intermolecular forces and finite volume of the molecules. Accordingly, volume and pressure corrections were applied to ideal gas equation to obtain van der Waals equation. Then we discussed about the critical phenomenon and in this context we defined critical constants. Their relationships with van der Waals parameters have also been established. The principle of corresponding states has been stated and explained. The necessary conditions for liquefaction of gases have also been discussed and the principles involved in two common methods for liquefaction of gases are described.

Towards the end of the unit, we took up viscosity of gases and derived a relationship between the coefficient of viscosity of gases and the mean free path. The effect of temperature and pressure on the viscosity of gases have also been discussed briefly.

9.10 TERMINAL QUESTIONS

1. Using the van der Waals parameters of nitrogen given in Table 9.1, estimate its critical constants and compare with the actual values given in Table 9.1.
2. What is the pressure change if two moles of steam at 5.000×10^2 K occupying 0.0300 m^3 of volume is heated upto 1.000×10^3 K at constant volume. Assume that steam behaves as a van der Waals gas.

   Given: a = 0.5536 Pa m^6 mol^{-2} and b = 3.049×10^{-5} m^3 mol^{-1}
3. Which of the substances listed in Table 9.1 can be liquefied at 298 K?
4. State the principle of corresponding states.
5. Why is the liquefaction of gases easier at low temperatures and high pressures?
6. A vessel of 1.000×10^{-3} m^3 volume contains 0.0180 kg of argon at 300.0 K. Calculate its pressure using ideal gas equation and van der Waals equations. Use Table 9.1.
7. Calculate the reduced pressure and reduced temperature for oxygen gas at 273.2 K and 1.013×10^5 Pa. Use Table 9.1.
8. Define coefficient of viscosity and give its SI units.

9.11 ANSWERS

Self-Assessment Questions

1. As van der Waals gas:

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Substituting the values and solving we get

$p = 9.898 \times 10^4$ Pa

As an ideal gas: $p = \dfrac{nRT}{V}$

Substituting the values and solving we get

$p = 9.917 \times 10^4$ Pa.

Thus, the values of pressure calculated from van der Waals equation and ideal gas equation are slightly different.

2. The liquefied petroleum gas is in the liquid state inside the cylinder, hence, the critical temperature of propane and butane must be higher than 298 K. (Their critical temperatures are 370 and 425 K, respectively).

3. Using p_c, V_c and T_c from Table 9.1, we get

$Z_c = 0.2892$

Substituting the expressions for p_c, V_c and T_c in terms of van der Waals constants in Eq. 9.29, we get

$Z_c = 0.375$

Hence, at the critical point, methane deviates from van der Waals equation.

4. $\pi = \dfrac{p}{p_c} = 7.171 \times 10^{-2}$

$\phi = \dfrac{V}{V_c} = 50.51$

Substituting these quantities in Eq. 9.38, θ is found to be equal to 1.371.

5. The inversion temperature of hydrogen is much lower than room temperature. Hence, Joule-Thomson expansion at room temperature causes heating.

6. The basis of frictional drag or viscosity are as under

   i) liquids: Intermolecular interactions

   ii) gases: Transport of momentum

Terminal Questions

1. Critical constant calculated as per Eqs. 9.25, 9.26 and 9.28 are:

$V_c = 1.174 \times 10^{-4}$ m^3 mol^{-1}

$p_c = 3.400 \times 10^6$ Pa

$T_c = 128.2$ K

2. Using van der Waals equation, the pressure values at 5.000×10^2 K and 1.000×10^3 K are 2.752×10^5Pa and 5.530×10^5 Pa. The pressure change is

   $(5.530 - 2.752) \times 10^5$Pa = 2.778×10^5Pa

3. CO_2, H_2O and NH_3 can be liquefied at 298 K since their critical temperatures are higher than 298 K.

4. According to the principle of corresponding states if any two gases have the same values for any two of the reduced quantities (π, ϕ and θ), then the values of the third reduced quantity will also be equal. In such a case the two substances are said to be in the corresponding states.

5. At sufficiently low temperatures, thermal motions are reduced, and do not disturb attractive forces between the molecules. Hence, the molecules are drawn together to form a liquid at low temperatures. Liquefaction is easier at high pressure when distances between molecules are smaller on the average and hence, the attractive interactions are higher.

6. According to van der Waals equation, pressure calculated is 2.440×10^6Pa, whereas as per ideal gas equation, it is 2.494×10^6 Pa.

7. θ = 1.765; π = 1.996×10^{-2}.

8. We can define the coefficient of viscosity as the tangential force that is required to maintain unit difference of velocity between two layers unit distance apart.

   The SI unit of coefficient of viscosity is N m^{-2}s.

UNIT 10

LIQUIDS

Structure

10.1 INTRODUCTION

In Units 8 and 9, we discussed the characteristics of ideal gases. We assumed that there is no attractive or repulsive interaction between the individual molecules. In the previous unit, this treatment was modified to account for the behavior of real gases at low-temperatures and high pressures and to explain the liquefaction of gases. Finite size of the gaseous molecules and their weak interaction were recognized. In Units 11 and 12, we are going to study the strong interactions in a solid crystal and the orderly arrangement of particles in it. In this unit, we will discuss the characteristics of liquids in contrast to those of gases and solids. Liquids are quite complex to understand since there is neither completely random arrangement (as seen in gases) nor a completely ordered arrangement of atoms or molecules (as seen in solids). Liquid state is a state of matter intermediate between that of crystalline solids and gases.

After that, we will describe the features of a model proposed for the structure of liquids. Then, we shall explain the correlation between the intermolecular forces and the properties of liquids such as surface tension and viscosity.

Finally, we will discuss the effect of temperature on surface tension and coefficient of viscosity of a liquid.

Expected Learning Outcomes

After studying this unit, the student should be able to:

- compare liquids with gases and solids;
- discuss different types of intermolecular forces;
- explain the model of structure of liquids;
- state the significance of surface tension and describe its determination;
- state the significance of viscosity of liquids and the determination of coefficient of viscosity; and
- understand the effect of temperature on the surface tension and viscosity of a liquid.

10.2 COMPARISON OF LIQUIDS WITH GASES AND SOLIDS

When a solid is heated or a gas is cooled under certain conditions, we can obtain liquid. Therefore, liquid state is in between solid and gaseous states. The crystalline solids have strong intermolecular forces which lead to orderly arrangement in them. As a result, a solid has definite shape whereas the liquids take the shape of their container. In contrast to this, the molecules in a gas are free to move randomly and have a disorderly arrangement. The gases can expand or contract to conform to the volume of the vessel. Hence, the gases have no definite shape or volume. The particles in a liquid are free to move from one point to another. In this respect, it resembles a gas. The ability of a liquid to flow enables it to assume the shape of its container. Yet it never expands or contracts to fill the container and thus resembles a solid. So, properties of liquids are those in between solids and gases. Let us now examine the structural aspects of liquids.

10.3 INTERMOLECULAR FORCES

In this section, we are going to discuss intermolecular forces which are the attractive forces that act between a molecule and another molecule. The intermolecular forces are also responsible for the conversion of gases into liquids and solids. Intermolecular forces are electrostatic in origin, i.e. they involve positive-negative interactions. So you see that there is no sharing of electron pairs between atoms and so, in these cases, the intermolecular forces are weaker than covalent bonds. Now let us discuss the various types of forces that operate in liquids.

10.3.1 van der Waals Forces

The van der Waals forces are the attractive intermolecular forces. The following are the different types of van der Waals forces:

i) Dipole-dipole forces (Interactions between molecules with permanent dipoles)

ii) Dipole-induced dipole forces (Interactions between polar and nonpolar molecules)

iii) Dispersion forces or London forces (Interactions between nonpolar molecules)

Hydrogen bonding is also a very strong type of dipole-dipole interaction. Since hydrogen bonding occurs in very few elements so it is dealt separately in sub-section 10.3.2. Let us discuss the different types of van der Waals forces one by one.

Van der Waals forces are named after the Dutch physicist Johannes Diderik van der Waals, who in 1873 first postulated the intermolecular forces in developing a theory to account for the properties of real gases.

Dipole-dipole forces

Polar molecules (which maybe of same or different kind), can attract each other electrostatically. The partial positive charge (δ^+) of one such molecule (dipole) is attracted to the partial negative charge(δ^-) of another as shown in Fig.10.1. Such an attraction is called dipole-dipole interaction. Dipole-dipole forces involve partial charges and so they are much weaker than ionic bonds. In the liquid state, although molecules are in continuous motion, they tend to align themselves so that, on the average, the intermolecular attractions are maximum.

Ion and dipole experience attractive force which is known as ion-dipole force and not van der Waals force.

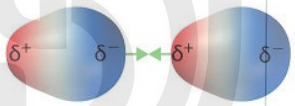


Fig. 10.1: Dipole–Dipole Interactions

The interaction energy between two polar molecules separated by a distance *r* is found to be

- directly proportional to the square of the product of the dipole moments of the two molecules
- inversely proportional to temperature
- inversely proportional to r^6.

Dipole-Induced dipole forces

The dipole-dipole interaction can explain the attractive forces between polar molecules at ordinary temperatures whereas at high temperatures it cannot. It was thought that induced dipole interactions must also be important. A polar molecule can induce a dipole moment in a neighbouring polarizable atom or molecule. Let us explain, the terms ‘polarizable’ and ‘polarizablility’. An atom or molecule is said to be polarizable, if its electron cloud can be distorted. The ability of a species to undergo electron distortion is described in terms of polarizability. The electron charge cloud of a larger atom (one with higher atomic number) can be easily distorted due to the following reasons:

- the electrons are more in number

- the influence of the nucleus is less due to longer distance.

So a larger atom has a higher polarizability than a smaller atom. For example, argon has higher polarizability than neon, ethane is more polarizable than methane, propane is more polarizable than ethane, and so on.

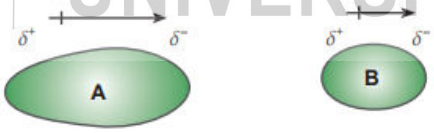
Just like a permanent magnet when brought near a magnetic substance can induce magnetism in it, a polar molecule (e.g. water) can induce, or create a dipole on molecules that do not have a permanent dipole. The dipole-induced dipole interaction between a polar molecule and a neighbouring polarizable molecule (in which dipole is induced) causes a lowering of energy. That is, such an attractive interaction adds to the stability. The interaction energy between a dipole and an induced dipole separated by a distance *r* has been estimated to be

- directly proportional to the square of the dipole moment of the polar molecule
- directly proportional to the polarizability of the molecule (in which dipole is induced),
- inversely proportional to the sixth power of *r*.

Unlike dipole-dipole interaction, dipole-induced dipole interaction is independent of temperature.

A typical example of such interaction is observed between a polar water molecule and a nonpolar O_2 molecule. Also it is observed between a polar ammonia molecule and a nonpolar benzene molecule. Let us understand this with the help of Fig. 10.2, where a polar molecule A approaches a nonpolar molecule B.

The dispersion force is one of the effects responsible for van der Waals attraction in gases.



Permanent dipole (a polar molecule) Induced dipole in a nonpolar molecule)

Fig. 10.2: Dipole-Induced dipole forces

Both the dipole-dipole interactions and dipole-induced dipole interactions are inversely proportional to the distance but the latter is of much smaller magnitude. So you see, this is the reason why polar and nonpolar liquids are often immiscible.

London or Dispersion forces

The two interactions mentioned earlier cannot explain the liquefaction of gases like hydrogen, oxygen, chlorine, helium and argon – which are all nonpolar. London gave an acceptable quantitative explanation for the attractive forces existing between nonpolar molecules and hence such forces are called London forces. At a given instant in time, the distribution of electrons around an individual atom may not be perfectly symmetrical (the electron cloud may be on one side of the nucleus). This atom will have an instantaneous polarity

(temporary dipolar arrangement of charges) which distorts a neighbouring atom due to the electrostatic attractions or the repulsions of their electron clouds. Look at Fig. 10.3, where origin of the London forces are explained with the help of the example of helium atoms.

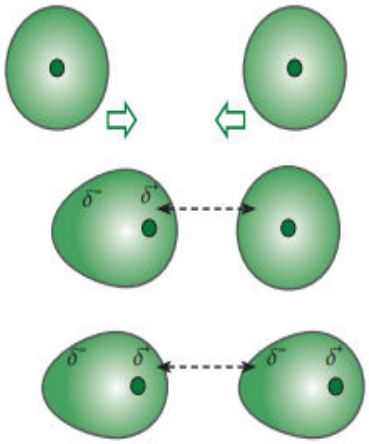


Fig. 10.3: London or Dispersion forces

The resultant instantaneous dipole-induced dipole attraction is both weak and short-lived. But this can be very significant for large atoms (or molecules) which have high polarisablility. For these interactions to become strong enough to produce a solid or a liquid, thermal motions must be decreased. This explains why noble gas elements have low liquefaction temperatures. The interactions explained above are also responsible for the liquefaction of nonpolar molecules like H_2, CH_4, CCl_4 and CO_2.

The interaction energy between two noble gas atoms or two nonpolar molecules separated by a distance *r* is

- directly proportional to the product of the polarizabilities of the two species
- inversely proportional to the sixth power of *r*.

10.3.2 Hydrogen Bonding

There are several specific types of interactions encountered between various types of molecules. Of these, hydrogen bonding is very significant which we shall study here in detail. The high boiling point of ammonia (NH_3), water (H_2O) and hydrogen fluoride (HF) are resulted from relatively strong dipole-dipole interactions called hydrogen bonding. When a hydrogen atom is covalently bonded to a small, strongly electronegative atom, such as oxygen, fluorine or nitrogen, the bond is much polar. Such a hydrogen atom would still possess large affinity for nonbonding electrons present on other oxygen, nitrogen or fluorine atom. The latter atom could be part of the same molecule or a neighbouring molecule. The strong interaction that results is called a hydrogen bond. It is a special type of dipole-dipole attraction. Hydrogen bonds are typically shown as dotted lines (……) between the atoms involved.

In Fig. 10.4 a is shown hydrogen bonding arising between hydrogen atom (positive end of the dipole) of one water molecule and the oxygen atom (negative end of the dipole) of the other. In Fig. 10.4 b is shown hydrogen bonding in hydrogen fluoride.

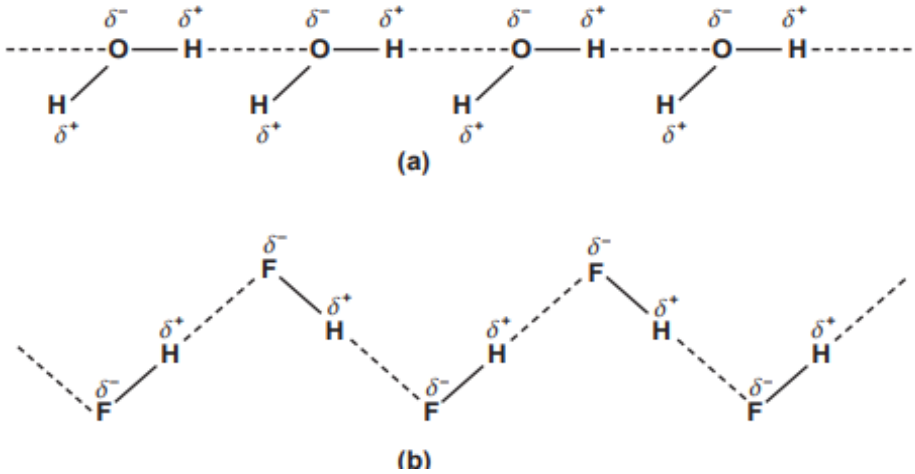


Fig. 10.4: Hydrogen bonding: a) in water b) in hydrogen fluoride (shown as dashed lines). (δ^+, δ^- shows the partial charges on hydrogen and oxygen or fluorine)

Before going to the next section try the following SAQ.

SAQ 1

Compare the dipole-dipole forces and London forces giving suitable examples.

10.3.3 The Total Attractive Interaction

Here we consider the molecules that are unable to participate in hydrogen bond formation. The total attractive interaction energy between rotating molecules is then the sum of the applicable van der Waals contributions discussed in section 10.3.1.

(Only the dispersion interaction contributes if both molecules are nonpolar.) In a fluid phase, all three contributions to the potential energy vary as the inverse sixth power of the separation of the molecules. So we may write that the total attractive interaction is

$$V = -\frac{q}{r^6} \qquad \text{.....(10.1)}$$

where q is a coefficient that depends on the identity of the molecules.

So we may express attractive interactions between molecules as in Eq.10.1, but this equation has only limited validity. We must remember the assumptions that we have made. The dipolar interactions of various kinds

have only been taken as they have the longest range and are the most dominant when average separation of the molecules is large. But, whenever we take total interactions, the quadrupolar and higher-order multiple interactions must also be taken into consideration, especially if the molecules do not have permanent electric dipole moments. Second assumption is that the molecules can rotate reasonably freely. Here we must understand that it is not true in most solids, and in rigid media where the dipole–dipole interaction is proportional to $1/r^3$.

10.3.4 Effect of Molecular Interactions on Physical Properties

Intermolecular forces have significant effect on the physical properties such as melting point, boiling point, solubility, surface tension, viscosity, density and so on. Here we will consider the effect of intermolecular forces on melting point, boiling point and solubility.

The unit of dipole moment is C m. C is coulomb, m is meter

i) Polar molecules have higher melting and boiling points than the nonpolar molecules of similar molecular size. It is so since in the polar molecules, in addition to London forces, dipole-dipole interactions are also present. In general, larger the dipole moment, the higher the melting and boiling points. See some illustrative data in Table 10.1.

Generally Relative molecular mass is known as molecular weight.

Table 10.1: Effect of Dipole-Dipole Interaction on Melting and Boiling Points

Compound	Relative molecular mass	Dipole moment/ 10^{-30} C m	Melting point/K	Boiling point/K
C_2H_6	30.1	0	89.7	184.4
CH_3F	34.0	6.17	131.2	194.6
SiH_4	32.1	0	88	161.2
PH_3	34.0	1.93	140	185.3
H_2S	34.1	3.24	187.5	212.3

ii) Among the noble gases, the boiling point increases with atomic number (Table 10.2). As explained earlier, the London forces are more in large atoms due to higher polarizability.

iii) Among a series of similar nonpolar molecules such as hydrocarbons, boiling point increases with the molecular size (Table 10.2). Again, the reason is that a larger molecule has higher polarizability and increased London forces.

iv) Among the hydrides of 15, 16 and 17 group elements in the periodic table, those having the highest boiling points are NH_3, H_2O and HF, respectively. This is due to the strong hydrogen bonding in these three compounds.

Table 10.2: Effect of London Forces on the Boiling Points

Noble gas	Atomic Number	Boiling point/K
He	2	4.1
Ne	10	27.0
Ar	18	87.3
Kr	36	120.7
Compound	**Relative molecular mass**	**Boiling point/K**
CH_4	16	111.5
C_2H_6	30	184.4
C_3H_8	44	231
C_4H_{10} (Butane)	58	272.4

v) There is a striking contrast in the boiling points of the isomeric compounds, ethanol (351 K) and dimethyl ether (249 K). The hydrogen bonding between the molecules of ethanol (Fig. 10.5) contributes to a much higher boiling point. On the other hand, the molecules of dimethyl ether are held together only by weaker dipole-dipole interaction (Fig. 10.6).

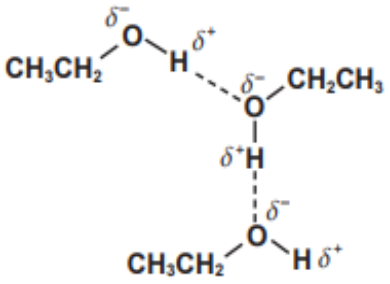


Fig. 10.5: Hydrogen bonding in ethanol

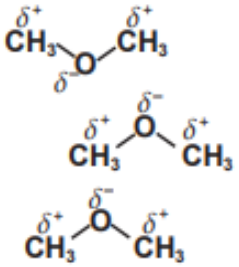


Fig. 10.6: Dipole-dipole interaction in dimethyl ether

vi) London forces also depend on the molecular geometry. For example, among the isomeric hydrocarbons, straight chain isomer has higher boiling point than the branched chain isomer. Let us illustrate this with a specific example. The straight chain isomer, butane, boils at 272.4 K whereas the branched chain isomer, 2-methylpropane, boils at 263 K. The molecules of 2-methylpropane are nearly spherical whereas those of butane are distorted rod-like (Fig. 10.7a and b).

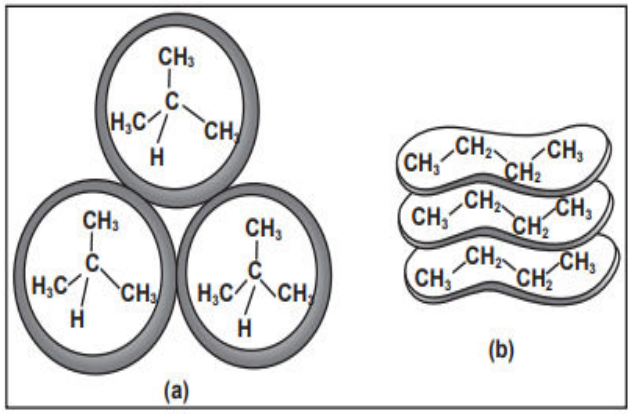


Fig. 10.7: (a) Interactions among nearly spherical molecules of 2-methylpropane (b) Interactions among distorted rod-like molecules of butane.

Hence the molecules of butane have a larger surface area for interaction with each other than those of 2-methylpropane. The stronger interactions in butane are reflected in its higher boiling point.

Care must be exercised in comparing the physical properties of molecules differing sharply in more than one way, viz., relative molecular mass, polarity and geometrical shape. Based on the principles developed above, answer the following SAQ.

SAQ 2

The melting points of Cl_2, Br_2 and I_2 are 172 K, 266 K and 386 K. Explain this variation.

10.4 STRUCTURE OF LIQUIDS

The particles in a liquid are not as much orderly as in a solid; also not as much disorderly as in a gas. To establish this, we cite the following three pieces of evidence:

Volume Change during Fusion and Vaporization

Fusion is the process in which a pure solid melts to give a liquid at a sharp temperature. It is generally seen that during fusion, volume increases by 10%. So that means that a substance to a much extent retains its orderliness during fusion. But during vaporization, which is the conversion of a liquid into vapour at its boiling point, the volume increases 100-1000 fold, indicating that the particles are changed into a more disorganized state.

Molar Enthalpy of Fusion and Vaporization

The amount of heat required at constant pressure to convert one mole of a solid into liquid at its melting point is called molar enthalpy of fusion ($\Delta_{fus}H^{\circ}$). Similarly, the amount of heat required at constant pressure to convert one mole of a liquid into its vapour at its boiling point is called the molar enthalpy of vaporization ($\Delta_{vap}H^{\circ}$). The values of $\Delta_{fus}H^{\circ}$, $\Delta_{vap}H^{\circ}$ and boiling point (BP) are given in Table 10.3 for some substances. It is seen that $\Delta_{vap}H^{\circ}$ is larger than $\Delta_{fus}H^{\circ}$ for all the substances. It requires more heat to convert a liquid into vapour than to convert a solid into a liquid. It seems reasonable to assume that a large enthalpy of vaporization during change of state is associated with a large increase in disorder. On this assumption, we can think that a liquid has considerable measure of orderly arrangement as compared to a gas.

The state of a substance under a given temperature and pressure is decided by the intermolecular forces operating in a substance. Fusion, vaporization etc. are dependent upon the external forces (such as pressure) applied on a substance.

Table 10.3: Molar Enthalpies of Fusion ($\Delta_{fus}H^{\circ}$) and Vaporization ($\Delta_{vap}H^{\circ}$) and Boiling Points (BP) of the Substances

Substance	$\Delta_{fus}H^{\circ}$ / kJ mol^{-1}	$\Delta_{vap}H^{\circ}$ / kJ mol^{-1}	BP/K
Methane	1.0	8.2	111.5
Ethane	2.9	14.5	184.4
Propane	3.5	19.0	231
Diethyl ether	7.6	26.9	308
Ethanol	5.1	39.1	351
Water	6.1	40.7	373
Benzene	10.1	31.1	353
Mercury	2.5	29.2	630
Silver	12.2	259	2430
Aluminium	10.9	292	2720

X-Ray Diffraction by Liquids

X-ray diffraction is the scattering of X-rays from a regular array of atoms, molecules or ions.

In the next unit, we shall study that the X-ray diffraction by a solid crystal gives rise to sharp diffraction pattern which is an indication of the orderly arrangement of atoms or ions in the crystal lattice. Gases, on the other hand, do not give rise to diffraction lines with X-rays. This is again due to the random arrangement and movement of molecules in a gas. Liquids do give diffraction patterns with X-rays, although the lines are diffuse (i.e., not quite sharp), which indicates that the order in the arrangement of particles is only partial but not total. Experimental data indicate that the first few neighbours of a particle in a

liquid are at fairly well-defined distances. However, the neighbours farther away are randomly distributed. This means that the arrangement of particles in a liquid exhibits short range order and long-range disorder. The number of nearest neighbours around the particles in different regions of a liquid is not the same. A model for the structure of liquids is shown in Fig. 10.8.

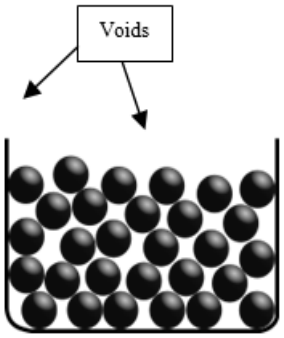


Fig. 10.8: A model for the structure of liquids.

The main aspects of this model of structure of liquids are summarized below:

- The particles in a liquid are fairly close.
- These particles have higher kinetic energy (and hence, speed) compared to those in a solid.
- Because of their speed, the individual particles occupy more space, and a liquid is less dense than the corresponding solid.
- To explain the relative densities of liquids and solids, it is further assumed that there are some voids between the molecules.
- These voids enable the liquid to flow.
- Particle close to one of the voids behaves like a particle in a gas.

Based on the above, answer the following SAQ.

SAQ 3

Liquids are less compressible than gases. State the reason.

In a gravity-free environment, as in the space shuttle in the orbit, the shape of liquid drop is governed by surface tension alone. If gravitational forces were to be absent on earth, the flat surface of water bodies like rivers and oceans would appear as an array of spherical drops.

10.5 SURFACE TENSION

We have already discussed the structure of liquids and now we will study the properties of liquids. Three of the characteristic properties of liquids are:

- Surface Tension
- Capillary action
- Viscosity

These properties are related to the strength of intermolecular forces in liquids. We will now discuss these properties.

10.5.1 Surface Tension

The presence of a surface in a liquid gives rise to the phenomenon of surface tension. Let's see how it arises. In the absence of external forces, liquids form spherical drops spontaneously. This is facilitated by the fact that for a given volume, a sphere has a smaller surface area than any other shape. The fascinating phenomenon is the reason for the spherical shape of water and mercury drops. Let us explain the origin of forces operating to minimize surface area.

The values of surface tension given in Table 10.4 are obtained when the liquids are in contact with their vapours and air. If measurement is made in presence of some other gas instead of air, the values will be different.

A molecule in the interior of a liquid is attracted by all the molecules surrounding it. It is pulled equally in all directions and the net force acting on it is zero. But a molecule at the surface of a liquid is attracted only by molecules below it (Fig. 10.9). It experiences a 'net' downward force.

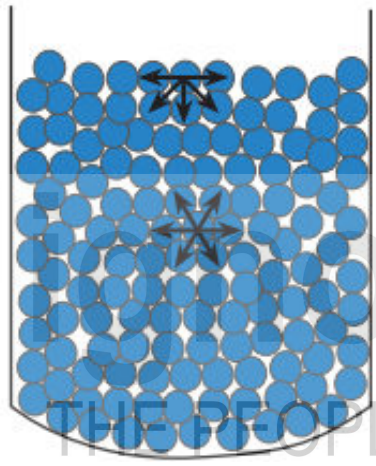


Fig 10.9: Molecules in the bulk and on the surface of liquid being attracted by neighbours.

Therefore, the molecules on the surface of the liquid are drawn inwards trying to minimize the surface area. Because of this tendency of a surface to contract, each point on the surface of the liquid is under pressure like a stretched rubber membrane. The resistance of a liquid to increase its surface area is correlated to its **surface tension**. It is defined as the force per unit length perpendicular to a liquid surface. Corresponding to this definition, SI unit of surface tension is N m^{-1}. It is represented by the Greek letter γ. Increase of temperature increases the thermal motion of the molecules in a liquid; this opposes the effect of intermolecular forces. Thus as temperature is raised, the surface tension decreases.

The values of surface tension of some liquids are given in Table 10.4.

Table 10.4: Values of surface tension (γ) of some liquids at 293 K

Liquid	$10^2 \times \gamma$/N m^{-1}
Water	7.28

Benzene	2.89
Carbon tetrachloride	2.64
Chloroform	2.67
Mercury	46.5

Some of the factors which influence the magnitude of surface tension are given below:

- Molecules having strong hydrogen bonds have high surface tension. The surface tension of water, for example, is about three times higher than that of nonpolar liquids like carbon tetrachloride.
- Metallic bonding also leads to high surface tension. For example, the surface tension of mercury is more than six times that of water.
- The dispersion forces are quite significant in molecules with large atoms and are often more important than dipole-dipole forces. In fact, surface tension of carbon tetrachloride is only slightly less than that of chloroform; the effect of London forces in the former is nearly equal to the combined effect of London and dipole-dipole forces in the latter.

Cohesion is due to attraction between molecules of the liquid, while adhesion is attraction between the molecules of a liquid and the molecules in the wall of the capillary.

Intermolecular forces give rise to **capillary action**. It is the rise of liquids through a capillary (narrow glass) tube (Fig. 10.10a). Two types of forces – **cohesive** and **adhesive** – are responsible for this property. The cohesive forces are the intermolecular forces among the molecules of a liquid. Adhesive forces exist between the liquid molecules and the molecules in the capillary walls. For example, glass contains many oxygen atoms; each oxygen atom (with partial negative charge) attracts (the positive end of) a polar molecule, such as water.

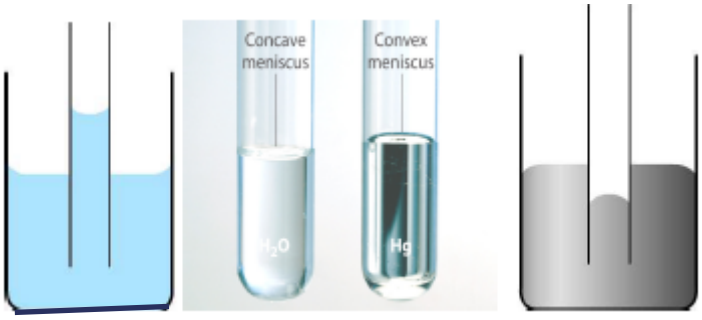
The phenomenon of surface tension is important for understanding chromatography, colloids, catalysis, detergent action of soaps, etc.

Some of the familiar instances of capillary action are:

- Movement of water through the soil.
- Rise of nutrient dissolved water from the roots to the tree top.
- Penetration of water into cement structure.

The adhesive forces enable water to “wet” the glass. The adhesive forces acting upward pull up a water column inside a capillary tube when the latter is in contact with water. The height of the water column inside the capillary tube is such that the adhesive forces acting upwards balance the gravitational force (in the form of weight of water column) acting downwards. The height of the water column inside the capillary tube has been found to be inversely proportional to the radius of the tube. Hence only in tubes of small radius, the capillary rise is meaningful.

The concave shape of the **meniscus** of water in a glass tube indicates that the adhesive forces of water towards the glass are stronger than its cohesive forces. A metallic liquid such as mercury (Fig. 10.10b) shows a lower level in a capillary tube and a convex meniscus. This behaviour is characteristic of a liquid in which the cohesive forces between its molecules are stronger than the adhesive forces between the molecules and glass.



(a) (b)

Fig. 10.10 : (a) A polar liquid such as water rises in a capillary tube – water has concave meniscus in a glass tube; (b) A metallic liquid such as mercury shows a depression of level – mercury has convex meniscus.

10.5.2 Determination of Surface Tension

There are various methods for determining the surface tension of a liquid. The names of such methods are given below:

i) Capillary rise method

ii) Torsion balance method

iii) Maximum bubble pressure method

iv) Stalagmometer method.

Here, we will be discussing the stalagmometer method only because this method you will be using in the determination of the surface tension in Experiment 1 of BCHCL 138. The stalagmometer is used to determine surface tension of liquids. This is shown in Fig. 10.11 and is called Traube's Stalagmometer. It is a simple apparatus and is frequently employed when the values of surface tension of two or more different liquids are to be compared.

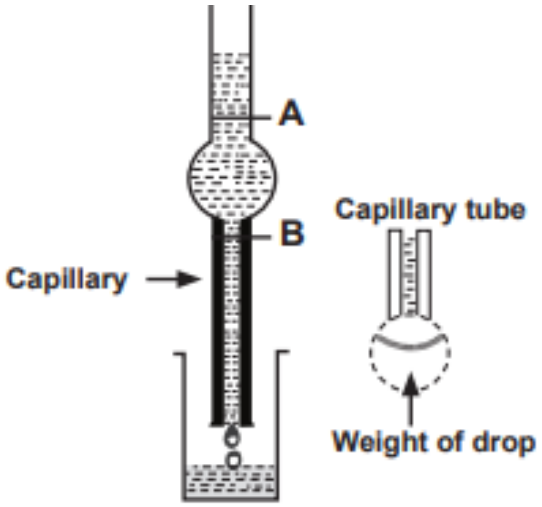


Fig. 10.11: Traube's Stalagmometer.

It consists of a bulbed capillary tube, the end of which is flattened and grounded carefully so that there is a large dropping surface. There are two marks, A and B, on it which are arbitrarily etched; one of them is above the bulb and the other is below the bulb. A liquid is sucked up to the level A and then allowed to flow at a slow rate drop by drop until it reaches the level B. The speed of the drop formation can be adjusted by attaching a piece of rubber tube with a screw pinch cock at the upper end of the tube.

When a liquid is allowed to flow through a capillary tube, a drop begins to form at its lower end, and increases in size to a certain extent, and then falls off. The size of the drop will depend on the radius of the capillary and the surface tension of the liquid. The total force of surface tension supporting the drop is $2\pi r\gamma$, where r is the outer Capillary radius of the capillary tube, see Fig. 10.12. The drop will fall when its weight w, just exceeds the force of surface tension acting along the circumference. Therefore,

$$w = 2\pi r\gamma \qquad \ldots(10.2)$$

where w, is the weight of the drop and $2\pi r$ is the outer circumference of the capillary tube.

From the above expression, it is clear that that surface tension of a liquid can be determined if the weight of a single drop w and the outer radius of the dropping tube, r are known.

If, we have two liquids, such that

$$w_1 = 2\pi r\gamma_1 \qquad \ldots(10.3)$$

and $$w_2 = 2\pi r\gamma_2 \qquad \ldots(10.4)$$

then, we can say that

$$\frac{w_1}{w_2} = \frac{\gamma_1}{\gamma_2} \qquad \ldots(10.5)$$

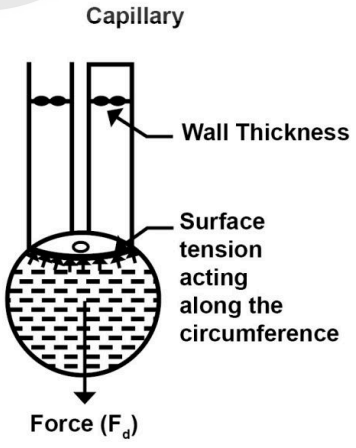


Fig. 10.12: Formation of a drop at the end of the capillary

If γ_1 for one of the liquids is known, γ_2 for other liquid can be determined without needing a measurement of r, the outer radius of the dropping end of the capillary, provided the weights of the individual drops of two liquids are known. This method of determination is also known as Drop Weight Method. Alternatively, the surface tension can also be determined using the Drop Number method as given below.

Drop Number Method

Instead of finding the weights of individual drops, it is easier to count the number of drops formed by equal volumes of two liquids. With two different liquids, the weights of equal volumes are proportional to their densities. If n_1 and n_2 are the number of drops formed by the same volume V of the two liquids, then; v_1, the volume of a single drop of first liquid (i.e., liquid one) = V/n_1.

Thus,

weight of the single drop of the first liquid = $w_1 = (V/n_1) \times d_1 \times g$ for first liquid, where d_1 is the density of the first liquid

and

weight of the single drop of the second liquid = $w_2 = (V/n_2) \times d_2 \times g$ for second liquid, where d_2 is the density of the second liquid

Weight of an object is the force experienced by it due to gravitation when it is freely suspended (as in spring balance). Therefore,

weight = mass × acceleration due to gravity

or $w = m \times g$

$w_1 = m_1 \times g$

and $w_2 = m_2 \times g$

Thus,

$$\frac{w_1}{w_2} = \frac{m_1 \times g}{m_2 \times g} = \frac{m_1}{m_2}$$

Substituting the above values of w_1 and w_2 in Eq. 10.5, we get

$$\frac{\gamma_1}{\gamma_2} = \frac{(V/n_1) \times d_1 \times g}{(V/n_2) \times d_2 \times g} = \frac{d_1/n_1}{d_2/n_2} = \frac{n_2 d_1}{n_1 d_2} \quad \ldots(10.6)$$

where, γ_1 and γ_2 and are the surface tensions of two individual liquids, and d_1 and d_2 are their densities, respectively. Thus, for the determination of surface tension of any liquid, the number of drops produced from equal volume of two liquids and their densities must be known, in addition to the surface tension of the reference liquid, e.g., water).

You can also check your understanding about the Eq. 10.6 involved in the determination of surface tension by answering the following SAQ.

SAQ 5

Calculate the ratio of number of drops of water to those of mercury if the values of density for mercury and water are 13.6 kg dm^{-3} and 1.00 kg dm^{-3}, respectively. Use the values of surface tension of the two liquids as given in Table 10.4.

10.6 VISCOSITY

10.6.1 Viscosity of a liquid

Another property of liquid that depends on intermolecular forces is **viscosity**; it is a measure of the resistance to flow. A liquid which has higher viscosity, flows slowly. It is represented by the Greek letter η (eta). Its unit is Pa s. It decreases with temperature. The viscosity of a few liquids are given in Table 10.5.

Table 10.5: Viscosity (η) of some liquids at 298 K

Liquid	η/Pa s
Water	8.9×10^{-4}
Benzene	6.0×10^{-4}
Glycerol	0.945
Chloroform	4.7×10^{-4}

Viscosity measurement help in evaluating relative molecular masses of polymers.

Liquids with stronger intermolecular forces flow slowly and are called viscous liquids. Liquids, in general, have an inherent tendency to flow. But this tendency to flow is not always the same for all liquids. It is a common experience that water flows more easily than honey. Therefore, water is said to have higher fluidity. On the other hand, honey is said to have lower fluidity. Those liquids which have lower fluidity (η) are said to be viscous. The examples being honey, castor oil and glycerol. The viscosity, therefore, measures the resistance of a liquid to flow, while the fluidity measures the ease with which a liquid can flow. The two quantities, the viscosity and the fluidity, are essentially reciprocal to each other. Thus, we can say that $\eta = 1/\phi$, where η is the coefficient of viscosity and ϕ is the fluidity.

Coefficient of viscosity is represented by the Greek letter η (eta).

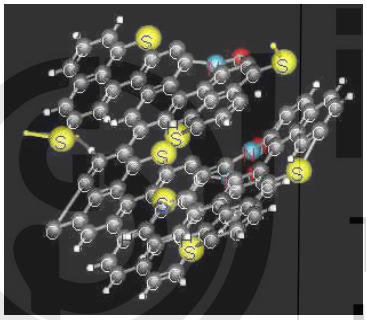
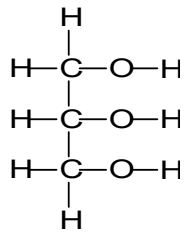


Fig. 10.13: Entangled molecules in the heavy hydrocarbon oil.

The viscosity is very much influenced by the shape, size and the chemical nature of the liquid molecules. The greater the size of the molecules and the higher the molar mass, the higher will be the viscosity because the greater will be the intermolecular interactions. The hydrogen bonds also enhance the coefficient of viscosity to a large extent. It is, indeed, the presence of a network of hydrogen bonds which accounts for the very high viscosity of glycerol. Incidentally, the larger the number of hydroxyl groups in a molecule, the more complex will be the network of hydrogen bonds and the greater will be the resistance of a liquid to flow. In long chain hydrocarbons or polymeric compounds the viscosity increases with the increase in the length of the molecular chain. Due to this reason, heavy hydrocarbon oil (Fig. 10.13) and grease (which are used as lubricants) have fairly high viscosity values.



Glycerol

The Coefficient of Viscosity

To define the coefficient of viscosity, let us consider a liquid flowing through a narrow circular tube. The flowing liquid can be viewed as being composed of parallel concentric cylindrical layers, See Fig.10.14(a). It is assumed that the layer of liquid in contact of the wall is stationary and each successive layer

starting from the wall towards the centre, moves faster than the previous one. In other words, the velocity increases to a maximum at the middle of the tube. Such a flow in which one layer slides smoothly relative to another, with regular gradation of velocity is called laminar flow and is shown in Fig. 10.14(b).

Parallel concentric cylindrical layers: cylindrical layers of liquids which have common central axis as shown in Fig. 10.14(a)

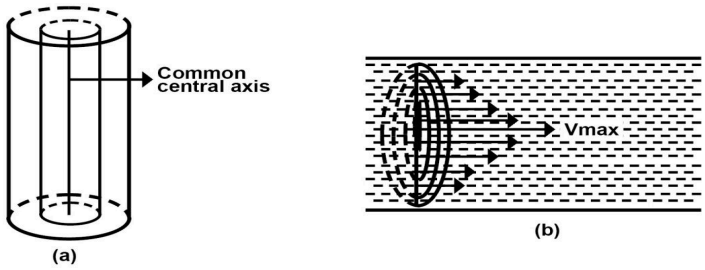


Fig. 10.14: (a) Parallel concentric cylindrical layers (b) Laminar Flow.

$\frac{dv}{dx}$ is called the velocity gradient.

Unit of $\frac{dv}{dx} = \frac{ms^{-1}}{m}$

$= s^{-1}$

For such flow, if, at a given temperature dv (m s^{-1}) is the velocity difference between two successive layers each of area A (m^2) which are at a distance dx (m), then the net resisting force F operating between two successive layers will be directly proportional to the area A and velocity difference dv, and inversely proportional to the distance dx, such that

$$F \alpha A.\frac{dv}{dx}$$

or

$$F = \eta . A.\frac{dv}{dx} \qquad \ldots(10.7)$$

where, η is the proportionality constant and is called the coefficient of viscosity of the liquid at the given temperature. Therefore, from Eq. 10.7, we can write

$$\eta = \frac{F}{A.\frac{dv}{dx}} \qquad \ldots(10.8)$$

$1\ \mathrm{N} = 1\ \mathrm{kg\,m\,s^{-2}}$

Hence,

$1\ \mathrm{Pa\,s} = 1\ \mathrm{N\,m^{-2}\,s}$

$= 1(\mathrm{kg\,m\,s^{-2}})\,\mathrm{m^{-2}\,s}$

$= 1\ \mathrm{kg\,m^{-1}\,s^{-1}}$

A liquid has a viscosity of 1 Pa s if a force of I N is required to move a plane of 1 m^2 at a velocity of 1 m s^{-1} with respect to a plane surface 1 m away and parallel with it.

If A is 1 m^2 and $\frac{dv}{dx}$ is 1 s^{-1}, then $\eta = F$.

Thus, the coefficient of viscosity of a liquid, η, at a given temperature may be defined as, **the force per unit area required to maintain a unit difference of velocity between two parallel layers at unit distance apart**. This is also obvious from the Eq. 10.8. For convenience, at times, the coefficient of viscosity is often called the viscosity of liquids. Having defined the coefficient of viscosity, let us now study its units.

Units

In SI system, from Eq. 10.8, we can say that

$$\text{Unit of } \eta = \frac{\text{Unit of } F}{\text{Unit of } \left(A.\frac{dv}{dx}\right)} = \frac{\mathrm{N}}{\mathrm{m^2}.\frac{\mathrm{m\,s^{-1}}}{\mathrm{m}}} = \mathrm{N\,m^{-2}\,s}$$

Since N m^{-2} = Pa (Pascal, unit of pressure)

$$\eta = \text{Pa s}$$

In c.g.s. system, the unit of coefficient of viscosity is **poise**. A liquid has a coefficient of viscosity of one poise if a force of 1 dyne (1 g cm s^{-2}) is required to move a plane of 1 cm^2 at a velocity of 1 cm s^{-1} with respect to a plane 1 cm away and parallel with it.

$$\text{Unit of } \eta = \frac{\text{Unit of } F}{\text{Unit of } \left(A.\frac{dv}{dx}\right)}$$

$$= \frac{\text{dyne}}{\text{cm}^2 \frac{\text{cm s}^{-1}}{\text{cm}}}$$

$$= \frac{\text{g cm s}^{-2}}{\text{cm}^2\,\text{s}^{-1}}$$

$$= \text{g cm}^{-1}\text{s}^{-1}$$

$$= \text{poise}$$

In other words, 1 poise = 1 g cm^{-1} s^{-1}

If you are interested in knowing the conversion from c.g.s. to SI units, go through the following steps:

$$1 \text{ poise} = 1\,\text{g cm}^{-1}\text{s}^{-1} = 1(10^{-3}\text{ kg})\,(10^{-2}\text{m})^{-1}\text{s}^{-1}$$

$$= 10^{-3}\text{ kg} \times 10^{2}\,\text{m}^{-1}\text{s}^{-1}$$

$$= 10^{-1}\text{ kg m}^{-1}\text{s}^{-1}$$

$$= 10^{-1}\text{ Pa s}$$

Hence, 10 poise = 1 Pa s

At this stage, it will be beneficial for you to answer the SAQ given below.

SAQ 6

i) How are the viscosity and the fluidity of a liquid related to each other?

ii) What does the viscosity of a liquid measure?

iii) Fill in the blanks with correct words.

Liquids having high……are said to have…….viscosity and the liquids with the high……..are said to have low…….

iv) The vertical flow of a liquid through a capillary is proportional to the. . ..... of the liquid.

v) For water-proof coating of wood, paraffin wax is used. Explain the reason.

The flow of liquid through a pipe or tube of radius *r*, is associated with Reynolds Number (*R*) which is given by the following expression,

$$R = \frac{2rvd}{n}$$

Where *v* is the average velocity of the liquid, *d* is the density and η is the coefficient of viscosity. If the value of *R* is less than 2100, the flow of liquid is said to be laminar or streamlined, and if *R* is greater than 4000, the flow is termed as turbulent.

The relationship, $p = hdg$ can be derived as follows:

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

$$= \frac{\text{mass} \times \text{acceleration due to gravity}}{\text{Area}}$$

$$= \frac{mg}{\pi r^2}$$ (cross-sectional areas of a cylindrical layer is πr^2)

$$= \frac{V d\ g}{\pi r^2}$$ (since mass = volume × density)

$$= \frac{\pi\ r^2 hdg}{\pi\ r^2}$$

$$= hdg$$

[Hint: Paraffin wax is a mixture of solid hydrocarbons]

vi) Among the alkanes – octane (C_8H_{18}), nonane (C_9H_{20}) and decane ($C_{10}H_{22}$) – which is expected to have the highest viscosity?

During the flow of the liquid, as the height (h) (level) of the liquid changes, there is a change in the pressure difference (p). But, for every position of the meniscus, p is proportional to density (d).

Thus, $p^1 \propto d^1$

and $p^2 \propto d^2$

or $\frac{p_1}{p_2} = \frac{d_1}{d_2}$

As a result of the change in driving pressure (p) the rate of flow of the liquid also changes all the time the flow is taking place. The rate of flow, i.e., the volume of liquid flowing per second (V) is inversely proportional to time. Thus, for the liquids, 1 and 2, we can say that

$\frac{V_2}{V_1} = \frac{t_1}{t_2}$

10.6.2 Determination of the Coefficient of Viscosity

The coefficient of viscosity of liquids is generally determined by using the following two methods:

i) Ostwald Viscometer technique

ii) Falling Sphere technique

We will discuss here the principles involved in the first method because in the laboratory (BCHCL-138) experiment, you will be measuring the coefficient of viscosity by this technique.

Ostwald Viscometer Technique

For the measurement of coefficient of viscosity of liquids having a laminar or streamlined flow, Poiseuille derived an expression, known as **Poiseuille's equation.** This expression is given below.

$$\eta = \frac{\pi p r^4 t}{8Vl} \qquad \ldots(10.9)$$

where η = coefficient of viscosity of the liquid

V = volume of the liquid flowing out of the tube

t = time in which the volume V flows

r = radius of the tube

l = length of the tube

p = driving pressure necessary to maintain uniform rate of flow of volume V, of the liquid

This involves the use of Ostwald Viscometer in which a fixed volume of a liquid is allowed to fall under its own weight or the force of gravity, and the time required for a given volume of the liquid to flow is noted. Obviously the driving pressure p is replaced by hdg, where h is the height of the liquid and d is its density and g is the acceleration due to gravity. Therefore,

$$p = hdg$$

Substituting hdg for p in Poiseuille's Equation (Eq. 10.9), we get,

$$\eta = \frac{\pi r^4 h d g t}{8Vl} \qquad \ldots(10.10)$$

If equal volumes of the two liquids (1 and 2) are allowed to fall through the same capillary tube under identical conditions of temperature and pressure then, from Eq. 10.10 by comparison, we have

$$\frac{\eta_1}{\eta_2} = \frac{d_1\ t_1}{d_2\ t_2} \qquad \ldots(10.11)$$

where η_1, d_1 and t_1 are, respectively, the coefficient of viscosity, density and time of flow for the liquid 1 under examination and η_2, d_2 and t_2 the corresponding values for the reference liquid (liquid 2). Thus, by knowing η_2, d_2, t_2, d_1 and t_1 the coefficient of viscosity of first liquid, η_1, could be determined.

Below is given the figure showing an Ostwald Viscometer, where A is the bulb, B is the capillary tube and C is the storage bulb.

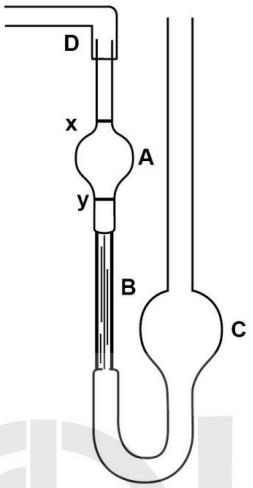


Fig. 10.15: Ostwald Viscometer

The viscosities of some liquids are shown in Table 10.6.

Table 10.6: Coefficient of Viscosity of Different Substances at 293 K

Substance	Coefficient of Viscosity (η /10^{-3} Pa s)
Acetic acid	1.314
Acetone	0.337
Chloroform	0.560
Methanol	0.593
Mercury	1.552

SAQ 7

i) Name the two methods which can be used for the measurement of the coefficient of viscosity of liquids.

ii) What are the units of the coefficient of viscosity in the c.g.s. and SI system?

10.7 EFFECT OF TEMPERATURE ON SURFACE TENSION AND COEFFICIENT OF VISCOSITY OF A LIQUID

10.7.1 Effect of Temperature on Surface Tension

As the temperature increases, the kinetic energy of the molecules increases. This causes a decrease in their intermolecular forces of attraction. This results in a decrease in the surface tension of the liquid. The surface tension of some liquids at various temperatures are given in Table 10.7. For the majority of compounds the temperature dependence of the surface tension can be given as, $\gamma = A - BT$ …(10.12)

Table 10.7: Surface Tension of some liquids at various temperatures ($10^2 x\gamma$/N m^{-1}).

Liquids	273 K	283 K	293 K	298 K
Acetone	2.62	-	2.37	-
Benzene	3.16	3.02	2.89	2.83
Ethanol	2.40	2.36	2.28	2.19
Methanol	2.45	-	2.26	2.22
Water	-	7.42	7.28	7.20

where, A and B are the constants and *T* is the temperature in degree celsius. The values of A and B for various compounds are available due to the research work done so far. A should be γ_0, that is the surface tension at 273 K temperature.

10.7.2 Effect of Temperature on Viscosity

Let us now study the effect of temperature on viscosity. In liquids, as the temperature rises, the kinetic energy of the molecules increases and the intermolecular forces of attraction become weak, resulting in the subsequent decrease in the viscosity. The value of the coefficient of viscosity appreciably drops as the temperature of liquid increases such that for each degree rise in temperature there is about two percent decrease in the viscosity. The viscosity and temperature are related to each other by the following expression:

$$\log \eta = \frac{A}{T} + B \quad \text{…(10.13)}$$

where A and B are constants for a given liquid and *T* is the absolute temperature. The plot of log η against $\frac{1}{T}$, therefore, gives a straight line, demonstrating the fact that the viscosity of a liquid rapidly decreases with the rise in temperature. see Fig. 10.16. (a).

On the other hand, if we plot a graph between coefficient of viscosity and temperature, we get a curve as shown in Fig. 10.16 (b).

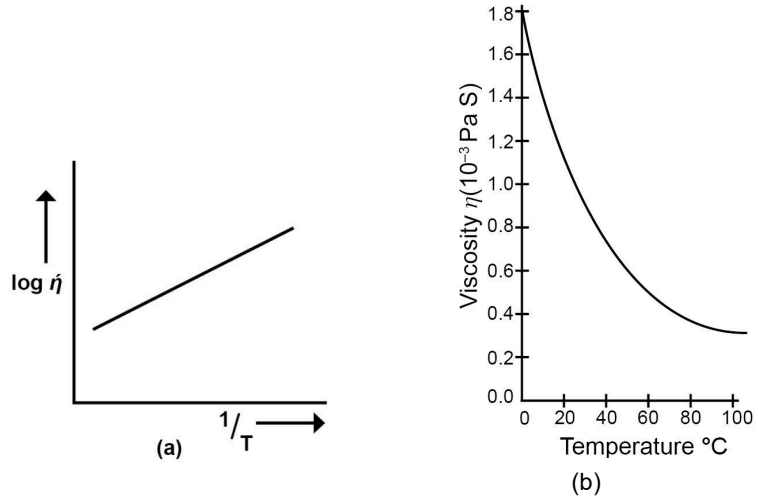


Fig. 10.16: Temperature dependence of viscosity of water.

The viscosities of some liquids at various temperatures are given in Table 10.8.

Table 10.8: Viscosities of some liquids at various temperatures (η/ Pa s)

Liquids	273 K	283 K	293 K	298 K
Acetone	4.0×10^{-4}	-	3.3×10^{-4}	3.1×10^{-4}
Benzene	9.0×10^{-4}	7.6×10^{-4}	6.5×10^{-4}	6.0×10^{-4}
Ethanol	17.7×10^{-4}	14.7×10^{-4}	12.0×10^{-4}	-
Methanol	8.1×10^{-4}	6.9×10^{-4}	5.9×10^{-4}	$5.5^{o}\times10^{-4}$
Water	-	13.1×10^{-4}	10.0×10^{-4}	8.9×10^{-4}

Before going to the next section you should answer the following SAQ.

SAQ 8

Fill in the blanks with correct words.

i) At higher temperature, the surface tension of a liquid ..... because ..... decreases.

ii) With the rise in temperature, the viscosity of a liquid…….

iii) The plot of log η against 1/T gives a …….

10.8 SUMMARY

In this unit we studied the characteristics of liquids and compared them with those of solids and gas. Next, the model proposed for the structure of liquid was discussed. Intermolecular forces were discussed in detail. Surface tension and viscosity of liquids were explained and the dependence of these characteristics on intermolecular forces was brought out. Lastly, the effect of

temperature on surface tension and coefficient of viscosity of a liquid were discussed.

10.9 TERMINAL QUESTIONS

(1) Comment on the fact that the densities of solid, liquid and gaseous nitrogen are 1.026, 0.8081 and 1.251×10^{-3} kg dm^{-3}, respectively.

(2) In a polythene tube, water meniscus is convex. Explain.

(3) At room temperature, among water, methyl cyanide and methanol, which one is expected to have the highest surface tension? State the reason.

(4) Why the viscosity of water at 373 K is one-sixth of its viscosity at 273 K?

(5) Generally why do surface tension decreases when temperature increases?

10.10 ANSWERS

Self Assessment Questions

(1) Comparison of the forces:

Type of Interaction	**Factors responsible for Interaction**	**Example**
Dipole-dipole	Dipole moment (depends on the electronegativities of the atoms and the structure of the molecule).	H_2O, HCl
Instantaneous dipole-induced dipole (London or dispersion forces)	Polarizability of nonpolar molecules.	I_2…..I_2

(2) The main intermolecular interactions in Cl_2, Br_2 and I_2 are London forces. Since the polarisability and hence London forces increase with relative molecular mass, the melting points are in that order.

(3) The voids in liquids have less space than those of gases.

(4) (i) Because of surface tension, a liquid develops a tendency to acquire smallest possible area for a given volume. A sphere has the smallest surface area for a given volume.

(ii) Capillary action is the rise of liquids through a capillary (narrow glass) tube (Fig. 10.10a).

(iii) Higher surface tension corresponds to stronger intermolecular forces.

a) one of these (CH_3COOH) has the ability to hydrogen bond. It will probably have the strongest intermolecular forces.

b) CH_3COOH is the only one of these molecules to have a dipole, and we already decided it has the strongest intermolecular forces.

c) of the molecules that are left, the largest one (C_3H_8) likely has the strongest London dispersion forces. The smallest CH_4 likely has the weakest intermolecular forces. The answer is: CH_4, C_2H_6, C_3H_8, CH_3COOH.

(5) let subscript 2 represent water & subscript 1 represent mercury.

Then Eq. 10.6 becomes,

$$\frac{\gamma_{Hg}}{\gamma_w} = \frac{n_w d_{Hg}}{n_{Hg} d_w}$$

or $$\frac{n_w}{n_{Hg}} = \frac{\gamma_{Hg}}{\gamma_w} \times \frac{d_w}{d_{Hg}}$$

$$= \frac{0.472}{0.07288} \times \frac{13.6}{1.00} = 88.1.$$ (rounded to three significant figures)

(6) i) They are reciprocal to each other.

ii) Viscosity of a liquid measures its resitance to flow.

iii) Fluidity, low, viscosity, fluidity.

iv) Density.

v) The cohesive forces between the molecules of water are stronger than the adhesive forces between water molecules and the hydrocarbon molecules in wax. Hence water does not “wet” the surface of wax.

vi) Decane is expected to have the highest viscosity due to increase London forces with chain length.

(7) i) Ostwald technique, Falling sphere technique.

ii) Poise, Pa s.

(8) i) decreases, cohesive forces.

ii) decreases.

iii) Straight line.

Terminal Questions

(1) The free space is the highest in gas, less in liquid and the least in a solid.

(2) The adhesive forces between water and the hydrocarbon molecules in polythene are weaker than the cohesive forces between water molecules.

(3) Due to strong hydrogen bonding, water must have the highest surface tension among the three liquids.

(4) With temperature increase, the kinetic energy of the molecules increase and the intermolecular forces of attraction become weak. The molecules can move easily leading to an increase in the flow rate; the viscosity decreases.

(5) Because cohesive forces decrease with an increase of molecular thermal activity.

Sources of Figures

Fig.10.1: https://chem.libretexts.org/

Fig.10.10: https://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0m/s15-03-unique-properties-of-liquids.html (CC-BY-NC-SA 3.0)

UNIT 11

SOLIDS-I

Structure

11.1 INTRODUCTION

In the earlier units, we had drawn a comparison amongst the three states of matter namely - solid, liquid and gas. These states of matter were described in terms of few physical properties like density, compressibility, etc. Now, instead of defining the states of matter in terms of the physical properties, we will think in terms of the binding forces (ionic, covalent, van der Waals, etc.,) which are involved in a particular state giving different properties to solids, liquids and gases. So we could say that, solid state is a state of a substance in which the neighbouring particles (molecules, atoms or ions) are close enough for even van der Waals forces to operate. Due to strong binding forces, the motion of the molecules is restricted with respect to its neighbours.

In this unit, we will be discussing the different types of solids, mainly – **crystalline** and **amorphous.** Again, different crystalline structures are associated with different physical properties. Hence, we shall discuss symmetry elements, crystal forms, Bravais lattice and crystal systems in this unit. Further, the laws of crystallography, specially the law of constancy of interfacial angles and the law of rational indices, followed by crystal planes and Miller indices are discussed in this unit. In the next unit you will be learning about X-ray diffraction, Bragg's law, structures of unit cells, formula of

a compound and number of voids filled in body-centred cubic (bcc) and face-centred cubic (fcc) structures, along with density calculations, defects in crystals, followed by glasses and liquid crystals. So, in this way you will be learning all about solids from Unit 11 and 12.

Expected Learning Outcomes

After studying this unit, you should be able to:

- differentiate between amorphous and crystalline solids;
- describe the symmetry elements;
- define lattice, basis and unit cell;
- describe the fourteen Bravais lattices and the seven crystal systems;
- state and explain the laws of crystallography-law of constancy of interfacial angles and law of rational indices; and
- denote the crystal planes in terms of Weiss and Miller indices.

11.2 AMORPHOUS AND CRYSTALLINE SOLIDS

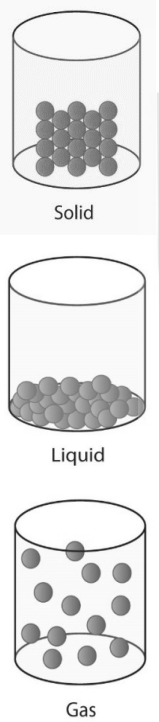


Fig.11.1: A Representation of the Solid, Liquid, and Gas States.

Now you can recall from your previous classes the general characteristics of solid state as follows:

i. They have definite mass, volume and shape.

ii. Their intermolecular distances are short and intermolecular forces are strong.

iii. The constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean position.

Solids are the least compressible and generally denser than the liquids.

According to structure, solids are generally classified into two broad types, namely **crystalline solids** and **amorphous solids.** Let us explain what a crystalline solid is. Those solids which are formed due to regular repetition of identical building blocks are called crystals. Now, have you seen how a wall is constructed out of bricks? In a similar way identical units build up a crystalline solid. But there may be solids which do not appear to have regular internal arrangement in every part and thus do not show regular form. Examples of amorphous substances are glass, polyethylene as in plastic bags, etc.

The structures of quartz (crystalline) and quartz glass (amorphous) are shown in Fig. 11.2 (a) and (b), respectively.

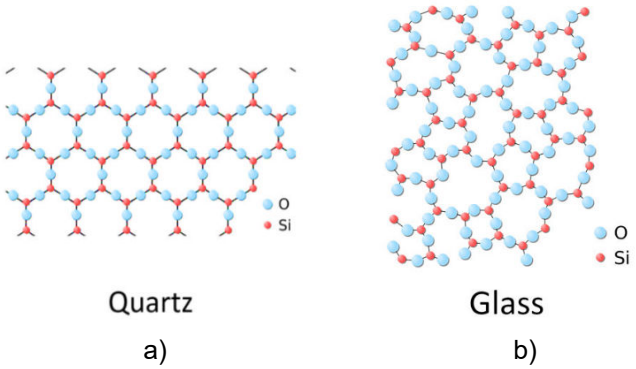


Fig. 11.2: Two dimensional structure of a) quartz and b) quartz glass.

Now let us understand the two forms of solid with the help of an example. Do you know what is quartz? Well, quartz is a form of SiO_2 (silica). It has tetrahedral SiO_4 (silicate) units which are orderly arranged in crystalline quartz as shown in Fig. 11.2a. If you slowly melt SiO_2 and then cool it, randomly joined amorphous quartz glass forms. Here SiO_4 units are there. But if you look at Fig, 11.2 a & b, do you observe any difference in their structures? In the amorphous quartz glass there is no long range order. The structure of amorphous solids is similar to that of liquids. Now the question is why do the two types of solids (amorphous and crystalline) differ in their properties? This we will discuss in the following section.

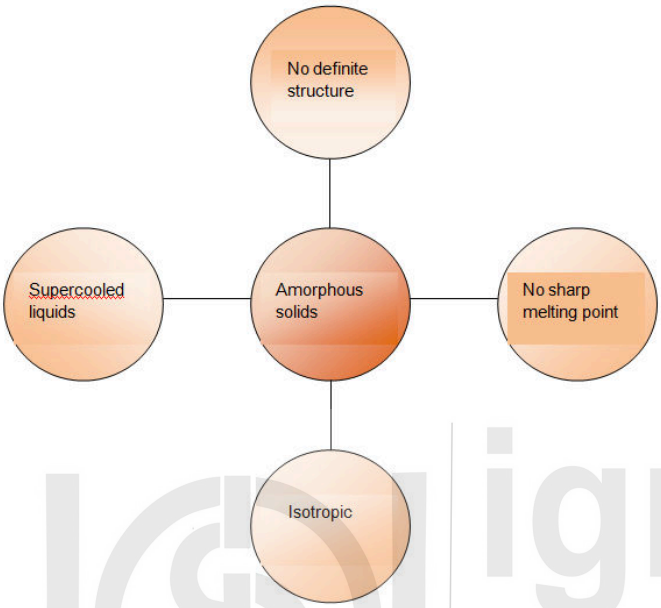


Fig. 11.3: Properties of Amorphous Solids

On heating, amorphous solids become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation. Amorphous solids are called pseudo solids or supercooled liquids because like liquids, they have a tendency to flow. Therefore glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

Amorphous solids

The definition of **amorphous solids** (Greek amorphos = no form) is that they are solids which do not possess a definite structure and sharp melting point, and the constituents (may be atoms, ions, molecules) do not have ordered arrangement. They are rigid, but do not have repeated periodicity or long-range order. So the amorphous solids have short-range order. Amorphous solids have identical properties along all axes and break to form irregular shapes. Also, they melt gradually over a range of temperatures.
Thus **amorphous material** are considered as supercooled liquids rather than solids. Amorphous solids include both natural and man-made materials. Additional examples include thin film lubricants, metallic glasses, polymers, and gels.

So can you summarise the properties of amorphous solids? Look at the following example.

EXAMPLE 11.1: State important properties of amorphous solids. What type of structure do they possess?

SOLUTION: The amorphous solids have short range order. They have irregular shapes. They do not have sharp melting point. They gradually soften over a range of temperatures. They do not have definite enthalpy of fusion. When cut with a sharp edged tool they cut into two pieces with irregular surfaces. Amorphous solids are isotropic (i.e. the properties of a material are

identical in all directions) in nature. It is because the arrangement of constituent particles is equally irregular along all the directions. Therefore, the value of any physical property (electrical resistance or refractive index) would be same along each direction.

Crystalline solids

Crystalline solids are solids which possess a definite structure, sharp melting point, and the constituents are arranged symmetrically. Crystalline solids are formed due to regular repetition of identical building blocks, almost similar to a collection of identical bricks which could be arranged regularly to construct a wall. Sodium chloride, potassium chloride, sugar, ice, quartz, metals and diamonds are some examples of crystals.

Properties of crystalline materials

1. Constituents may be atoms, ions or molecules.
2. Definite regular geometry exists as a result of regular arrangement of the constituent particles. Ordered arrangement of the constituents of fixed pattern extends over a large distance. So they show long range order as well as short range order. The crystalline solids have definite characteristic shape. Generally they show symmetry too.
3. Crystalline solids have a sharp melting point as a result of regular pattern of their constituent particles. Therefore, crystalline solids have definite enthalpy of fusion.
4. Crystalline solids show cleavage property. Cleavage refers to the tendency to break along planes of weak bonds. When cut with a sharp edged tool (e.g. knife) they split into two pieces and the newly generated surfaces are plain (flat) and smooth. But the opposite will happen for amorphous solids. It would cut into surfaces with rough, uneven edges. Crystalline solids are therefore said to have cleavage property, and amorphous solids do not show cleavage property. This is explained through Fig. 11.4 and can be seen in Fig. 11.5.

Fig. 11.5: Green fluorite with prominent cleavage.

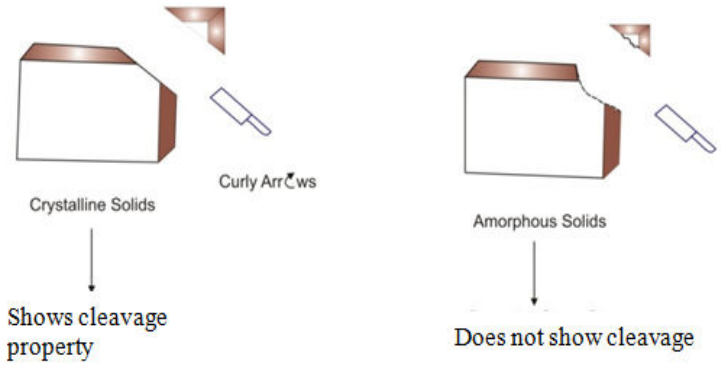


Fig. 11.4: Cleavage Property of Solids.

When some external pressure is applied to a crystalline solid, it changes into small crystals of the same size and shape as that of the original one. When a large crystal breaks up into smaller one with identical of shape it is called cleavage. The plane which contains the direction of cleavage is called cleavage plane as shown in Fig. 11.6.

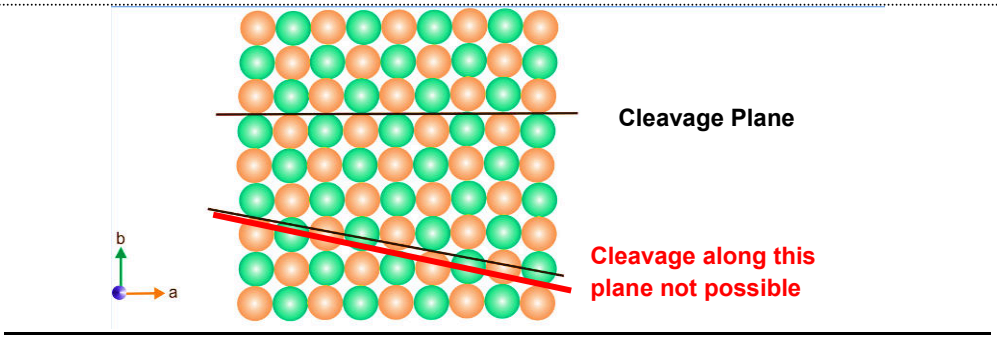


Fig. 11.6: Cleavage Plane (black), cleavage not possible along the other(red).

5. Crystalline solids are anisotropic (i.e. the properties of a material depend on the direction. The arrangement of constituent particles is different in different directions. For example, in a NaCl crystal (Fig.11.7), if you move in different directions you will come across different set of ions. Therefore, the value of any physical property (electrical resistance or refractive index) would be different along each direction.

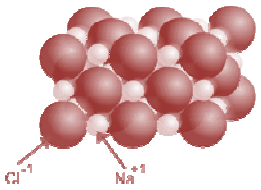


Fig. 11.7: Ionic solid (NaCl).

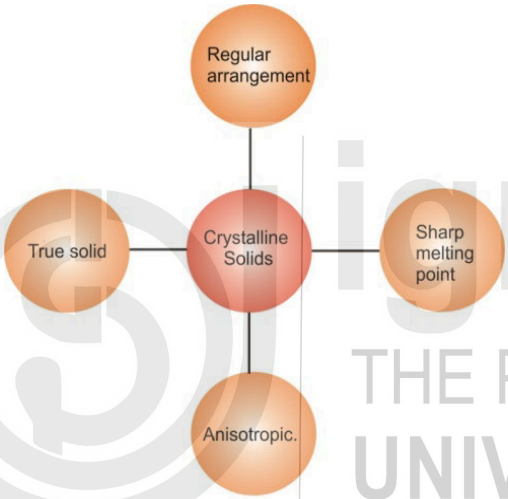


Fig. 11.8: Properties of Crystalline Solids.

Before going further try to answer the following SAQ.

SAQ 1

i) Below are given the criteria on which you should compare the solid and liquid states. Give the answer in a table form.

   a. rigidity of structure.

   b. long-range order.

   c. short-range order.

ii) In a tabular form give the difference between amorphous solids and crystalline solids based on the various characteristics.

iii) Which type of solid behaves like a supercooled liquid?

iv) While synthesizing a chemical in a laboratory, a solid product was obtained whose melting point was determined. It was found that it melted over a wide range of about 10 ºC. After slow cooling, when again the

melting point was measured, a sharp melting point was observed which was characteristic of the desired product. Explain the reason for the change in the melting point.

Classification of Crystalline Solids

Based on the type of intermolecular forces involved, the crystalline solids can be classified into the following five types:

a. Molecular solids, b. Ionic solids

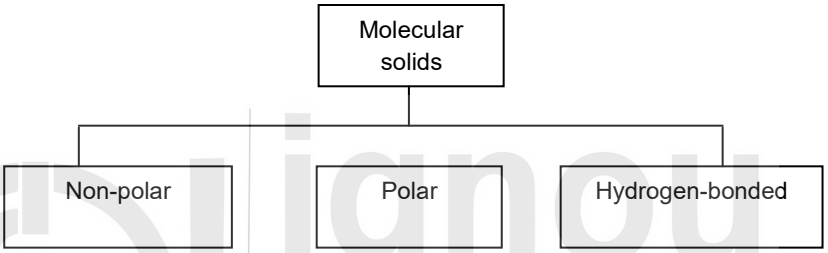
c. Covalent or network solids, d. Metallic solids

London Dispersion Forces

The unsymmetrical distribution of electrons about the nucleus in an atom can result in an instantaneous dipole in the atom. Another atom or molecule in the neighbourhood of this atom develops an induced dipole that leads to an electrostatic attraction between either atoms or molecules.

a) Molecular Solids

Molecular solids are crystalline substances made up of molecules. Dispersion forces or London forces, dipole-dipole forces or hydrogen bonds are responsible to hold together the constituent molecules. Molecular solids are of three types as shown below:



Nonpolar molecular solids: Atoms, (e.g., argon and helium) or molecules formed by nonpolar covalent bonds, (e.g. H_2, Cl_2 and I_2) are the constituent particles of these. In these solids, the atoms or molecules are held by weak dispersion forces or London forces for which an example is illustrated in Fig.11.9.

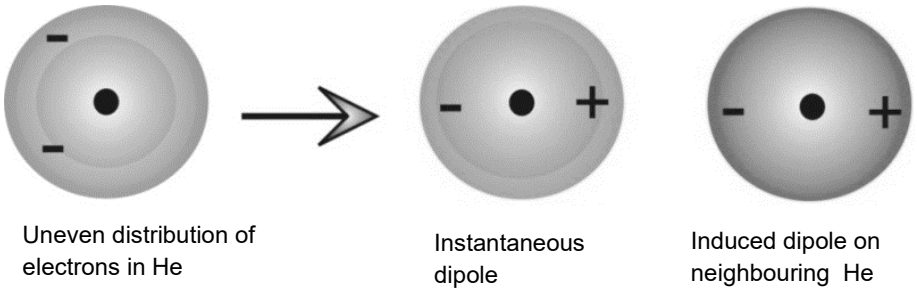


Fig.11.9: Example of London Dispersion forces in an inert gas (Helium).

The characteristics exhibited by them are:

(i) Low melting points.

(ii) Soft.

(iii) Mostly liquid or gaseous at room temperature and pressure.

(iv) They are made up of neutral molecules in solid state and even when dissolved and so they are non-conductors of electricity.

Polar molecular solids: The molecules like HCl, SO_2, etc. are having polar covalent bonds. Such solids are held by relatively stronger dipole-dipole

interactions in their molecules, e.g. solid SO_2 and solid NH_3. Their characteristics are:

(i) Soft.

(ii) Non-conductors of electricity.

(iiii) Low melting and boiling points, although higher than those of non-polar molecular solids.

(iv) Mostly gases or liquids under room temperature and pressure conditions.

Hydrogen bonded molecular solids: Their molecules have strong hydrogen bonds generally between H and F, O or N atoms, e.g. H_2O (ice). Their characteristics are:

(i) Hard and brittle.

(ii) Non-conductors of electricity.

(iii) Usually higher melting and boiling points than those of non polar molecular solids and polar molecular solids. Now with the following example, compare the properties of different types of molecular solids.

EXAMPLE 11.2: Give a comparison of the different types of molecular solids.

Non-polar	**Polar**	**H-bonded**
Soft	Soft	Hard
Non-conductors of electricity	Non-conductors of electricity	Non-conductors of electricity
Very low melting point	Low melting Point	Low melting point
Intermolecular Forces - Dispersion or London forces	Intermolecular Forces - Dipole – dipole interaction	Intermolecular forces - Hydrogen bonding
Example – Ar, CCl_4, H_2, CO_2	Example – HCl, SO_2	Example – H_2O (ice)

b) Ionic Solids

Ionic solids consist of cations and anions which are placed in a regular manner. Strong coulombic (or electrostatic) forces hold the ions together.

Their characteristics are:

(i) The ions in ionic solids are tightly held in a lattice as they have the strong electrostatic forces of attraction in between the cations and anions. This results in their hard and brittle nature. Now, can you explain why they are brittle? Well, if you apply large force along a certain plane of these solids, then the ions shift along that layer, displacing that layer with respect to other. Thereafter repulsion occurs between like charges as they are closer. This repulsion shatters the crystal lattice of the ionic compound as shown in Fig. 11.10.

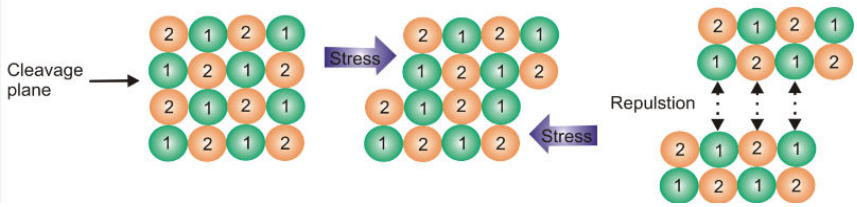


Fig. 11.10: Stress and repulsion in crystal lattice.

(ii) Very high melting and boiling points

(iii) Insulators in solid state as they are poor conductors of electricity. This happens as the ions are not free to move about. When in the fused state or when in dissolution(aqueous solution), the ions become free to move about and then conduct electricity.

(iv) Have high enthalpies of fusion and vaporization.

(v) Ionic crystals are water soluble and also dissolves in other polar solvents. They are insoluble or very slightly soluble in non-polar solvents such as benzene, carbon tetrachloride and carbon disulphide, e.g., salts like NaCl, KNO_3, LiF, Na_2SO_4, etc.

c) Covalent or Network Solids

Covalent crystals are made up of nonmetal atoms which are bonded to the adjacent atoms by covalent bonds throughout the crystal. There is a continuous network of covalent bonds forming a giant three dimensional structure as shown in Fig. 11.11.

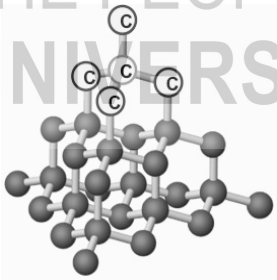


Fig. 11.11: Giant three-dimensional structure of covalent solids.

Covalent bonds are strong and directional in nature and so the atoms in these solids are held very strongly at their positions. Their main characteristics are:

i) Hard.

ii) Extremely high melting points.

iii) Poor conductors of electricity and are insulators.

E.g.: diamond, carborundum (silicon carbide), quartz (SiO_2), boron nitride (BN), etc. Diamond is a three-dimensional network solid. In diamond each carbon atom is connected to surrounding atoms by four covalent bonds. So you see each crystal is basically one giant molecule held together by covalent bonds. This structure makes diamond chemically very non-reactive, very hard and electrical insulator.

Graphite is soft and a conductor of electricity. Look at the extreme right of Fig.11.12, you can see the structure of graphite where carbon atoms are in sheets or layers. Each atom is covalently bonded to three of its neighbouring atoms of the same layer. Here, you may have the question in mind that why is graphite conducting? Well, it must have free electrons. Indeed, the fourth valence electron of each atom is present between different layers and is free to move about. These free electrons make graphite a good conductor of electricity. Each layer can slide one over the other which makes graphite a soft solid and a good solid lubricant.

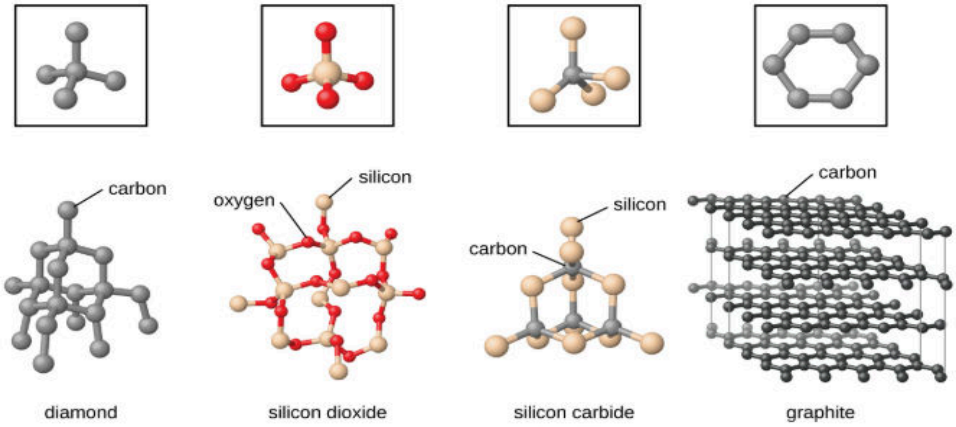


Fig. 11.12: Structures of covalent crystals of diamond, silicon dioxide, silicon carbide and graphite.

d) Metallic Solids

Metallic solids are made up of positive ions (called kernels) immersed in a sea of mobile electrons which are there in the entire crystal. This is called the electron-sea model. Can you tell what is the origin of these electrons? If you look at Fig. 11.13 you can easily follow that the metal atoms contribute them. That makes these metals have from each atom one or more electrons to this sea of mobile electrons. This is responsible for their high electrical and thermal conductivities.

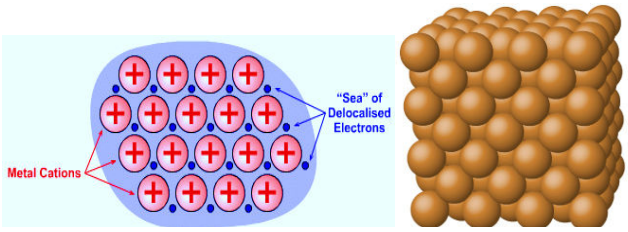


Fig.11.13: Copper is a metallic solid.

These electrons flow through the network of positive ions whenever electric field is applied. The free electrons uniformly spread the thermal energy throughout the crystal when heat is supplied to one portion of metal. Metallic bonds are the forces in the metals. The characteristic of metallic crystals are:

(i) Hard or soft.

(ii) Good conductors of heat and electricity.

(iii) Have metallic lustre.

(iv) They are malleable and ductile. That is, can be beaten into sheets and drawn into wires.

(v) They have moderate enthalpies of fusion. The examples of metallic crystals are common metals such as nickel, copper and alloys.

So we have discussed the different types of crystalline solids. Now, do try the following SAQ.

SAQ 2

i. Give examples of molecular, ionic, metallic and covalent solids.

ii. What are the differences between polar molecular solids and hydrogen bonded molecular solids.

iii. Name the force of attraction between the atoms or molecules in solid argon and solid CO_2.

iv. Compare the type of bonding in the following:

a) Diamond and copper.

b) KNO_3 and SiC.

11.3 SYMMETRY ELEMENTS

The term symmetry is derived from the Greek word "symmetria" which means "measured together".

In this section, we are going to discuss the symmetry elements. Now let us look around us in nature you will find that symmetry is there. About this, some examples are given in Fig.11.14.

Fig. 11.14: Symmetry in nature.

Look at one part (e.g. one side) of an object is it the same as all of the other parts? Well, then it is said to be symmetric. Now refer to the different objects in Fig. 11.14 and tell if they are symmetric or not. Let us discuss the methods by which we can exactly predict whether an object is symmetric, or not.

Group theory depends on a very powerful mathematical tool, to understand chemistry and simplify its many problems. A group consists of a set of symmetry elements (and associated symmetry operations) that completely describe the symmetry of an object. Symmetry is a state in which parts on opposite sides of a plane, line, or point display arrangements that are related to one another via a symmetry operation such as translation, rotation, reflection or inversion.

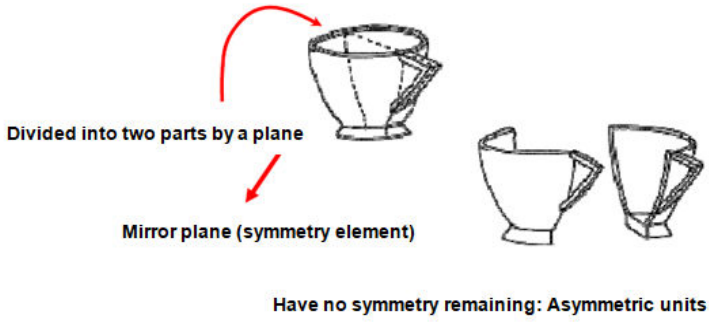


Fig. 11.15: Symmetric element and asymmetric units.

Point group of elements have symmetry about a single point at the centre of mass of the system.

The total number of planes (axes) and centres of symmetry of a crystal is called its elements of symmetry. Next, let us discuss the different elements of symmetry.

Elements of symmetry

1. Plane of symmetry: A crystal is said have a plane of symmetry if an imaginary plane which passes through the centre of crystal gives two parts of it, so that each part is the mirror image of the other part. There may be numerous planes of symmetry in a crystal as shown below in Fig. 11.16 (b and c).

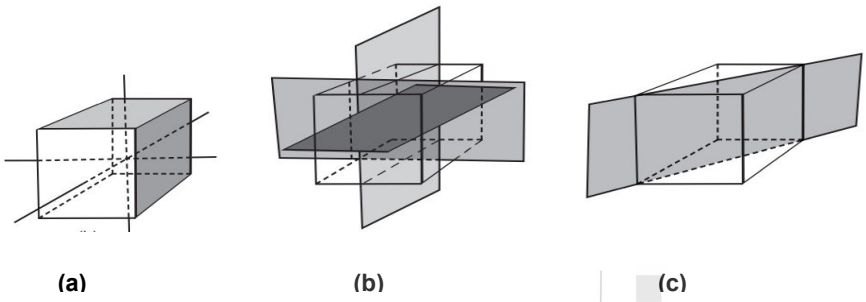


Fig. 11.16: (a) Four-fold symmetry in the cubic system (three axes) (b) Rectangular plane of symmetry (three) in cubic system (c) Diagonal plane of symmetry (six) in cubic system.

There are two naming systems commonly used in describing symmetry elements

1. The Schoenflies notation used by spectroscopists.
2. The Hermann-Mauguin or international notation used by crystallographers.

2. Axis of symmetry: It is that imaginary line which passes through the centre of a crystal, so that if the crystal is rotated about this line, then the crystal gives the same appearance more than one time in a complete 360º angle rotation. Look at Fig. 11.17 below, the number of times the crystal appears unchanged on a complete rotation, it gives that many-fold axes of symmetry. So the axis has two-fold symmetry if the equivalent configurations occurs twice in any revolution (i.e. after every 180º). Similarly, if thrice, four times and six times then three-fold, four-fold and six-fold axes of symmetry. Please note that five-fold symmetry does not exist in crystals.

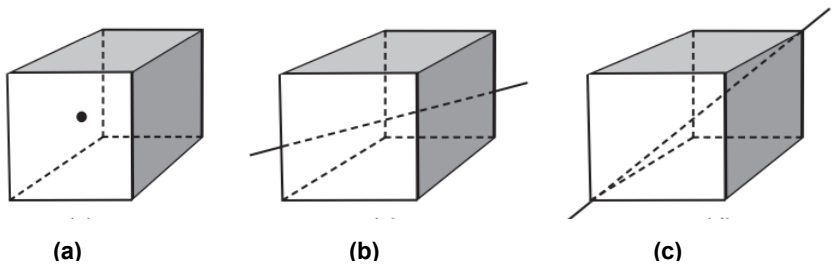


Fig. 11.17: (a) One centre of symmetry in cubic system (b) Two-fold symmetry in cubic system (six axes) and (c) Three-fold symmetry in cubic system (four axes).

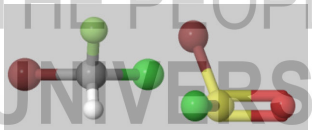
3. **Centre of Symmetry:** Centre of symmetry is a point in a crystal so that if any imaginary line is drawn through it will meet the surface of the crystal at equal distances on the either side.

Symmetry operations: In the above part, the various types of symmetry elements have been discussed. Here we will learn about symmetry operations which are generated by the symmetry elements. A symmetry operation may be defined as a movement of a body, so that, after the movement is carried out, every point of the body will lie upon an equivalent point (maybe even the same point) of the body as it was originally.

Point groups: Point groups are combinations of symmetry elements. A point group tells us about all the symmetry operations that can be performed on a molecule which result in the same spatial arrangement of atoms in the molecule as that of the original. From group theory it can be found out that the maximum number of point groups (or classes) for any symmetrical object is 32. So the different crystal actually fall into 32 classes (point groups). Each of these classes, have the same elements of symmetry i.e. same axes, planes and centre of symmetry. The 32 point groups (classes) can be grouped into seven different categories, namely, cubic, tetragonal, orthorhombic, monoclinic, rhombohedral (or trigonal), hexagonal and triclinic.

Now let us discuss in the following section the five symmetry elements and know their Schoenflies notation.

1. **Identity**-There is no change to the object by the identity operation. Every object (and therefore all molecules) have at least the identity element. The following molecules have only the identity operation as the symmetry operation.



CHFClBr **SOClBr**

Here a rotation by 360° taken around randomly chosen axes is done. Thereby the molecule comes back to its original position. Any direction in any object is a C_1 axis; rotation by 360° restores original orientation. Where C is the symbol given to a rotational axis, 1 indicates rotation by 360°.

Notation: E, Operation: act of rotating molecule through 360°

2. **Rotation**-The centre of rotation is the point around which all the points in the asymmetric unit are turned around. The centre of rotation is the only invariant point (or fixed point). Rotations are counterclockwise about the axis according to convention. Axis of rotation is the line with respect to which the rotation operations occur.

Proper rotation (C_n): If we take *n* as the order of the axis, a proper rotation is said to be performed by rotating the molecule by 360°/*n* about the rotation axis. If you find that the configuration at the end of rotation is the same as the original, then it is called an *n*-fold proper rotation axis (or C_n axis) in the molecule.

Operation: act of rotation; Element: rotation axis

Symbol for a symmetry element for which the operation is a rotation of 360°/*n*:

C_2 = 180°, C_3 = 120°, C_4 = 90°, C_5 = 72°, C_6 = 60° rotation, etc.

C_n indicates that the molecule has an *n*-fold axis of symmetry.

An object may possess several rotation axes and in such a case the one (or more) with the greatest value of *n* is called the principal axes of rotation. Let us understand this with the following Fig. 11.18 & 11.19. Here we are taking water as the molecule where each atom is given a number so that they can be distinguished from each other.

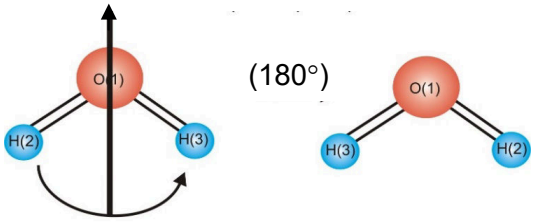


Fig. 11.18: 2-fold (180°) rotation in water.

n-fold rotation – a rotation of 360°/*n* about the C_n axis (*n*=1 to ∞). C_2 axis is there in water, and thus a 2-fold (180°) rotation can be done to get the identical arrangement of atoms.

Now next let us take the molecule ammonia. We number the atoms so that they can be distinguished from each other.

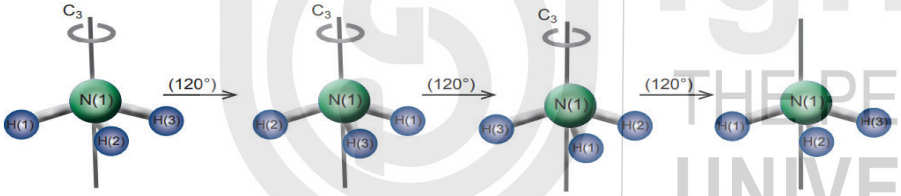
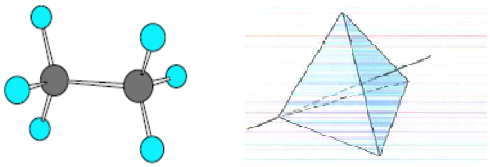


Fig. 11.19: 3-fold (120°) rotation in ammonia.

You will see from Fig.11.19 that ammonia has a C_3 axis and thus 3-fold (120°) rotations can be done so that identical arrangement of atoms are obtained.

Next we are going to discuss what is the principal axis in this context. Well, the principal axis in an object is the highest order rotation axis. You have to identify the principal axis and usually you can assign it to the z-axis in case you use cartesian coordinates. You will understand this better with the help of Fig.11.20.



(a) (b)

Fig. 11.20: a) The principal axis is the three-fold axis containing the C-C bond in ethane. b) The principal axis in a tetrahedron is a three-fold axis going through one vertex and the centre of the object.

3. **Reflection**-The mirror is the line over which all the points of the asymmetric unit are flipped over and thereby changes the handedness of any figures in the asymmetric unit. All the invariant points which are the points along the mirror line are under a reflection. Now, what steps should you follow when you hope to have the operation of reflection. Atoms in the molecule should be taken and moved one by one toward the reflection plane along a line perpendicular to that plane. After that, the atom should be taken through the plane to a point equidistant from the plane on the opposite side of the plane. After this the configuration that you get is it indistinguishable from the original? If it is so then you can conclude that there exists a symmetry plane in the molecule.

Mirror planes involve mirror reflection through a plane.
Operation: act of reflection; Element: mirror plane
Horizontal mirror plane (σ_h): plane perpendicular to the principal rotation axis.

Vertical mirror plane (σ_v): plane includes principal rotation axis
Dihedral mirror plane (σ_d): Here the plane has a principal rotation axis and bisects the angle between a pair of 2-fold rotation axes that are normal (perpendicular) to principal rotation axis.

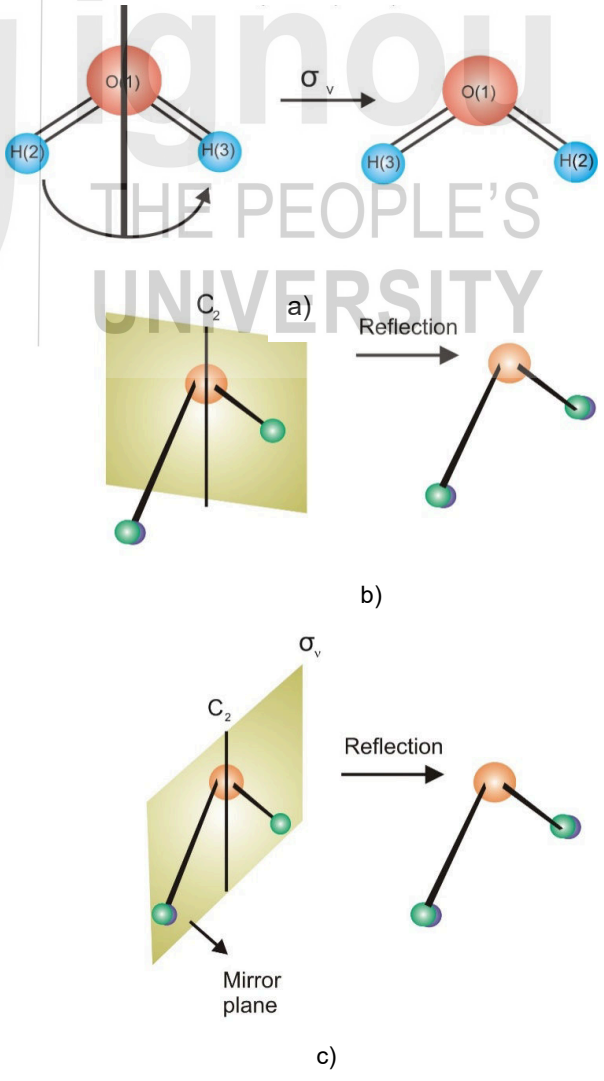


Fig. 11.21: Reflection across a plane of symmetry.

In the above Fig. 11.21 you can see mirror planes which are “vertical” mirror planes as there is the principal axis. In Fig. 11.21 is shown a reflection, which is perpendicular to the plane of the water molecule. The plane shown on the bottom lies in the same plane as that of the water molecule.In both Fig. 11.21 and 11.22, reflection of water molecule is shown.

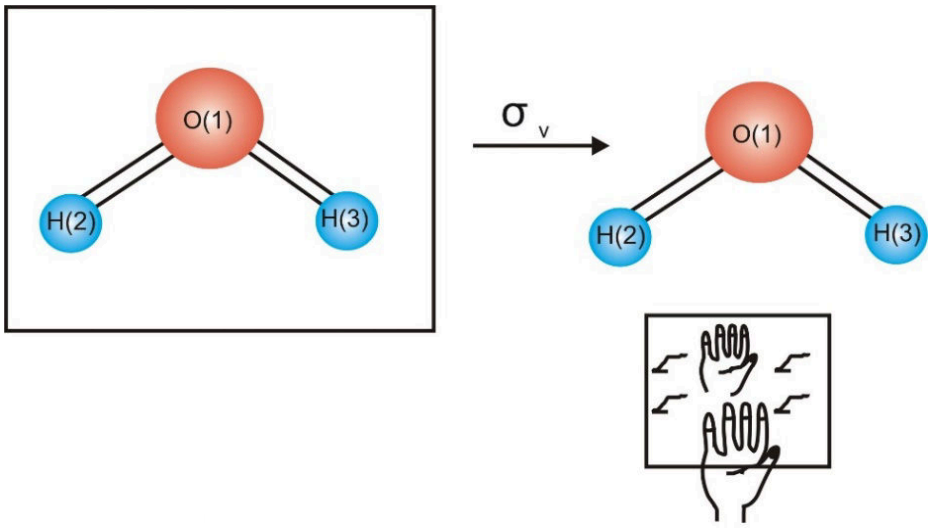


Fig. 11.22: Handedness is changed by reflection.

At this stage, can you predict what will be the result of two successive reflections? Yes, it will be equivalent to the identity operation (nothing is moved). So what are the essentials for reflective operations? Let us summarize them:

- One half of the object is reflected in reflection of the other half.
- Reflection planes may be vertical (σ_v), horizontal (σ_h) or dihedral (σ_d)
- The result of two successive reflections is the same as the identity operation (nothing is moved)

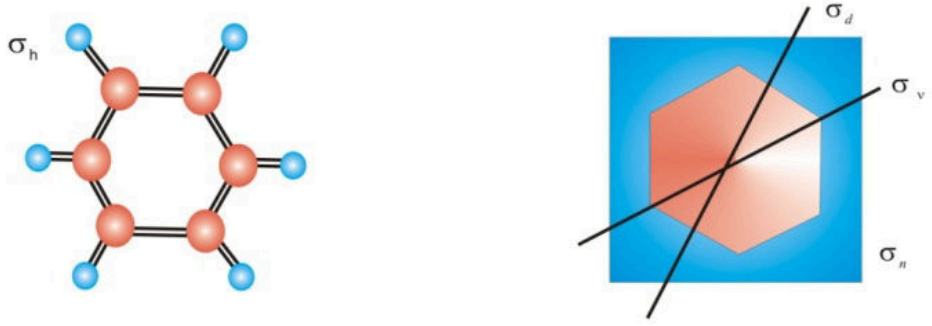


Fig. 11.23: The mirror planes in benzene molecule.

A “horizontal” mirror plane, σ_h, is perpendicular to the principal axis. This must be the xy-plane if the z-axis is the principal axis. In the left side of Fig. 11.23, you can see that, the σ_h is the plane of the molecule of benzene – it “reflects” each atom onto itself. In the right side of Fig. 11.23 you can see benzene contains six vertical planes (σ_v and σ_d). so total benzene has seven reflection planes.

In Fig. 11.24 the vertical and dihedral mirror planes of geometric shapes are shown.

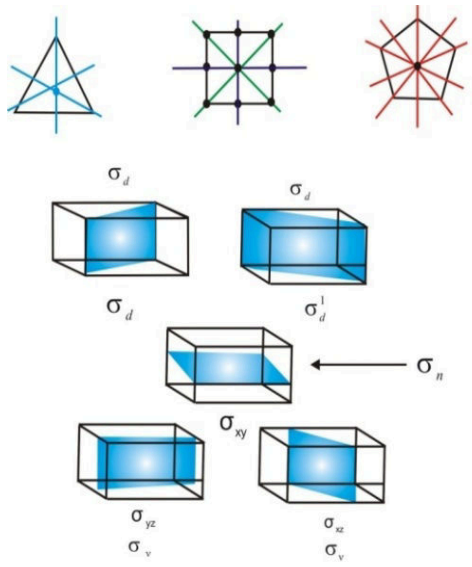


Fig. 11.24: Vertical and dihedral mirror planes of geometric shapes.

4. **Inversion** - every point on one side of a centre of symmetry has a similar point at an equal distance on the opposite side of the centre of symmetry.

Centres of inversion (centre of symmetry, *i* or 1)
Operation: inversion through this point
Element: point

If you draw a straight line through centre of inversion from any point of the molecule you will be joining it with an equivalent point at an equal distance from the centre on the other side.

Notation: *i*
Molecules possessing a centre of inversion are centrosymmetric.

In Fig. 11.25, the inversion of a molecule is illustrated.

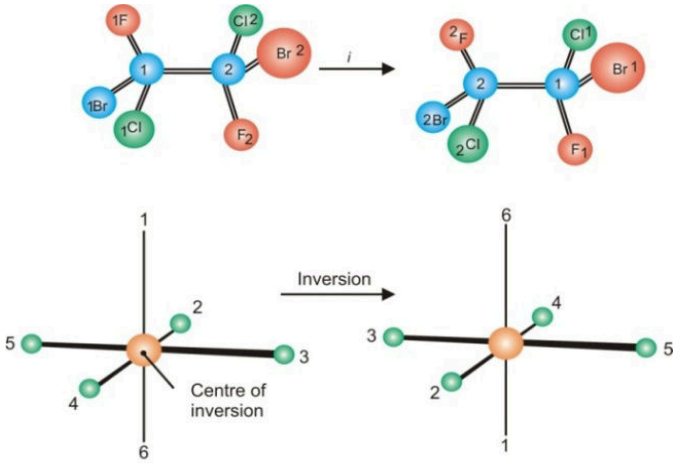


Fig. 11.25: Inversion.

5. **Improper Rotation** (S_n): An improper rotation is performed by rotating the molecule 360°/*n* followed by reflection through the plane perpendicular to the rotation axis. At the end of this if the configuration is indistinguishable from the original, then you may say an *n*-fold improper rotation axis (or S_n axis) is there in the molecule. It involves a combination of elements and operation.

Notation: S_n
Element: axis of rotatory reflection
Improper rotation involves a combination of rotation by 360°/n(C_n) followed by reflection in a plane normal (σ_h) to the S_n axis.($S_n = \sigma_h C_n$)
In Fig. 11.26 is illustrated improper rotation in methane. The first step of this improper rotation is rotation through 90° through the rotation axis which bisects the H-C-H bond. So it is a C_4 that is 4-fold proper rotation. Next it is reflected through a plane that is perpendicular to the original rotation axis(σ_h) and thereby the final configuration is indistinguishable from the original.

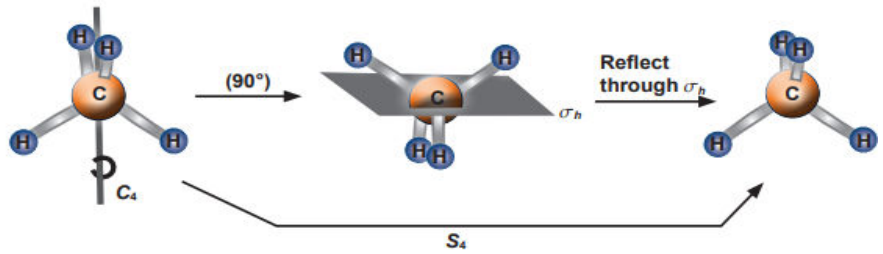


Fig. 11.26: Improper rotation.

Note that: $S_1 = \sigma$, $S_2 = i$, S_2 is the same as inversion and sometimes $S_{2n} = C_n$(e.g. in box). Note that S_1 is the same as reflection and The molecule shown above has two S_2 axes.

So let us summarise the 5 Symmetry Elements and related operations that are found in molecules:

Element	Operation
Rotation axis, C_n	n-fold rotation
Improper rotation axis, S_n	n-fold improper rotation
Plane of symmetry, σ	Reflection
Centre of symmetry, i	Inversion
	Identity, E (doing nothing)

The matrix approach to each of the symmetry operations in this section is not done. But let us at least do it for the inversion operation. The inversion operation takes a point or object at [x, y, z] to [-x, -y, -z].The inversion operation occurs through a single point called the *inversion centre*, i, located at the centre of the molecule. (Note that the inversion centre may or may not be an atom in the molecule)

So, we have discussed the different symmetry elements along with their suitable examples. In the next section we are going to discuss the definition of terms used in crystal systems. Before moving to the next section, try out the following SAQ.

SAQ 3

What are the five symmetry elements? Give the Schoenflies notation for them.

11.4 DEFINITIONS OF TERMS USED IN CRYSTAL SYSTEMS

A parallel net-like arrangement of points space is known as lattice.

Now we will discuss the definitions of terms used in crystal systems. If you go back to section 11.2 you will see that the definition of crystal involves a regular and repetitive arrangement of particles (atom/molecules/ions) in space. The

Atom is used in general sense in this unit; it stands for an atom or an ion or a molecule.

study of crystals and their structures involve certain terms which constitute a crystallographic language. Let us now look at the definitions of some of these terms. Let us start this section on crystalline solids with simple elemental metals as they have one type of atoms only. A pure metal is a crystalline solid with metal atoms packed closely together in a repeating pattern. Have you wondered why metal properties like malleability and ductility exist? The atoms are arranged in a regular pattern in the metals. The different metals have different atomic sizes and the spatial arrangements of those atoms cause different properties. Let us discuss now in details the terms used in crystal systems one by one.

11.4.1 Lattice

The basis may be defined as a group of atoms around a lattice point.

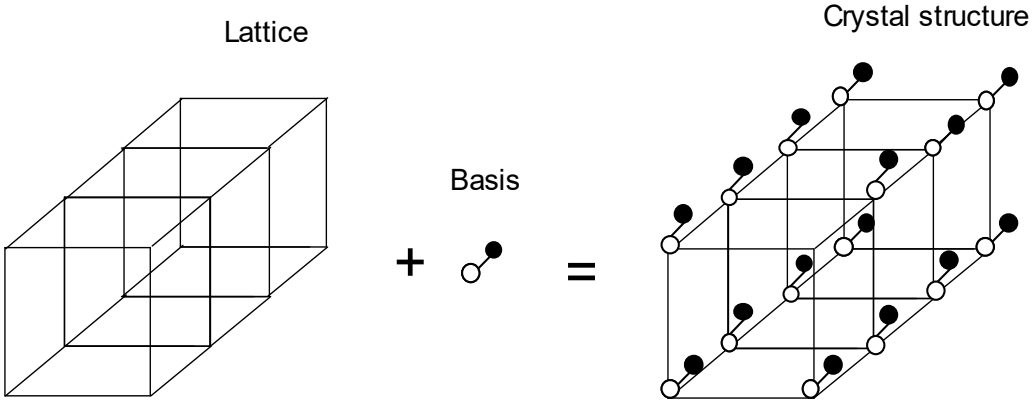
When we study the crystal structure the first and foremost thing is atomic arrangement and symmetry. Crystal structure is a combination of lattice and basis. A periodic arrangement in space of a set of points is lattice. The lattice is defined by three fundamental translation vectors which may or may not lie in same plane. Basis is the building block or group of atoms attached to lattice.

Lattice is an arrangement of geometrical points in a definite pattern in space (Fig. 11.27a). Alternately we can say that a lattice is a regular periodic arrangement of points in space. You must note that lattice point is an imaginary concept but the crystal is real.

Fig. 11.27: Representation of a) lattice in two dimensions, b) basis (with two atoms), c) crystal structures, showing the basis of two atom in relation to lattice points.

By adding basis (atoms) to every lattice points of the lattice the formation of the crystal structure takes place. Basis may have one or more than one atoms. The same may be illustrated in another way as in Fig.11.28.

Mathematically, **Crystal structure = lattice + basis.**



Identical repetition of basis about each lattice point in three dimensions gives a crystal structure.

Fig. 11.28: Crystal structure = lattice + basis.

The crystal lattice has the following characteristics:

(a) Each point in a lattice is called lattice point or lattice site.

(b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.

(c) Lattice points are joined by straight lines to bring out the geometry of the lattice.

11.4.2 Basis

A crystal forms as a group of atoms get arranged in a regular pattern at each lattice point which is called the basis (Fig. 11.27b). It comprises of the atoms, their spacings and orientation. Fig. 11.27c shows the resulting crystal structure. Most crystals have the basis with a few atoms. For example, the basis in iodine crystal is I_2 molecule whereas in the ice crystal, H_2O molecule is the basis.

11.4.3 Unit Cell

The unit cell is the fundamental unit in crystal. In the Fig. 11.29 four rows of spheres representing atoms in a close-packed structure in two dimension. If we join the centres or any other point, say, gaps between the spheres, in three successive rows, we get a cell of the type a, b or c. All the other rows of atoms are a repetition of the first three rows. It is immaterial whether the unit cell chosen is a, b or c, but it is the simplest representation which on repetition in two dimensions will produce the entire assembly as shown in Fig 11.29.

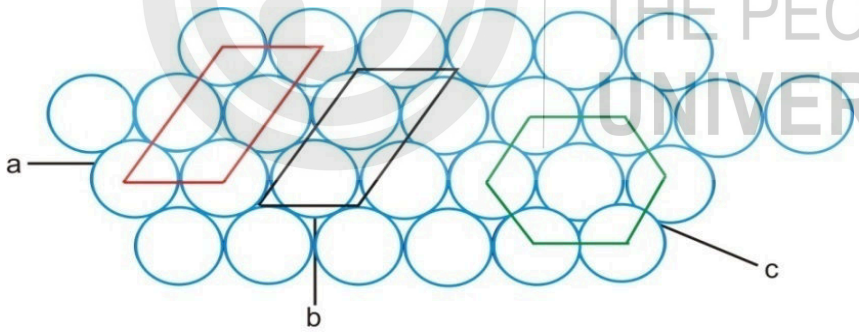


Fig. 11.29: Choice of unit cell.

The situation in a crystal is somewhat similar to the above except that the unit cell and the resulting crystal are three dimensional. Thus, we can say that the simplest repeating unit in a crystal is called a unit cell.

It is true that the unit cell must have some regularity in structure. Would any type of regular shape constitute a unit cell? The answer is no. To understand this, let us consider the covering of a floor space by tiles without leaving a gap. Can we use any type of tiles - triangular, square, pentagonal, hexagonal, heptagonal or octagonal? Again the answer is no.

A crystalline solid can be constructed from a "Unit Cell" plus translational operators.

You can cover the floor space completely with triangular, square or hexagonal tiles but not with pentagonal, heptagonal or octagonal tiles (Fig. 11.30). Note the gaps in the interior floor space when pentagonal, heptagonal or octagonal tiles are used.

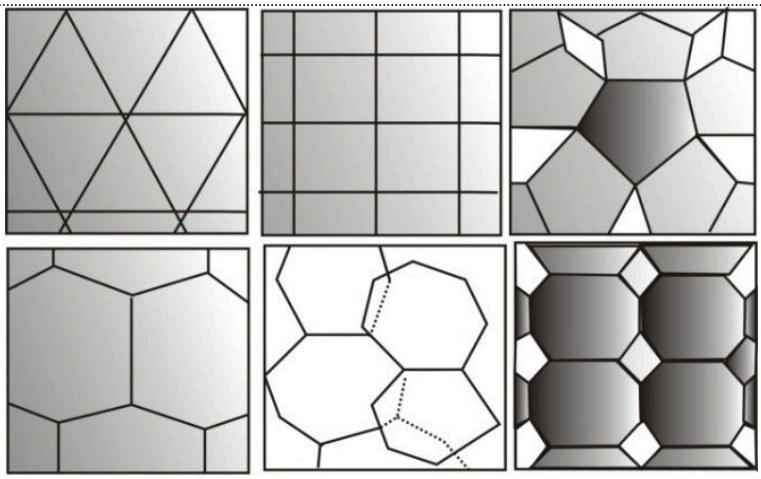


Fig. 11.30: Of all the regular polygons, only triangles, squares and hexagons can fill a floor space without gap.

Just as identical bricks make up a wall, a unit cell is the smallest unit resulting in a crystal. If you displace the unit cell in three dimensions it will produce the crystal. You may have different unit cells to represent the crystal. However, whatever the unit cell, it should be the simplest representation which if repeated in three dimension would produce the crystal. In Fig. 11.31 the illustration of the unit cell and when it is translated one after another along three dimensions is given.

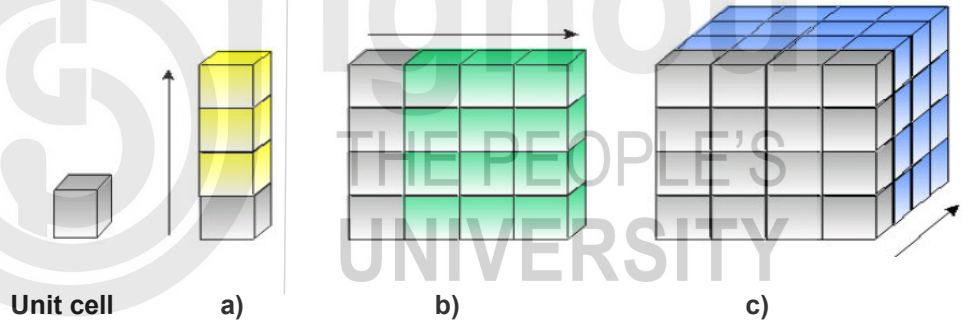


Fig. 11.31: Unit cell when translated one after another along a) first dimension b) second dimension c) third dimension.

In Fig. 11.32, a portion of a three dimensional cubic lattice and its unit cell (three different possibilities) is shown.

A parallelepiped is a three dimensional model of a parallelogram.

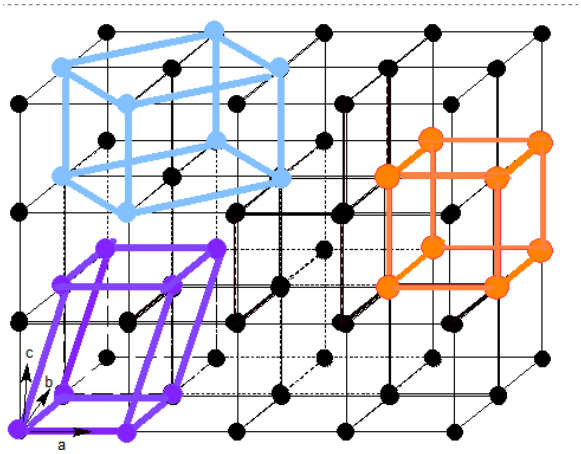
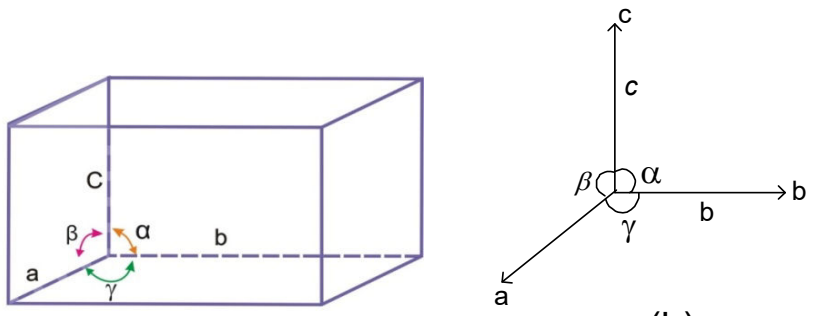


Fig. 11.32: A portion of a three dimensional cubic lattice and its unit cell.

Now let us look at Fig. 11.33, to follow the characteristics of a unit cell:

(i) Its dimensions are along the three edges, a, b and c. These edges may or may not be mutually perpendicular.

(ii) Angles between the edges are α (between b and c), β (between a and c) and γ (between a and b). Thus, a unit cell is characterised by six parameters, a, b, c, α, β and γ.



(a) (b)

Fig. 11.33: Illustration of parameters of a unit cell: a) parallelepiped, three coordinate axes, cell-edge lengths and b) the angles between axes.

So we have discussed the definition of terms used in crystal systems in this section. Before moving to the next section where we discuss the Bravais lattices and crystal systems, try out the following SAQ.

SAQ 4

a) What is the 'basis' of crystal structure? Give your answer with pictorial representation.

b) What is the essential characteristic of a unit cell?

11.5 BRAVAIS LATTICES AND CRYSTAL SYSTEMS

Let us now discuss the details of Bravais lattices and crystal systems. The basic shape of a unit cell is described by a parallelepiped. (Fig.11.32a).A unit cell has three coordinate axes, **a, b** and **c**. The cell-edge lengths in the three axes are a, b and c, respectively (Fig. 11.32a). The angles between **a** and **b** axes, **b** and **c** axes, and **c** and **a** axes are γ, α and β, respectively. The quantities a, b, c, α, β and γ are called lattice parameters (or constants) or unit cell parameters.

Based on the relationship among the axial angles and the edge-lengths, there are seven crystal systems as given in Fig. 11.34 and Table 11.1.

For a cubic crystal, the cell-edge lengths are the same along the three axes.

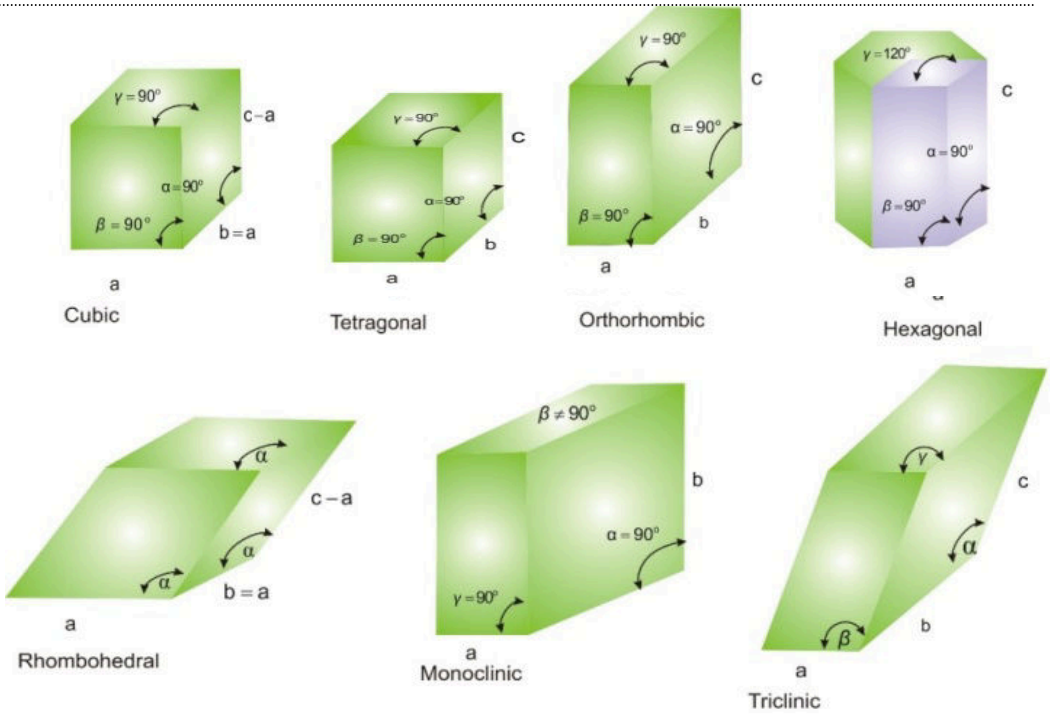


Fig. 11.34: Seven primitive unit cells in crystals.

Table 11.1: The Seven Crystal Systems

Systems	Axes	Angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^o$	NaCl, CsCl
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^o$	TiO_2 (rutile)
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^o$	$CdSO_4$, $HgBr_2$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^o$	$CaCO_3$ (calcite)
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^o; \gamma = 120^o$	SiO_2
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^o; \beta \neq 90^o$	KIO_3, $NaHCO_3$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^o$	$NaHSO_4$, CuF_2

11.5.1 Cubic System Geometry

Of the seven crystal systems, we are particularly interested in cubic system due to its simplicity and symmetry. A cube has the same value for all the three lattice parameters ($a = b = c$). Next let us discuss the geometry of a cube. Now, you imagine that you are sitting in a cubical room. Each wall (including floor and ceiling) of your room is called a face. A cubical room has **six faces** – four walls, the ceiling and the floor. The ceiling and the floor are the horizontal walls!

Each point where three faces of a cube (similar to the point where three walls in your room) meet is called a corner. A cube has **eight corners** and these indicated by A to H in Fig. 11.35a.

Each face has four corners. Try to join the corners of a face diagonally. How many face diagonals do you get? Yes, two. For example, in Fig. 11.35b, the lines AC and BD (obtained by joining A and C or B and D, respectively) are two of the twelve face diagonals in a cube. The centre point of a face where the two face diagonals meet is called a face-centre; one of the six face-centres is indicated by M in Fig. 11.35b.

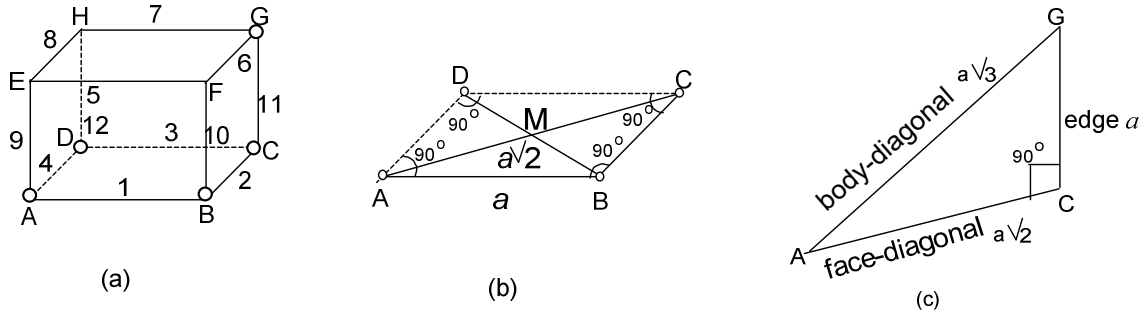


Fig. 11.35: a) Eight corners in a cube indicated by letters A to H - each corner is marked by red dot; twelve edges indicated by number 1 to 12; b) bottom face ABCD of the cube shown; AC and BD are the face diagonals and M is face-centre; c) The right-angled ΔACG.

In ΔABC, $\angle ABC = 90^o$

Length of face diagonal, AC

$= \sqrt{AB^2 + BC^2}$

$= a\sqrt{2}$

In ΔACG, $\angle ACG = 90^o$

(See Fig. 11.34c)

Length of the body diagonal, AG

$= \sqrt{AC^2 + CG^2}$

$= a\sqrt{2a^2 + a^2}$

$= a\sqrt{3}$

By joining any two opposite corners which are not in the same face, a body diagonal is obtained. There are, four body diagonals in a cube - AG, BH, FD and EC in Fig. 11.35a. All the body diagonals meet at the body-centre. The definitions of face, corner, edge, face-centre and body-centre apply to other crystal system also.

11.5.2 Bravais Lattice

In this sub-section Bravais lattices will be discussed. In the Bravais lattice, all atoms/molecules are of the same type and all lattice points are equivalent. Whereas, in the non-Bravais lattice, atoms/ions maybe of different type and some lattice points may not be equivalent.

Some crystal systems, may have one or more types of lattices depending on the number of lattice points.

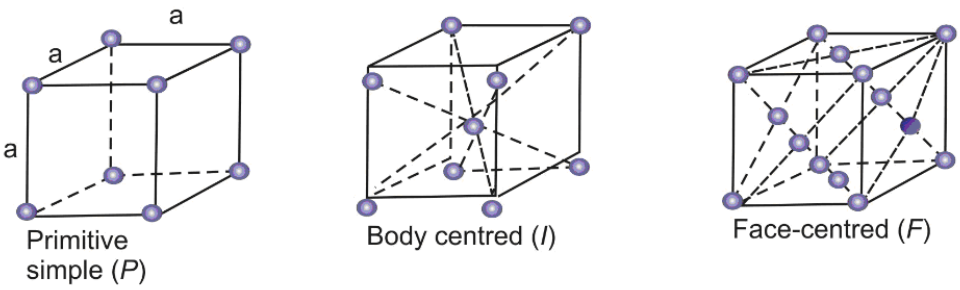
A non-Bravais lattice structure is composed of two or more sub lattices.

- A simple or primitive (*P*) cell is there when the lattice points are only at the eight corners of a unit cell.
- A cell which has lattice points at the eight corners and the six face centres is called a face-centred (*F*) cell.
- A cell that has eight lattice points at the corners and two more at the centres of a pair of any two opposite faces is called an end-centred (*C*) cell.
- If a cell has eight lattice points at the corners and one at the body centre, it is called body-centred(*I*) cell.

In a body-centred unit cell, all the lattice points are the same.

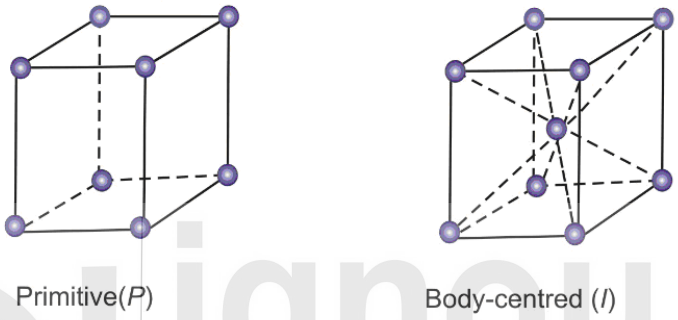
The unit cells of the type *F*, *C* and *I* are called non primitive cells. Based on the presence of lattice points in the seven crystal systems, there are fourteen Bravais lattices in three dimensional arrangement; these are given in Fig. 11.36.

Cubic



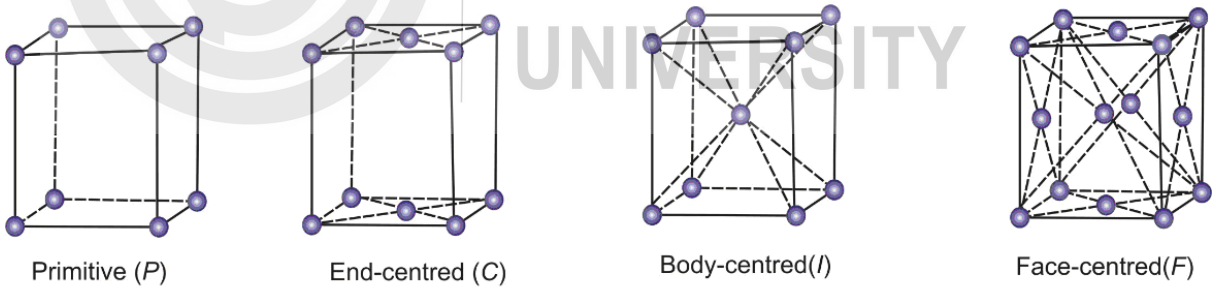
The three cubic lattices: all sides of same length, angles between faces all 90°

Tetragonal



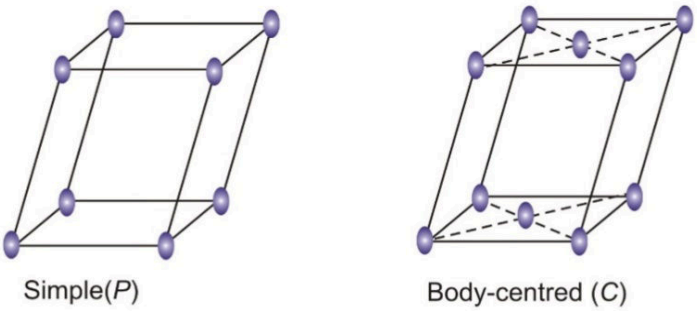
The two tetragonal: one side different in length to the other. two angles between faces all 90°

Orthorhombic



The four orthorhombic unequal sides, all angles between faces equal to 90°

Monoclinic



The two monoclinic lattices: unequal sides. two faces have angles different to 90°

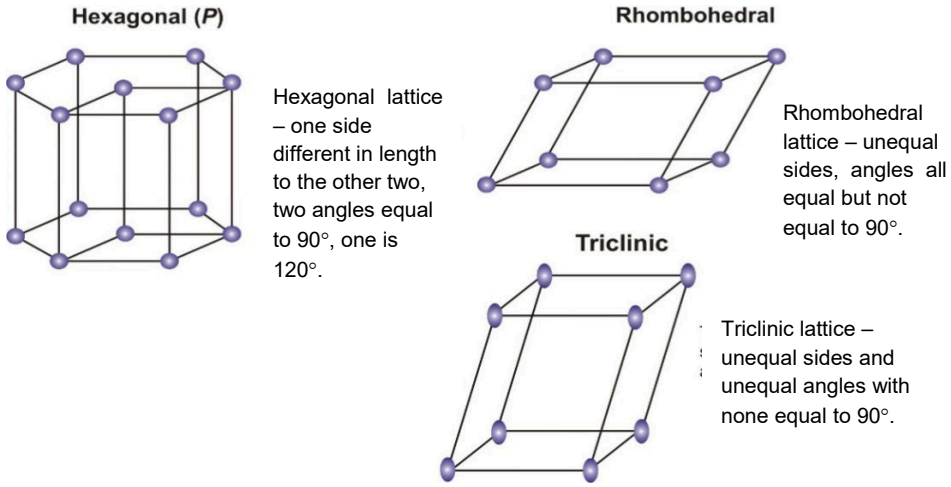


Fig. 11.36: Fourteen Bravais Lattices.

Of these Bravais lattices, we shall consider simple cubic (sc), body-centred cubic (bcc) and face-centred cubic (fcc) lattices only. In the next section, let us see how to represent the crystal planes. Before that, try out the following SAQ.

Crystallographic Laws: Nicholas Steno, a Danish physician and natural scientist, in 1669 discovered Steno's law. While measuring at the same temperature, samples of the same mineral, had constant angles between similar crystal faces regardless of the size or the shape of the crystal.

SAQ 5

Describe the following: simple cubic, body-centred cubic and face-centred cubic crystals.

11.6 LAWS OF CRYSTALLOGRAPHY

In this section we will discuss the Laws of Crystallography, namely the Law of Constancy of Interfacial Angles and the Law of Rational Indices

Steno's Law is the law of Constancy of Interfacial Angles: The law of the constancy of interfacial angles (also called the 'first law of crystallography') states that the angles between the two corresponding crystal faces of a given species are constant, whatever the lateral extension of these faces and the origin of the crystal, and are characteristic of that species (Fig.11.37). Look at Fig. 11.38, which shows how the interfacial angle between faces of crystal can be measured. You can see that the angle is measured between lines drawn perpendicular (or normal) to each face. The Steno's law paved the way for Haüy's law of rational indices.

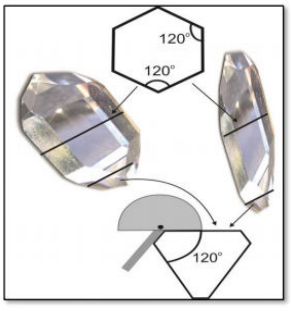


Fig. 11.37: Cross section along prism and rhombohedral faces indicating constancy of interfacial angles even if the quartz crystal is flattened along one axis.

The idea of the law of rational indices was confirmed about a century later when X-ray diffraction studies made the intercept arrangement of particles (atoms, ions molecules) clear.

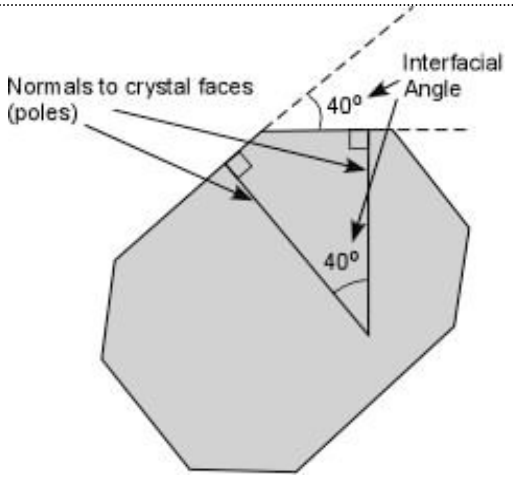


Fig. 11.38: Interfacial angle between two crystal faces.

Hauy's laws of Rational intercepts or Indices: This law states that the intercepts of planes of various faces of a crystal are integral multiples of the intercepts by the standard (or unit) plane.

Look at the Fig. 11.39 below, OX, OY and OZ may be taken as three crystallographic axes and ABC the unit plane. The unit intercepts may then be taken as a, b and c as shown in Fig. 11.39. If any plane PQR cuts the three axes with intercepts, p, q and r, then according to the law of rational intercept, OP = p = *x*a, OR = q = *y*b, OQ = r = *z*c, where intercepts of unit plane ABC on three axes are OA = a, OB = b, OC = c.

The multiples *x, y* and *z* are small whole numbers or fractions.

The three ratios *x, y* and *z* discussed above are known as the Weiss indices of the plane. These are difficult to use and hence were replaced by Miller indices.

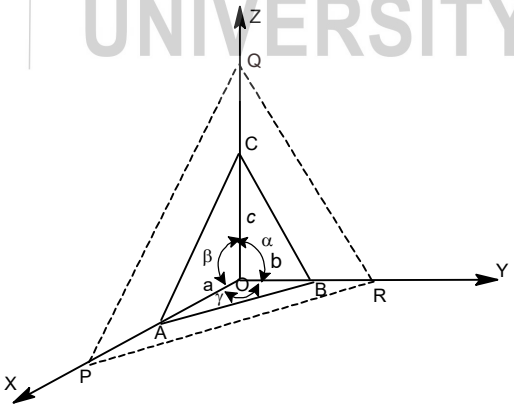


Fig. 11.39: Law of rational indices.

Hence, the ratio between the intercepts on the axes of different faces of a crystal can always be expressed by rational numbers as 1: 2, 1: 3, 1: 4. Thus the laws of crystallography have been discussed. Next, in the following section crystal planes and Miller indices will be discussed. Before that try out the following SAQ.

SAQ 6

What is the law of constancy of interfacial angles?

11.7 CRYSTAL PLANES AND MILLER INDICES

In this section you are going to learn about crystal planes and Miller indices. You already have the idea of Weiss indices from the previous section. Now, let us first understand how these two terms are related. Miller indices are more commonly used as they have advantage over the Weiss indices. The Miller indices of a plane are obtained by taking the reciprocals of Weiss indices (i.e. *x, y , z*) and when it is needed, the reciprocals are made simple (small) integers by multiplying then by the smallest number (i.e. least common multiple). So if Weiss indices are *x, y , z* then Miller indices are $\frac{1}{x},\frac{1}{y},\frac{1}{z}$.

Crystal planes are represented by certain numbers which are the Miller indices. Following are the ways in which these indices are determined:

i) A crystal plane on the axes, **a, b** and **c** in cell-edge lengths, *a, b* and *c* should be taken and you have to find the intercepts. Let us assume that a crystal plane makes intercepts 3*a*, 2*b*, 2*c* as shown in Fig.11.40.

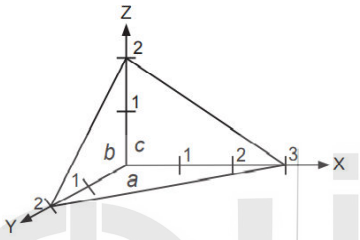


Fig. 11.40: Miller indices.

ii) Next you should divide the intercepts by the respective cell-edge (*a, b* and *c*). If you take the crystal plane in Fig. 11.40, this step gives $\frac{3a}{a},\frac{2b}{b},\frac{2c}{c}$, i.e., 3, 2, 2. These numbers are Weiss indices.

iii) Now, take the reciprocal of the Weiss indices. Corresponding to Fig. 11.40, this step gives $\frac{1}{3},\frac{1}{2},\frac{1}{2}$ as the answer.

iv) Lastly take the fractions given above and bring them to the smallest integers having the same ratio. You should enclose these numbers in parentheses without comma; so you get the Miller indices of the given crystal plane. What are the Miller indices of the figure given in Fig.11.40? They are (233) which we call two three three plane.

Miller indices are generally represented as (*hkl*). Here you may note that one set of Miller indices represents a series of equivalent and parallel planes. So if the planes have intercepts 3*a,* 2*b*, 2*c* or a, $\frac{2b}{3},\frac{2c}{3}$ or 9*a*, 6*b*, 6*c*, etc., they are all represented by a set of Miller indices (233). In general, Miller indices of crystal faces are small integers, as well as zero.

Whenever a face is parallel to an axis, theoretically it has the intercept equal to ∞. Now let us understand this with the following illustration, let us draw a crystal plane of a cubic cell which makes intercepts a, ∞, ∞. That is, the plane is parallel to **b** and **c** axes. Applying the above steps in order, we get the Miller

indices for this plane as (100). Remember $\frac{1}{\infty}$ is equal to zero. The origin (O) and the axes directions are shown in Fig. 11.41a. The (100) plane is indicated in Fig. 11.41b. Similarly, corresponding to the planes with intercepts a, a, ∞ and *a, a, a,* the Miller indices are (110) and (111), respectively; these are shown in Figs. 11.41 c and d, respectively.

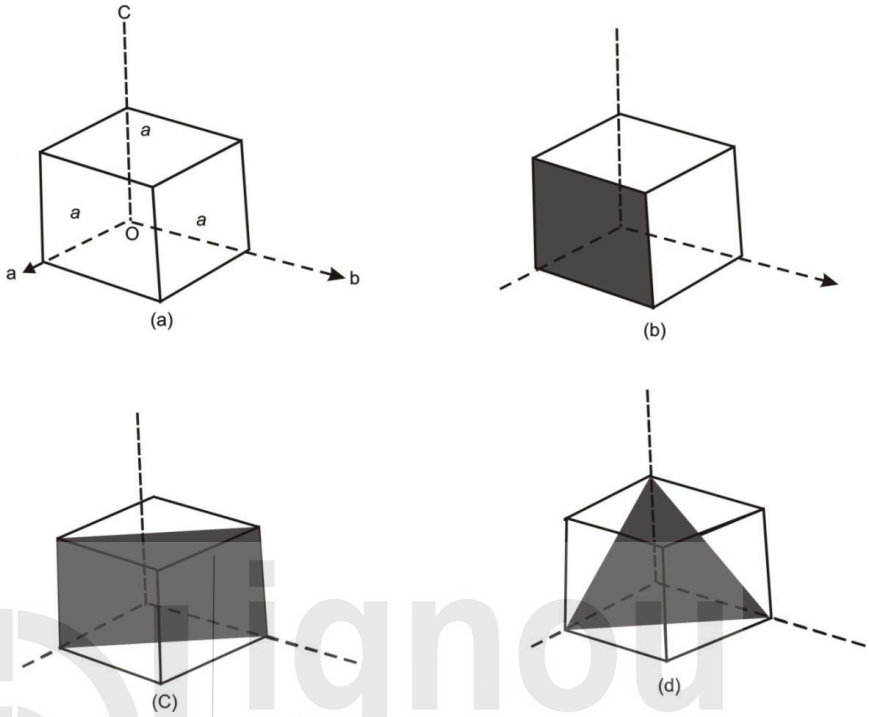


Fig. 11.41: a) The origin, O, the axes and cell-edge length a in a cubic cell; b) (100) plane; c) (110) plane; d) (111) plane.

We can calculate the distance between the adjacent planes labeled by the same Miller indices (*hkl),* but no generalised formula can be written. The actual formula in a particular case would depend upon the crystal structure. For example, the distance d_{hkl} between the (*hkl)* planes of a cubic lattice is given by,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad \ldots (11.1)$$

Where *a* is the cell-edge length of the cell and (*hkl)* the Miller indices. Thus, in sodium chloride crystal, the cell-edge length is 5.63 X 10^{-10} m. The distance between (111) planes is given by Eq. 11.1,

$$d_{111} = \frac{5.63\times10^{-10}\text{m}}{\sqrt{1^2+1^2+1^2}} = \frac{5.63\times10^{-10}\text{m}}{\sqrt{3}} = 3.25\times10^{-10}\text{m}$$

Eq. 11.1 could be used only for cubic crystals. For an orthorhombic cell, the equation for d_{hkl} turns out to be,

$$\frac{1}{d^2{}_{hkl}} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2 \qquad \ldots(11.2)$$

Using Eq. 11.2, work out the following SAQ.

SAQ 7

An orthorhombic crystal has the following parameters:

$a = 8.2 \times 10^{-10}$ m; $b = 9.4 \times 10^{-10}$ m; $c = 7.5 \times 10^{-10}$ m.

What is the distance between (123) planes?

11.8 SUMMARY

In this unit, we have briefly described solid substances, both amorphous and crystalline. We have also given a hint at the usefulness of crystal studies. We summarise below what we have studied so far:

- The different types of solids, amorphous and crystalline were discussed,
- The five symmetry elements were dealt with,
- The terms-lattice, basis and unit cell-were explained,
- Seven crystal systems and fourteen Bravais lattices were discussed,
- The laws of crystallography, law of constancy of interfacial angles and law of rational indices were discussed, and
- The crystal planes in terms of Weiss and Miller indices were explained.

11.9 TERMINAL QUESTIONS

1. What are solids?
2. Will the following characteristic favour the formation of an amorphous solid? Justify your answers.
   a) slow cooling of pure molten material
   b) weak intermolecular attractive forces
3. Show that for a simple cubic cell, the ratio of the volume occupied to the volume of the unit cell is 0.52.(Hint : Assume (i) atoms are spherical and (ii) they touch along the cell-edge, i.e., radius = a/2).
4. In the following cases. mark '√' for correct statement and 'X' for wrong statement :
   i) The Miller indices of a crystal plane which makes intercepts 2*a*, 3*b*, 2*c* are (232).
   ii) The basis in ice crystal is H_2O molecule.
   iii) A cube has twelve edges.
   iv) The unit cell of caesium chloride crystal contains two formula units of CsCl.
5. What are the separations of the planes with Miller indices (111), (211) and (100) in a cubic crystal having cell-edge length of 432 pm?
6. Identify the type of attractive forces (or bonding) mainly responsible for crystal bonding in the following cases:
   i) diamond ii) potassium bromide iii) aluminium iv) helium

11.10 ANSWERS

Self Assessment Questions

1. i) The comparison:

Terms of	Solid state	liquid states
rigidity of structure	Rigid	Not rigid
long-range order	Yes	No
short-range order	Yes	Yes

ii)

Property	Crystalline solids	Amorphous solids
Shape	Have definite characteristic geometrical shape	Have irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces thereafter generated surfaces are plain and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Enthalpy of fusion	Have a definite and characteristic enthalpy of fusion	Do not have fixed enthalpy of fusion
Anisotropy	Anisotropic	Isotropic
Nature	True solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order as well as short range order	Only short range order.

iii) The amorphous solids behave like a supercooled liquid.

iv) The initial solid contained the desired compound in an amorphous state, as indicated by the wide temperature range over which melting occurred. Slow cooling of the liquid caused it to crystallize, as evidenced by the sharp second melting point observed at the expected temperature.

2. i) Molecular solids - P_4O_{10}, I_2; Covalent solids- Graphite, SiC;
Metallic solids- Brass, Ag; Ionic solids- MgO, LiBr.

ii) See Example 11.2.

iii) Dispersion forces

iv) a) Diamond is having covalent bonds whereas copper has metallic bond (electron-sea model).

b) KNO_3 has electrostatic force of attraction, whereas SiC has covalent bonding.

3.

S.No.	Symmetry Elements	Schoenflies notation
1.	Identity	E
2.	*n*-Fold Rotations	C_n
3.	Reflection	$\sigma_h, \sigma_v, \sigma_d$
4.	Inversion	*i*
5.	Improper *n*-Fold Rotation	S_n

4. a) The basis may be defined if we have a group of atoms around a lattice point (Fig. 11.27).

   b) A unit cell is the smallest unit chosen which when repeats itself three dimensions generates the crystal lattice.

5. Simple cubic - lattice points at the eight corners only;

   bcc - lattice points at the eight corners and the body-centre;

   fcc- lattice points at the eight corners and the six face-centres.

6. The law of the constancy of interfacial angles (also called the 'first law of crystallography') states that the angles between the two corresponding crystal faces of a given species are constant, whatever the lateral extension of these faces and the origin of the crystal, and are characteristic of that species.

7. $d_{123} = 2.132 \times 10^{-10}$ m

Terminal Questions

1) Solids have definite shape and volume. Solids are those substances in which the neighbouring particles (molecules, atoms or ions) are close enough for even van der Waals forces to operate.

2) a. Slow cooling of pure molten material - does not form amorphous material as this condition favours formation of pure crystals.

   b. weak intermolecular attractive forces – favour of formation of amorphous solids as they have short range order.

3) Since the spheres touch along the edge, the cell-edge length (*a*) is twice the radius of a sphere ***(r),*** i.e., $r = a/2$.
The volume of a sphere $= 4\pi r^3/3 = \pi a^3/6$
A simple cubic lattice has one net sphere only per unit cell. Hence,

volume occupied in a unit cell $= \pi a^3/6$

But the volume of the unit cell $= a^3$

Fraction of the volume filled = (Volume occupied)/(unit cell volume)

$$= (\pi a^3)/6a^3 = 0.52$$

4) (i) X (ii) √ (iii)√ (iv) X.

5) 2.49 X 10^{-10} m; 1.76 X 10^{-10} m and 4.32 X 10^{-10} m.

6) i) Covalent bonding ii) Electrostatic forces (ionic bonding)

iii) Metallic bonding iv) van der waals interaction.

References

https://symotter.org/

https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Book%3A_Symmetry_(Vallance)/02._Symmetry_operations_and_symmetry_elements

https://nroer.gov.in/home/file/5682818e81fccb068727ff86?selected=5652f5e281fccb0b8ec652ff

https://opentextbc.ca/chemistry/chapter/10-6-lattice-structures-in-crystalline-solids/

Sources of Figures

Fig.11.2: Wikipedia; Fig.11.5: Wikimedia; Fig.11.10, Fig.11.12: https://opentextbc.ca/chemistry/chapter/10-5-the-solid-state-of-matter/, Fig.11.13: https://www.open.edu/openlearncreate/

UNIT 12

SOLIDS-II

Structure

12.1 INTRODUCTION

In the previous unit, you have learnt about those solid substances which can be classified as crystals as we dealt with the different types of solids, namely amorphous and crystalline. Also, you have learnt about the five symmetry elements, lattice, basis, unit cell, seven crystal systems, fourteen Bravais lattices, the laws of crystallography, namely, law of constancy of interfacial angles and law of rational indices. Thereupon you have studied the crystal planes in terms of Miller indices. In this unit we will be discussing X-rays diffraction and Bragg's Law along with characteristics of cubic unit cells. Thereafter we will be dealing with defects in crystals and at the end you will learn about glasses and liquid crystals.

1895 – Willhelm Röngten discovered X-rays.

Expected Learning Outcomes

After studying this unit, you should be able to:

- state Bragg's law;
- describe the determination of crystal structure by X-ray diffraction method;

- ❖ compair the characteristics of different types of cubic unit cell;
- ❖ explain the defects in crystals; and
- ❖ describe glasses and liquid crystals.

12.2 X-RAYS DIFFRACTION

In 1912, Max von Laue at University of Munich in Germany suggested that since the order of the magnitude of the wavelength of X-rays and the crystal lattice distances are the same, we should expect diffraction of X-rays by crystals. This was soon confirmed experimentally by Friedrich and Knipping.

X-rays are reflected from the atoms in a solid crystal, the phenomenon is known as diffraction. Crystal structures are generally determined with the help of X-rays. Even radiations having similar properties - like a beam of neutrons or electrons could also be used. But we will limit the discussion to the use of X-rays only. X-rays get diffracted by a crystal because the wavelength of X-rays matches the inter-atomic spacing in the crystals. These have wavelength of the order of 1 Å (10^{-8} cm). This X-ray diffraction technique is based on the elastic scattering of X-rays from structures that have long range order (solid crystals). Let us explain the principle of diffraction, in general, and the diffraction of X-rays by crystals in particular.

12.2.1 Principle of Diffraction

The diffracted X-rays generate a pattern which gives the structural orientation of each atom in a given compound. Diffraction pattern arises due to interference of waves. When the waves are in phase, the intensity is increased, (this is known as constructive interference; Fig. 12.1a) and when they are out of phase (known as destructive interference), the intensity is decreased (Fig. 12.1b). If there are two waves starting from a common source, their **phase difference** will be directly proportional to their path difference.

The amplitude is directly related to the intensity of the beam.

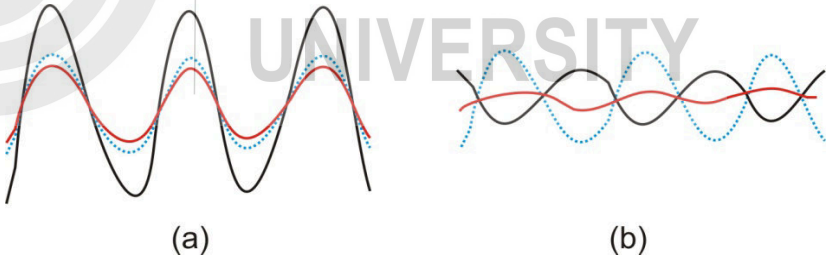


Fig. 12.1: Two waves (shown by dotted and solid lines) giving rise to a resultant (shown by red colour): a) constructive interference (in-phase wave - greater amplitude); b) destructive interference (out-of-phase wave - smaller amplitude).

X-ray crystallography is a scientific method used to determine the arrangement of atoms of a solid crystal in 3-D space.

The bending of light around the edges of an obstacle is called diffraction. Consider a beam of light passing through two slits (S_1 and S_2), cut near to each other on a screen and falling on a second screen placed beyond the slits (Fig. 12.2). A series of dark and bright bands are observed on the screen, which are due to the constructive and destructive interference of the two beams passing through the two slits. When their amplitudes are in phase, the intensity is enhanced and when their amplitudes are out-of-phase, the intensity is decreased. Whether the beams are in-phase or out-of-phase will depend on the path difference between the two rays. The diffraction pattern is considered

the fingerprint of the crystal because each crystal structure produce unique diffraction patterns.

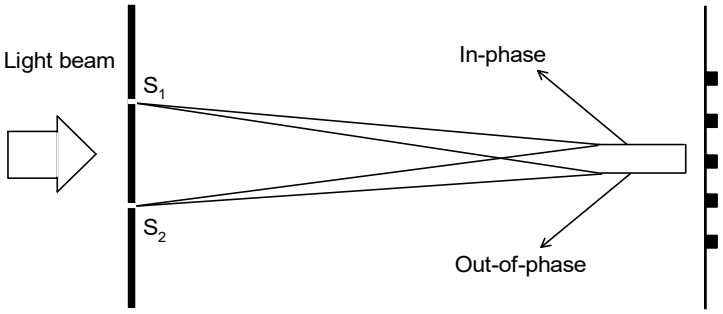


Fig. 12.2: In-phase and out-of-phase waves.

The bright and dark spots which appear on a photographic film are called diffraction pattern; but diffraction phenomenon is just the bending of light around the edges of an obstacle.

12.2.2 Bragg's Law

W.L. Bragg showed in the early 19th century that diffracted X-rays behave as if they were 'reflected' from the different planes within crystals. Bragg's law is the theoretical basis of X-ray diffractometer. If the path difference between the two rays is an integral multiple (n =1, 2, 3,…) of the wavelength of X-rays, then the two rays will be in-phase and the diffraction pattern will be bright (i.e. with enhanced intensity).

Bragg's law orequation assumes that incident X-rays are reflected just as in a mirror. such that the angle of incidence is equal to the angle of reflection. This assumption is convincing only because it explains the experimental results.

Bragg's law gives the general relation between the wave length of the incident X-rays, angle of incidence and the spacing between two crystal planes for diffraction to occur. It is expressed as:

$$n\lambda = 2d \sin \theta \qquad \ldots (12.1)$$

Eq. 12.1 is known as Bragg's law or Bragg's equation. It is useful in crystal structure determination. In this equation, λ is the wavelength of X-rays used, d is the distance or the spacing between the planes. The value of n gives the order of reflection.

If n = 1, it is first-order reflection.

If n = 2, it is second-order reflection and so on.

After reading the above section you should be able to solve the following SAQ.

SAQ 1

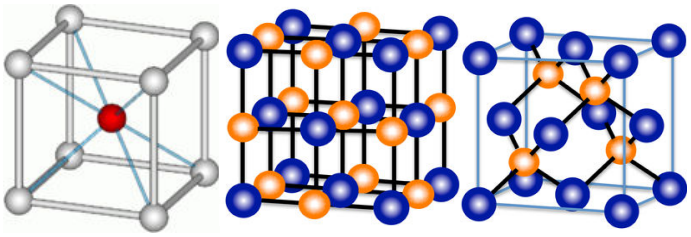
a) If the separation between the lattice layers in crystal is 404 pm and the wavelength of X-rays used is 1124 pm, what would be angle of incidence at which reflection would occur? Assume n = 1.

b) Does XRD help in determining the crystal structure and molecular formula of a crystalline compound?

12.3 CHARACTERISTICS OF CUBIC UNIT CELLS

In this section you will study the characteristics of the unit cell.

The structures of cubic unit cells for some salts are shown below.



CsCl NaCl ZnS

Fig. 12.3: Structures of CsCl, NaCl and ZnS

12.3.1 Number of Net Atoms in a Cubic Unit Cell

You have learnt in the previous unit that crystal lattice is made up of many unit cells and each of its points is occupied by its constituent particles (atom, molecule or ion). In this section we will discuss only three types of cubic unit cells. We also make the assumption that its constituent particles are atoms. First let us calculate the number of atoms belonging to a unit cell in different types of cubic cell.

Primitive cubic unit cell

It has atoms only at its corners. Look at Fig. 12.4, here eight adjacent cubic unit cells share one atom which is at a corner. Four unit cells in the same layer and four unit cells of the upper (or lower) layer are there.

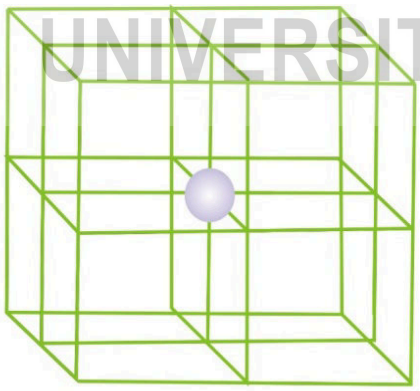


Fig. 12.4: Eight unit cells share one corner atom in a simple cubic unit cell.

Therefore 1/8th of an atom (or molecule or ion) belongs to a particular unit cell. In Fig. 12.5, the primitive cubic unit cell has been depicted in three different ways. Look at Fig. 12.5a, where, each of the dark-shaded spheres depicts the centre of the particle. It does not signify its actual size. This sort of structure is known as open structure. Fig.12.5 (b) depicts the space-filling model of the primitive cubic unit cell and Fig. 12.5(c) depicts its unit cell with actual portions of atoms. Each cubic unit cell has 8 atoms on its corners and each corner atom contributes 1/8th portion to the unit cell, so the total number of atoms in one unit cell is 8×(1/8) = 1 atom.

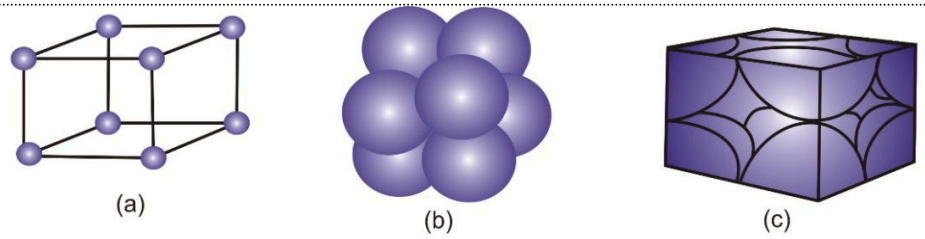


Fig. 12.5: A primitive cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atom belonging to one unit cell.

The number of other particles that each particle in a crystalline solid is in contact with is known as its **coordination number**. For an atom in a simple cubic array, the coordination number is, therefore, six. This is depicted in Fig. 12.6.

Open structures are preferred to show unit cells as it is simpler to follow the arrangement of particles here.

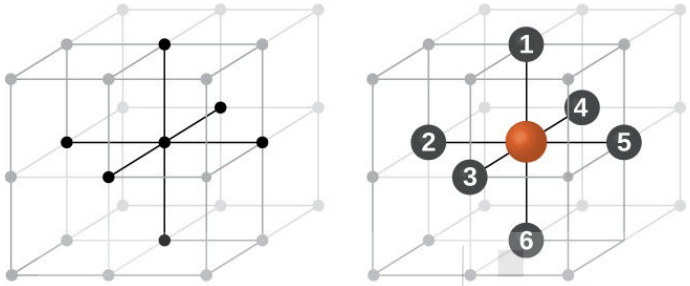


Fig. 12.6: An atom in a simple cubic lattice structure contacts six other atoms, so it has a coordination number of six.

Body-centred cubic (bcc) unit cell

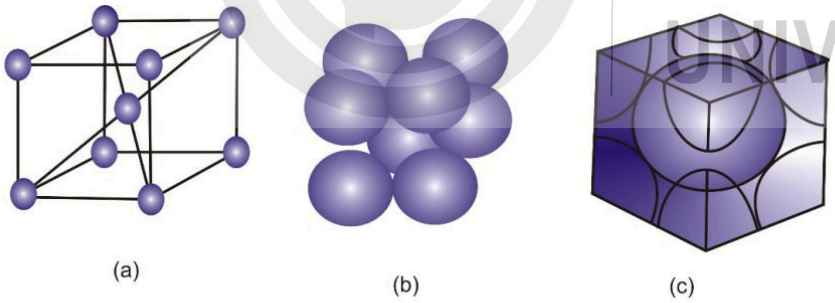


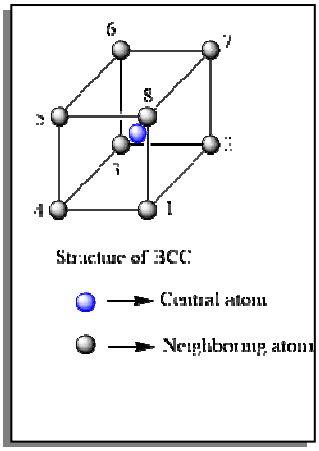
Fig. 12.7: A body-centred cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.

Look at Fig. 12.7a, it is a body-centred cubic unit cell. Fig. 12.7 (a), (b), (c) depicts open structure, space-filling structure and the actual portions of atoms belonging to one unit cell. You can see that an atom at the body-centre of a unit cell belongs to that cell only (Fig. 12.7a). An atom at the corner of a unit cell will be shared by eight unit cells. Hence, we can say that one eighth of an atom in a corner belongs to a particular unit cell. A body-centred cubic unit cell has an atom in each corner of the unit cell and one atom at its body centre. Therefore in body-centred cubic unit cell:

i) 8 corners × 1/8 per unit cell = 8 × 1/8 = 1 atom

ii) 1 body-centred atom= 1 × 1 = 1 atom

So, there are two atoms per unit cell of body-centred cubic structure.



Atoms in bcc arrangements are much more efficiently packed than in a simple cubic structure, occupying about 68% of the total volume. Isomorphous metals with a bcc structure include K, Ba, Cr, Mo, W, and Fe at room temperature. In Fig. 12.3 is given CsCl, which has a bcc structure.

Similar to simple cubic cell if we try to find out the coordination number of body-centred cubic cell we find that the central atom is connected to eight neighbouring atoms and so its coordination number is eight.

Fig. 12.8 depicts (a) open structure (b) space-filling model and (c) the unit cell with actual portions of atoms.

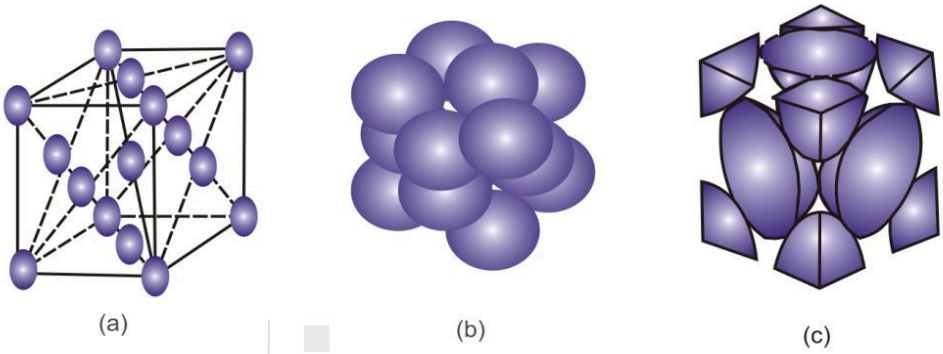


Fig. 12.8: A face-centred cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms

In a face-centred cubic (fcc) unit cell, atoms are there at all the corners and also at the centres of all the faces of the cube. Look at Fig. 12.9, you can see that each atom which is there at the face-centre is common for two adjacent unit cells and only half of each atom belongs to a unit cell.

(Elements or compounds that crystallize with the same structure are said to be **isomorphous**.)

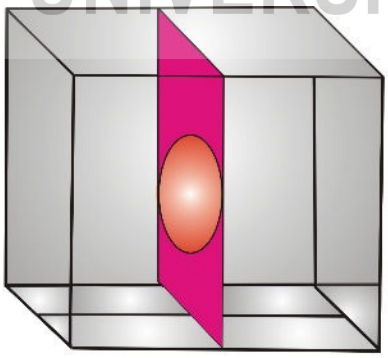


Fig. 12.9: An atom at face centre of unit cell is shared between two unit cells.

Thus, in a face-centred cubic (fcc) unit cell:

(i) 8 corners atoms ×1/8 atom per unit cell =8×1/8 = 1atom

(ii) 6 face-centred atoms×1/2 atom per unit cell = 6 ×1/2= 3 atoms

∴ Total number of atoms per unit cell = 4 atoms

In Fig 12.8, you can see that the coordination of the central atom in a fcc unit cell will be 12. Also, look at Fig. 12.3 where NaCl and ZnS both have fcc structure.

Close Packing in crystalline solids in one dimension

In one dimension close packing, spheres are arranged in a row so that the neighbouring atoms are in contact with each other. The number of atoms which are the nearest neighbours is its coordination number. In one dimensional close packing, coordination number is two as in Fig. 12.10.

Fig. 12.10: Close packing of spheres in one dimension

Close Packing in Two Dimensions:

Now let us see the close packing in two dimensions. Two dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres. There are two ways in which this can be achieved.

(a) Square close packing: Look at Fig. 12.11. See, the first row, then look at the spheres of the second row. They are exactly above those of the first row. If we call the first row as 'A' type row, then the second row is also of 'A' type as both are same type. In this way more rows may be there to obtain AAA type of arrangement as shown in Fig. 12.11.

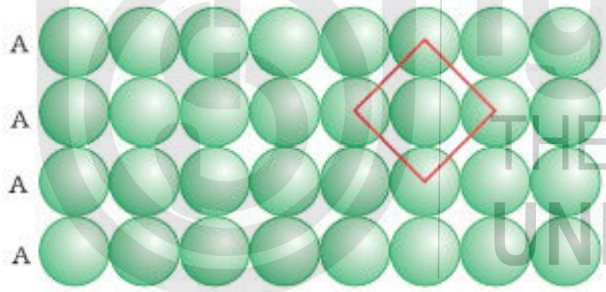


Fig. 12.11: Square close packing of spheres in two dimensions. (AAA type of arrangement).

Now take any sphere in Fig. 12.11, how many spheres are in contact with it? Yes, four of its neighbours are in contact. So, **the two dimensional coordination number is 4**. Also, if the centres of these 4 immediate neighbouring spheres are joined, a square is formed as marked in Fig.12.11. Hence this packing is called square close packing.

(b) Hexagonal close packing: Here the situation is different. Try to place the second row above the depressions of the first row. Here if you call arrangement of spheres in the first row as 'A' type, the second row is different and may be called 'B' type. This arrangement is of ABAB type as shown in Fig. 12.12. The closest packing of spheres in two dimensions has hexagonal symmetry where every sphere has six nearest neighbours. Each atom has six nearest neighbors in hexagonal close packing. Its two dimensional coordination number is 6 and thereby it is more efficient than square close packing.

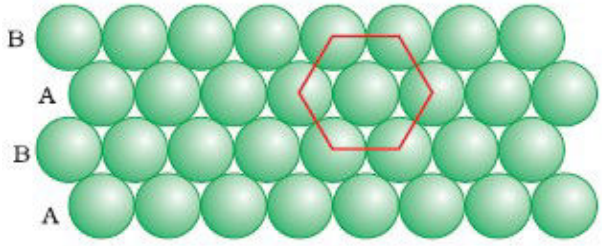


Fig. 12.12: Hexagonal close packing of spheres in two dimensions (ABAB type arrangement).

Close Packing in Three Dimensions:

Three dimensional close packing from two dimensional hexagonal close packed layers is to be discussed in this section. Here first the second layer comes over the first layer such that the spheres of the second layer fit into the depressions in the first layer.

(a) Look at Fig. 12.13. In the first layer the spheres are arranged in a hexagonal manner in which each sphere is in contact with six other spheres. This layer has triangular voids which are of two types. Apex of some triangular voids are pointing upwards while those of others downwards. There are alternate rows of these two types of triangular voids.

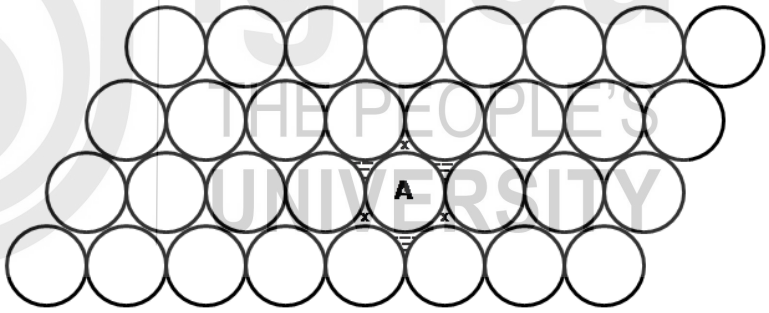


Fig. 12.13: Close packing of spheres of first layer in a hexagonal manner.

(b) For a close packed structure, the spheres of the second layer occupy triangular voids (depressions) of one type. Spheres of the second layer are aligned differently, and thus this layer is called B. When a sphere of the second layer is above the void of the first layer (or vice versa), these voids are called tetrahedral voids(as a tetrahedron is formed when the centres of these four spheres are joined). They have been marked as 'T' in Fig.12.14. One such void has been shown separately in Fig. 12.15. You will find that some triangular voids in the second layer are above the triangular voids in the first layer. But there is one difference to be noted. The triangular shapes of these voids do not overlap. The apex of the triangles of one layer point upwards and those of the other layer point downwards. These voids have been marked as 'O' in Fig.12.14 as they are surrounded by six spheres and they are called octahedral voids. You can see such a void separately in Fig.12.15.The number of spheres in the close packed structure determine the number of tetrahedral and octahedral voids.

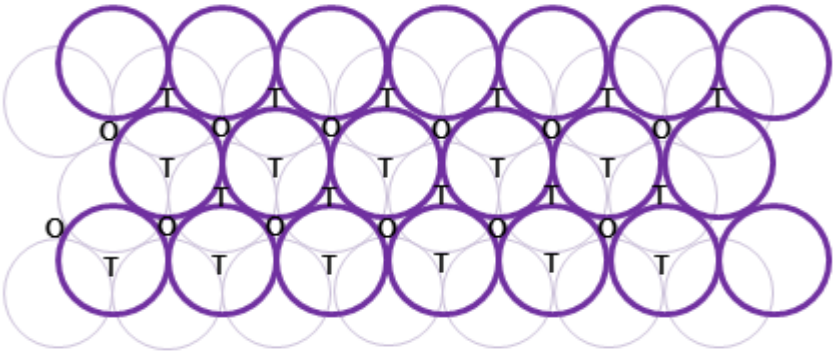


Fig. 12.14: A stack of two layers of close packed spheres and voids generated in them. (T = Tetrahedral void; O = Octahedral void)

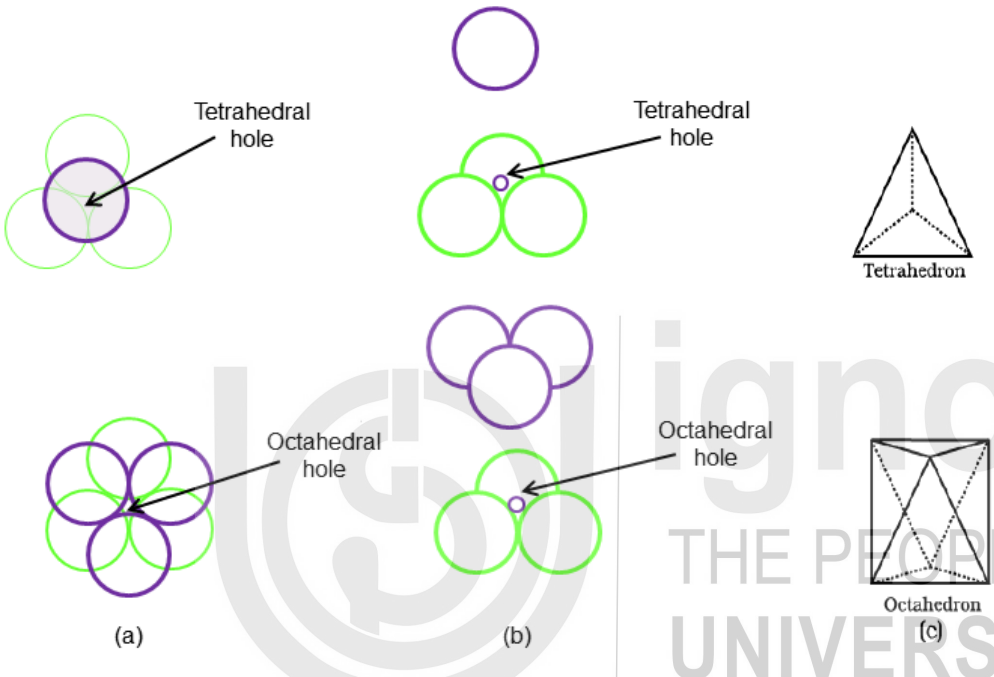


Fig 12.15: Tetrahedral and octahedral voids (a) top view (b) exploded side view and (c) geometrical shape of the void.

Let us assume that the number of close packed spheres is N, then,

The number of octahedral voids generated = N

The number of tetrahedral voids generated = 2N

(c) When the third layer is placed over the second layer then, there may be two cases:

i) Look at Fig.12.16(a). The spheres of the third layer may cover tetrahedral voids of the second layer. In this case the spheres of the third layer and first layer becomes aligned with each other. So you see in alternate layers the same pattern appears again. This pattern is often written as ABAB ..... pattern. This structure results in hexagonal close packed (hcp) structure. Here each sphere is in contact with twelve other spheres, six spheres surrounding it in the same layer and three spheres each of the two adjoining layers. So here the coordination number is 12.

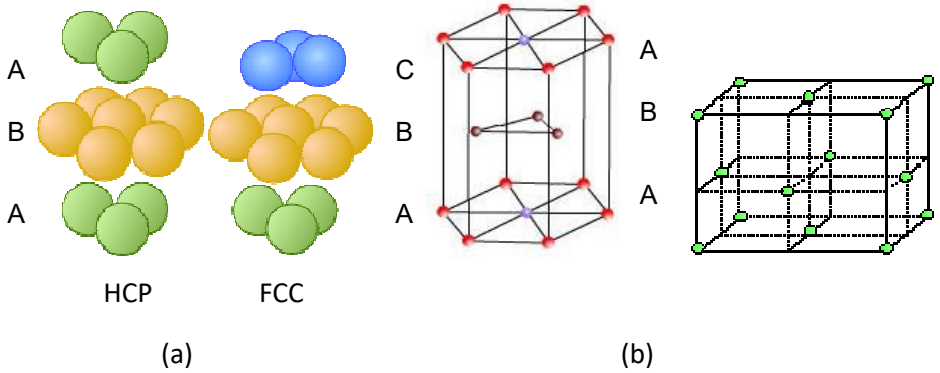


Fig. 12.16:(a) Hexagonal packing(HCP) and cubic close-packing(CCP or FCC) exploded view showing stacking of layers of atoms and (b) geometry of packing.

(ii) Covering Octahedral Voids (Cubic closed packing): When the third layer places itself above the second layer, its spheres may cover the octahedral voids. In this case, the spheres of the third layer do not form alignment with the first or the second layer. So it is a new arrangement which may be called "C' type. Only when fourth layer is placed, its spheres are aligned with layer A. This leads to the arrangement **ABCABCABC**……..as shown in Fig. 12.17a. The resulting three dimensional structure is called cubic closed packed (ccp) (or) face centred cubic (fcc) structure as shown in Fig. 12.17b. Here each sphere is in contact with twelve other spheres, so here coordination number is 12.

These two diagrams in Fig. 12.16 (a) that show exploded views of the vertical stacking further illustrate the rather small fundamental difference between these two arrangements— but, as you will see below, they have widely divergent structural consequences. Note the opposite orientations of the A and C layers.

Fig. 12.17 shows the formation of a face centred cubic (fcc) unit cell as a result of ABCABC…….. type of arrangement.

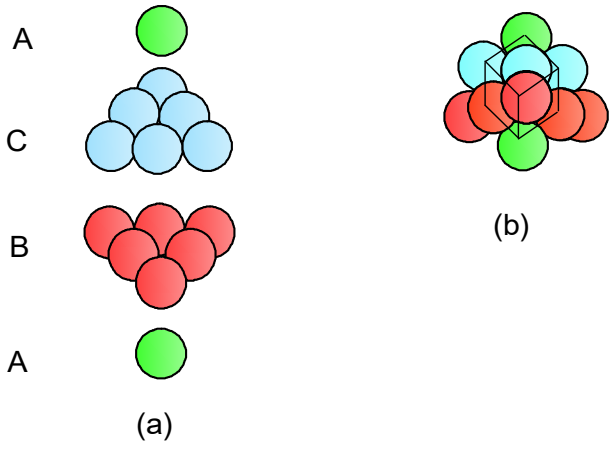


Fig. 12.17: (a) ABCABC... arrangement of layers when octahedral void is covered (b) fragment of structure formed by this arrangement resulting in cubic closed packed (ccp) or face centred cubic (fcc) structure.

12.4 Formula of a Compound and the Number of Voids Filled

You have already learnt that close packed particles form either ccp or hcp structure. In these structures two types of voids are generated. You must note that the number of octahedral voids present in a lattice is equal to the number of close packed particles. But the number of tetrahedral voids in it is two times this number. Now the question is in ionic solids, anions or cations, which of them occupy the voids? Well, the bigger ions (the anions) form the close packed structure and the smaller ions (the cations) occupy the voids. Tetrahedral voids are occupied by small cations and octahedral voids are occupied by not so small ones.

Remember that all octahedral or tetrahedral voids are not occupied. The fraction of the octahedral or tetrahedral voids that are occupied is dependent on the chemical formula of the compound. At this stage you should go through the examples given below to understand the above concepts in a better way.

EXAMPLE 12.1

Two elements X and Y form a compound. Atoms of the element Y (as anions) make ccp and those of the element X (as cations) place themselves in all the octahedral voids. What is the formula of the compound?

SOLUTION:

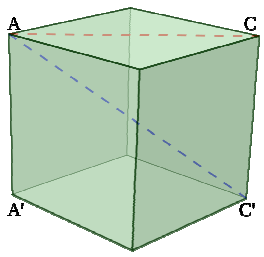
The element Y forms the ccp lattice. So the number of octahedral voids generated is the same as the number of atoms of Y present in it. Also the atoms of X occupy all the octahedral voids. So their number is the same as those of the element Y. So, X and Y are present in equal numbers or are in 1:1 ratio. Therefore, the formula of the compound is XY.

EXAMPLE 12.2

If atoms of element B form hcp lattice and 2/3rd of tetrahedral voids are occupied by those of the element A. What is the formula of the compound formed by the elements A and B?

SOLUTION:

The number of tetrahedral voids formed is two times the number of atoms of element B and atoms of element A occupies only 2/3rd of these. Hence the ratio of the number of atoms of A and B is 2 × (2/3):1 or 4:3 and the formula of the compound is A_4B_3.



AC (shown in red) is a face diagonal while AC' (shown in blue) is a body diagonal. (source: Wikimedia).

12.4.1 Packing Efficiency

Now we will understand the concept of packing efficiency, that is how the constituent particles (atoms, molecules or ions) are packed in the crystal lattices. Voids are the free space which are there in the crystal lattices. Packing efficiency is the percentage of total space filled by the particles. Now we will do the calculations involving the packing efficiency in different types of structures.

In a Simple Cubic Lattice

Here we will study about the packing efficiency in a simple cubic lattice. In a simple cubic lattice the atoms are located only on the corners of the cube (Fig. 12.18).

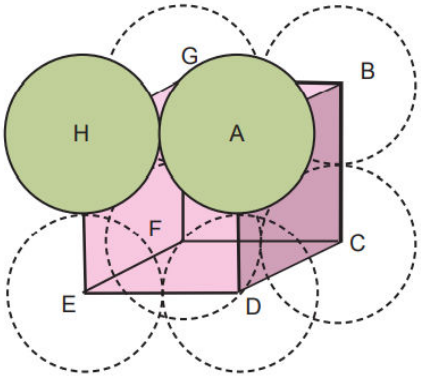


Fig 12.18: Packing in a Simple cubic lattice

The edge length or side of the cube = 'a',

The radius of each particle = *r*

From the Fig 12.18, a = 2*r*

The volume of the cubic unit cell = $a^3 = (2r)^3 = 8r^3$

In section 12.3.1 you have studied that a simple cubic unit cell contains only 1 atom. We know that the volume of one atom occupied space = $4/3\pi r^3$

So we get,

Packing efficiency = (Volume of one atom / Volume of cubic unit cell) x100%

= $(4/3\pi r^3 / 8r^3)$ x 100%=52.36% =52.4%

Look at Fig. 12.18 above which shows packing in a simple cubic lattice.

Ina Body-Centred Cubic Lattice

Next, let us look into the packing efficiency in a body-centred cubic lattice. The atoms (A, B, C, D, E, F, G & H) are located at the corners of the cube and one atom at the centre of the cube as shown in Fig. 12.19.

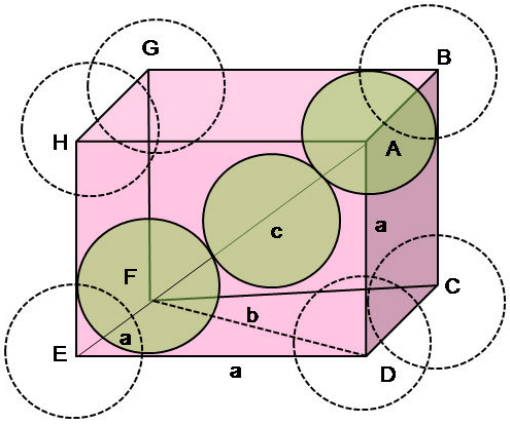


Fig.12.19: Body-centred cubic unit cell (sphere along the body diagonal are shown with solid boundaries).

The atom at the centre will just be touching the two atoms which are arranged diagonally. In the right angled Δ EFD, drawn on the face CDEF.

$b^2 = a^2 + a^2 = 2a^2$

$b = \sqrt{2}a$

Here b is the face diagonal

Now in the right angled Δ AFD

$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$

$c = \sqrt{3}a$

The length of the body diagonal c is equal to 4*r*, Therefore,

$\sqrt{3}a = 4r$

$a=(4/\sqrt{3})r$

Thus, $r = \sqrt{3}a/4$

The volume of the two atoms $= 2X(4/3)\pi r^3$

Volume of the cube, $a^3 = (4/\sqrt{3})^3 r^3$

Therefore,

Packing efficiency

$$= \frac{\text{Volume occupied by two spheres in the unit cell}}{\text{Total volume of the unit cell}} X100\%$$

$$= \frac{2X(4/3)\pi r^3}{(\frac{4}{\sqrt{3}}r)^3} X100$$

$$= \frac{(8/3)\pi r^3}{64(3\sqrt{3})r^3} X100$$

= 68%

In a Face-Centred Cubic (HCP and CCP) Structures

A face-centred cubic unit cell is shown below.

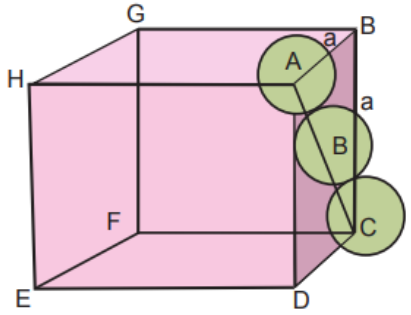


Fig. 12.20: Cubic close packing (Only one side shown for the purpose of clarity).

In Fig. 12.20 let the unit cell edge length be '*a*' and face diagonal AC = b.

In the right-angled Δ ABC

$AC^2 = b^2 = BC^2 + AB^2 = a^2 + a^2 = 2a^2$

or $b = \sqrt{2}\, a$

If r is the radius of the sphere, we can say

$b = 4r = \sqrt{2}\, a$

or $a = 4r/\sqrt{2} = (2\sqrt{2})r$

Also $r = a/(2\sqrt{2})$

We know, that each unit cell in fcc structure has 4 atoms.

Total volume of four spheres is equal to $4 \times (4/3)\, \pi r^3$

Volume of the cube is a^3 or $(2\sqrt{2}r)^3$

Therefore, Packing efficiency =

$$\frac{\text{Volume occupied by four spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100\%$$

The number of net atoms per unit cell are one, two and four in simple cubic, bcc and fcc structures.

$$= \frac{4 \times (4/3)\pi r^3}{(2\sqrt{2}r)^3} \times 100$$

$$= \frac{(16/3)\pi r^3}{16\sqrt{2}r^3} \times 100$$

= 74%

We have seen earlier that ccp and hcp lattices have equally efficient packings, hence the packing efficiency of hcp lattice is also 74%. So what can you say about the ccp and hcp structures? Well they have the maximum packing efficiency. The density of a crystal depends on the number of atoms, their mass and the volume of the unit cell. Next we will check the calculation of the densities of these three types of unit cells.

12.4.2 Calculations involving dimensions of the Unit Cell

Let us write the formula for density of the unit cell,

$$\text{Density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

In this unit, the cell-edge lengths and the distance between the planes are given in pm units; but it is usual to state such data in Å unit also.

1 Å = 10^{-10} m.

Calculation of the volume of the unit cell (using SI units):

Cell edge of the unit cell = a m

Volume of the unit cell = $a^3\, m^3$

Calculation of the mass of the unit cell:

Mass of the unit cell = (Number of atoms per unit cell) × (mass of each atom)

We know that mass of one mole (6.022×10^{23}) atoms or molecules is equal to its molar mass.

$\therefore$Mass of 1 atom = $\frac{\text{molar mass}}{N_A} = \frac{M}{N_A}$ kg

$\therefore$Mass of the unit cell $= \frac{zM}{N_A}$ kg

$\therefore$Density of the unit cell $= \rho = \frac{zXM}{N_A X\, a^3}$ kg m^{-3}

$a^3 = \frac{zXM}{N_A X \rho}$

Where z = Number of atoms per Unit cell, N_A = Avogadro's constant

Now with the following examples you can have a better concept of such calculations.

EXAMPLE 12.3

An element has a body-centred cubic (bcc) structure with a cell edge of 288 pm. The density of the element is 7.2 g/cm^3. In 208 g of the element how many atoms are present?

SOLUTION:

Volume of the unit cell = (288 pm)^3

= (288 x 10^{-12} m)^3 = (288 x 10^{-10} cm)^3

= 2.39 x 10^{-23} cm^3

Volume of 208 g of the element = mass/density

= 208 g / 7.2 g cm^{-3}

= 28.88 cm^3

Number of unit cells in this volume = (20.88 cm^3/2.39 x 10^{-23} cm^3 unit cell)$^{-1}$ = 12.08 x 10^{23} unit cells

In each unit cell of bcc two net atoms are there. Therefore, number of atoms in 208 g is 12.08 x 10^{23}x 2 = 24 x 10^{23} atoms.

EXAMPLE 12.4

Silver has a fcc lattice. The edge length of its unit cell is 4.077×10^{-8} cm and its density is 10.12 g cm^{-3}. What is the molar mass of silver?(N_A =6.022× 10^{23})

Solution:

Since the lattice is fcc, the number of silver atoms per unit cell = z = 4

Molar mass of silver = M

Edge length of unit cell = a = 4.077×10^{-8} cm

Density = 10.12 g/cm^3

We know that, $d = (z \times M) / (N_A \times a^3)$

Molar mass = M = $(d \times N_A \times a^3) / z = 10.12 \times 6.022 \times 10^{23} \times (4.077 \times 10^{-8})^3 / 4$

= 103.2 g mol^{-1}.

SAQ 2

Tungsten forms *bcc* crystals. Its cell-edge length is 3.16 x 10^{-10} m. Find the density of tungsten. (Given: Molar mass of tungsten = 183.84 g per mol).

So in this section you have learnt the details about the packing efficiency of the crystals and also how to calculate the dimensions of the unit cell. In the next section you are going to learn about the defects in crystals.

12.5 DEFECTS IN CRYSTALS

You have already learnt in the previous unit that the solids can be classified into crystalline solids and amorphous solids. The basis of such classification is the regularity in the arrangement of their constituent particles.

There is of course a definite repetitive pattern in the crystals. In this section, the possibilities of different types of irregularities that can occur in the arrangement of constituent particles and the effect of these defects on the properties of the crystals will be discussed. Crystalline solids have long range order but are not perfect. An ideal crystal is one which has the same unit cell containing the same lattice points throughout the crystal. It is very difficult to grow a perfect or an ideal crystal. Usually a solid consists of an aggregate of large number of small crystals. Single crystals are formed when the process of crystallisation occurs at an extremely slow rate, which may also have defects.

So you see, the irregularities in the arrangement of constituent particles are its defects. These irregularities are also called **crystal defects**. The properties of the crystals change due to the imperfections and new properties also arise. The defects can be broadly classified as point defects, line defects and plane or surface defects. Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance. Line defects are the irregularities or deviations from ideal arrangement in the entire rows of lattice points. Surface defects are irregularities on the whole surface of the solids. In this section, discussion will be limited to point defects only.

Point Defects

Following are the three types of point defects:

1. Stoichiometric defects

2. Impurity defects

3. Non-stoichiometric defects

Stoichiometric defects

The point defects that do not disturb the stoichiometry of the solids are called stoichiometric defects which are also called intrinsic or thermodynamic defects. Basically these are of two types, namely, vacancy defects and interstitial defects.

(i) Vacancy defect*:* As shown in Fig. 12.21, when some of the lattice sites are vacant, the crystal is said to have vacancy defect. There is a decrease in density of the substance as a result of these unoccupied positions. This type of defect could form if the substance is heated.

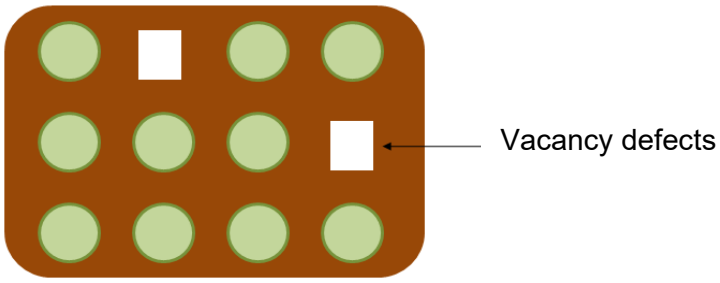


Fig. 12.21: Vacancy defects

(ii) Interstitial defect*:* If the interstitial sites (vacant places between the lattice sites) are occupied by any particles (atoms or molecules), the crystal has interstitial defect (Fig. 12.22). This defect increases the density slightly.

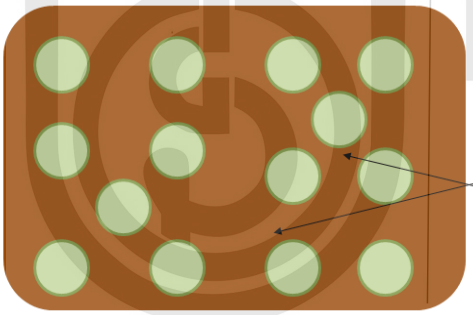


Fig. 12.22: Interstitial defects

At this point you should note that vacancy and interstitial defects are shown by non-ionic solids. Ionic solids do not show these simple vacancy and interstitial defects, but they show Schottky and Frenkel defect.

(iii) Schottky defect*:* The German scientist Schottky discovered this defect in 1930. It arises if some of the ions are missing from their normal lattice sites. You can say it is a vacancy defect in ionic solids. The lattice sites which are unoccupied are called lattice vacancies or holes.

To maintain electroneutrality in the crystal, equivalent number of cations and anions are missing (Fig. 12.23). Ionic compounds have this type of defect whenever cations and anions are of almost similar sizes. For example, NaCl, KCl, KBr, CsCl and AgBr which are ionic solids, show Schottky defects.

Let us take the example of NaCl. It has approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus,

there is one Schottky defect per 10^{16} ions. Such large number of vacancies in crystals gives rise to significantly lowering of its density.

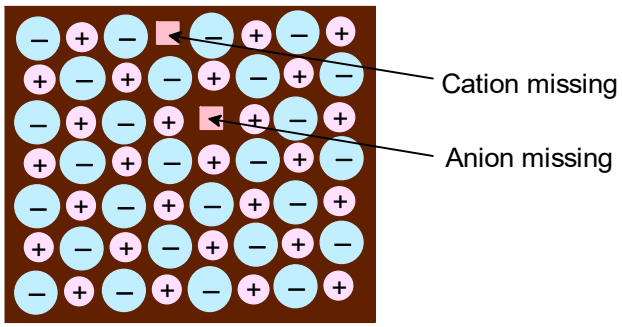


Fig. 12.23: Schottky defect

(iv) *Frenkel Defect*: The Russian scientist Frenkel in 1926 discovered this defect. The defect is said to occur when an ion migrates from its normal position (causing a vacancy or a hole) and occupies an interstitial site between the lattice points (Fig. 12.24). A vacancy defect thus arises in the original site and an interstitial defect in the new location.

Here electroneutrality is maintained because the number of cations and anions remains the same. When the coordination number is low and the size of anion is much larger than the size of cation. Frenkel defect is generally shown. These defects can be in AgCl, AgBr, AgI and ZnS because of the small size of Ag^+ and Zn^{2+} ions. Please note, AgBr shows both Frenkel as well as Schottky defects.

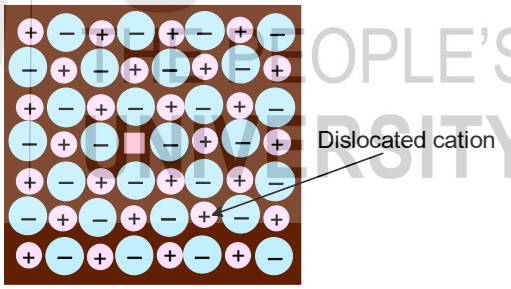


Fig. 12.24: Frenkel defect

Consequences of Schottky and Frenkel defect:

1. Schottky and Frenkel defects increase the electrical conductivity of crystals. If you apply an electrical field, a nearby ion moves from its lattice site to occupy a “hole”. Thus another “hole”is created and this way another nearby ion moves into it and this process continues. Thus, a hole moves from one lattice site to another lattice site, as a result of which electricity is conducted throughout the crystal.

2. The density of the substance showing Schottky defects decreases as holes are present in the crystal.

3. As a result of Frenkel defects, there is no change in density of the substance.

4. These ‘holes’ also decrease the lattice energy or the stability of the crystal and a lot of them can cause a partial collapse of the lattice.

5. In Frenkel defects similar charges near each other cause to increase the dielectric constant of the crystals.

Impurity Defects

When a foreign particle (atom or ion) enters in the crystal lattice this extrinsic defect happens. It may place itself in the interstices or it may replace the particle from the lattice site. When molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+}. Each Sr^{2+} replaces two Na^+ ions to maintain electrical neutrality. One Sr^{2+} cation replaces one Na^+ ion and the other site remains vacant producing cationic vacancies. Another example is the solid solution of $CdCl_2$ and AgCl.

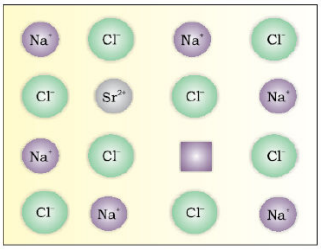


Fig. 12.25: Impurity defect

EXAMPLE 12.5

If some $CaCl_2$ impurity enters during the crystal formation of KCl, will the density of KCl crystal formed change?

SOLUTION:

In KCl crystal, the Ca^{2+} ion from $CaCl_2$ will replace K^+ ions. To maintain electroneutrality one Ca^{2+} ion will replace two K^+ ion, thereby decreasing the density of KCl crystal.

Non-stoichiometric defects

Non-stoichiometric compounds are those compounds in which the ideal chemical formula is not there.

The defects in these compounds are called non-stoichiometric defects. Vanadium oxide, for example, has the formula VO_x where x lies between 0.6 and 1.3. Similarly, iron(II) oxide of ideal composition FeO are difficult to obtain. It maybe $Fe_{0.912}O$, $Fe_{0.93}O$ upto $Fe_{0.96}O$). ZnO generally has excess of zinc atom than oxygen atom. The electrical neutrality of the crystal is maintained. Mostly transition metal compounds show such behaviour. Even lanthanoids and actinoids do show this too. Non-stoichiometric defects are of two types, that is, metal excess defects and metal deficient defects.

Colour of crystals arise out of the excitation of the electrons when they absorb the energy from the visible light which falls on the crystal.

(i) Metal excess defects: Here, the positive ions are in excess which happens in the two ways given below:

(a) Anionic vacancies

(b) Presence of extra cations in interstitial sites.

(a) Anionic Vacancies: Here, negative ions leave their lattice sites forming holes there, where electrons get trapped to maintain the electrical neutrality as shown in Fig.12.26. But, the crystal remains electrically neutral even if there is an excess of positive (metal) ions. This is found in crystals which generally form Schottky defects. If you heat alkali metal halides crystals in the presence of the alkali metal vapour, anion vacancies are produced. For example, if the crystals of NaCl are heated in an atmosphere of sodium vapour, the excess of sodium atoms are deposited on the surface of the crystal. Then the Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. That is

$$Na \longrightarrow Na^+ + e$$

$$Na^+ + Cl^- \longrightarrow NaCl$$

These electrons move into the crystal and get trapped at the anion vacancies. They are then referred to as **F-centres** (from **German word farbenzentrum meaning colour centre**)which give yellow colour to the crystal of NaCl.

In the same way potassium in KCl makes the crystal appear violet (or lilac), and the excess of lithium ion in LiCl makes the crystal appear pink

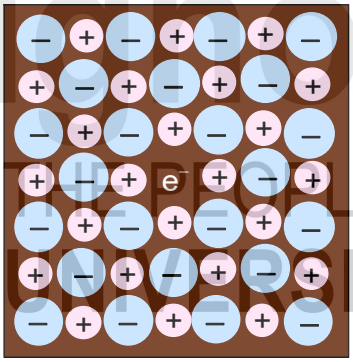


Fig. 12.26: Metal excess defect and the formation of F-centre

b) Excess cations occupying interstitial sites: Here positive ions are in excess and occupy interstitial sites to maintain electroneutrality. The defect may arise when non-metal atoms leave their electrons behind. The excess metal ions occupy interstitial positions. Crystals which show Frenkel defect have this defect. Example is zinc oxide (ZnO) which is white in colour at room temperature. If you heat it at high temperature, oxygen is lost in a reversible reaction and the crystal turns yellow in colour. The excess of both Zn^{2+} ions and equal number of electrons in sites are trapped to maintain electrical neutrality.

Now the question is what happens as a result of metal excess defects? The free electrons conduct electricity but, the conductivity is very low as their number is very small. This sort of low conductivity as compared to conductivity of metals gives its name as semiconductors. These compounds are also called **n-type semiconductors** because the conduction of electricity is due to the movement of negative charge of electrons.

EXAMPLE 12.6

Why is common salt often yellow instead of being pure white?

SOLUTION:

This happens due to presence of electrons in some lattice sites in place of anions. These sites act as F-centres and impart colour to common salt by the excitation of these electrons when they absorb energy from the visible light falling on the crystal.

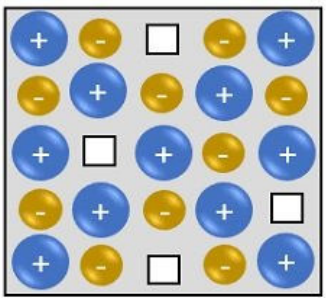
(ii) Metal deficient defects: If the number of positive ions are less than negative ions in the crystal it leads to metal deficient defects. This may happen due to the following two reasons: Cationic vacancies and extra anions occupying interstitial sites.

Cationic vacancies: There may be extra negative charge in the crystal due to missing positive ions. A nearby metal ion may become more positively charged and balance the extra negative charge. Of course such metals should show variable oxidation state, e.g. ferrous oxide, ferrous sulphide and nickel oxide. The interesting case of the iron pyrites crystal which has metallic lustre should be seen now. In the case of iron pyrites (FeS) crystal, there are both Fe^{2+} and Fe^{3+} ions. This gives rise to exchange of electrons from one Fe^{2+} to Fe^{3+}ion and the ions are interchangeable which gives the crystal metallic lustre.

Do you know what is fool's gold? Iron pyrites and some samples of minerals shine like gold and have been nick named as fool's gold. They have the shine due to cationic vacancies. Also FeO is found with a composition of $Fe_{0.912}O$ (range from $Fe_{0.93}O$to $Fe_{0.96}O$). In crystals of FeO, some Fe^{2+} are missing and the loss of positive charge is balanced by conversion of some Fe^{2+} ions to Fe^{3+} ions. Through the exchange of electrons between the metal cations with different valencies, the substances become conductors.

EXAMPLE 12.7

A portion of the defective crystal is given below:



i) What are these type of vacancy defects given in the illustration above called?

ii) Will the density of a crystal change as a result of these defects?

iii) Give one example of an ionic compound that exhibit this type of defect in the crystalline state.

iv) Give the effect on the stoichiometry of the compound as a result of this defect?

SOLUTION:

In the figure of the example you can count and see that an equal number of cations and anions are missing from their respective lattice sites. So it may be concluded:

i) It is Schottky defect.

ii) As the density of the crystal decreases, the number of constituent particles in the given volume of crystal decreases.

iii) KCl shows this type of defect.

iv) Equal number of cations and anions are missing and thus stoichiometry of the compound remains unchanged.

SAQ 3

(i) What are defects in crystals?

(ii) Compare the Schottky and Frenkel defects in a tabular form.

12.6 GLASSES AND LIQUID CRYSTALS

Glass

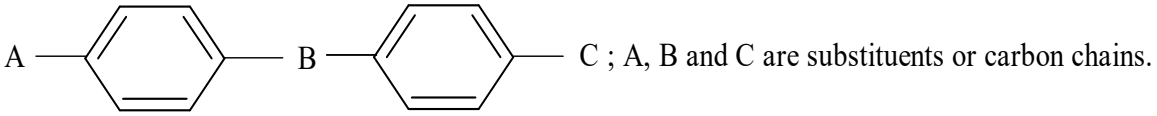
When glass is made, the material (generally containing silica) is quickly cooled from its liquid state. When its temperature drops below its melting point, the material is a supercooled liquid, an intermediate state between liquid and glass. If the material is cooled further, below the glass-transition temperature, then it becomes an amorphous solid. The material thereafter becomes glass which is not as organized as a crystal, but it is more organized than a liquid. Now, it is often seen that glass panes fixed to windows or doors of old buildings become thicker at the bottom. This happens because the glass is supercooled liquid and it flows down very slowly and makes the bottom portion thicker.

Liquid Crystals

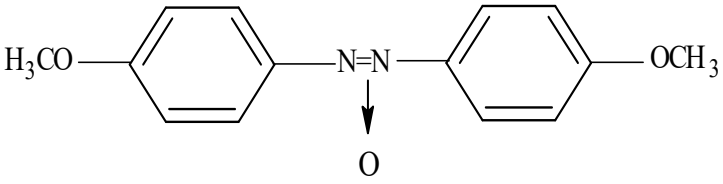
A liquid crystal is a substance which behaves like something between a liquid and solid. The slimy mess you find at the bottom of a soap dish is actually a liquid crystal, which is much similar to the material on a laptop screen. Liquid crystals can flow, take the shape of the container, and form drops as regular isotropic fluids do. But its molecules (mesogens) point along a common axis, called the director, which is in contrast to molecules in the liquid phase. In the solid state, molecules are highly ordered and have little translational freedom. So the liquid crystal state is in between the traditional solid and liquid phases and so they are also termed as mesogenic state. Liquid crystals are anisotropic like crystals of solids are.

Some organic compounds often have two melting points. On heating such a crystal, it melts into a turbid liquid at a definite temperature; and on heating further, the turbid liquid becomes clear at another temperature. The turbid liquid is called **'liquid crystal'**.

A number of compounds of the following type exist as liquid crystals:



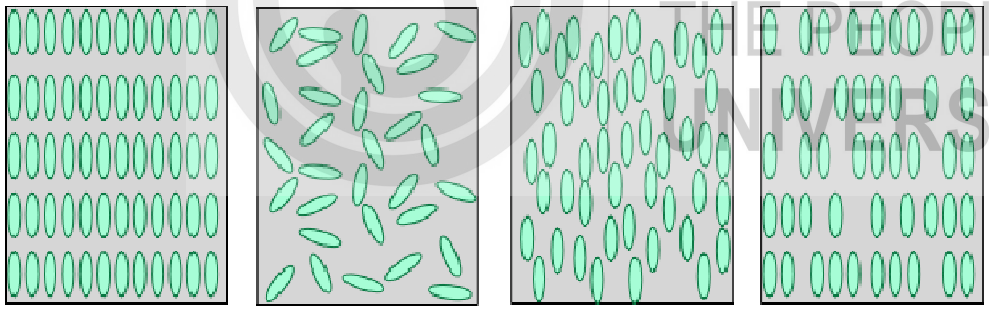
An example is *p*-azoxyanisole.



***p*-Azoxyanisole**

These molecules have a length which is greater than its breadth. In general, the arrangement of molecules in liquid crystals resembles a pile of cigars. Depending upon the structural pattern of molecules, liquid crystals can be classified as follows:

Smectic liquid crystals



Solid phase: Orientation and periodicity

Liquid phase: No orientation or periodicity

Nematic phase: Orientation, no periodicity

Smectic phase: Orientation with some periodicity

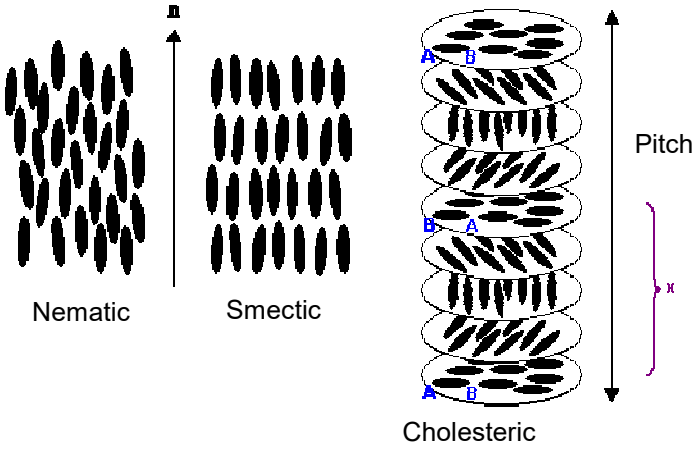


Fig. 12.27: Structure of a single crystal, liquid and liquid crystals.

The word "smectic" is derived from the Greek word for soap. The thick, slippery substance often found at the bottom of a soap dish is a type of smectic liquid crystal. These have molecules arranged in parallel layers or planes which are at equidistance. The molecules in all the planes have same orientation. The only difference between a solid crystal and a smectic liquid crystal is that in the former, the particles are arranged at regular intervals within a plane; whereas in the latter it is not so (Fig. 12.27). Molecules in the smectic phase show a degree of translational order. There is only motion within these planes, and different planes flow past each other. So the smectic state being more ordered is more "solid-like" than the nematic.

Nematic liquid crystals

The nematic liquid crystal phase sis characterized by molecules that have no positional order but tend to point in the same direction (along the director). These have all the molecules with the same orientation (Fig. 12.27). Here the molecules are not arranged in planes and their orientation changes when electric field is applied. Thereby their optical properties changes. It is this anisotropic character that makes a nematic liquid crystal useful in LCD (liquid crystal display) watches and calculators.

This anisotropic nature facilitates cholesteric liquid crystals being used in thermometers and in devices for indicating the temperature of the skin or of electrical devices. Temperature changes as small as 0.001 K can be detected using sensitive cholesteric liquid crystals.

Cholesteric liquid crystals

The cholesteric (or chiral nematic) liquid crystal phase is typically composed of nematic mesogenic molecules containing a chiral centre which produces intermolecular forces that favour alignment between molecules at a slight angle to one another. In this structure, the directors actually form in a continuous helical pattern about the layer normal. These have a multiple layer structure, but each successive layer is inclined or twisted slightly. Fig. 12.27 illustrates the cholesteric liquid crystal structure. For comparison, the typical disorderly arrangement of molecules (accounting for isotropy) in a liquid is shown in Fig. 12.27.

The successive twist in structure makes the cholesteric liquid crystals coloured. This class of liquid crystals received their name from the fact that many derivatives of cholesterol pertain to this type.

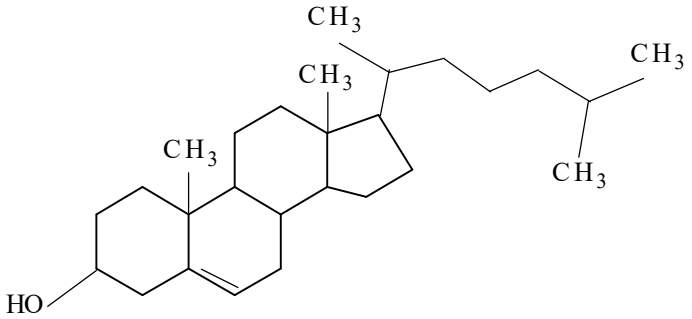


Fig. 12.28: Cholesterol

We see that a difference in the orientation of molecules in a nematic or a cholesteric liquid crystal causes a difference in its optical properties, thereby pointing to its anisotropic nature.

Columnar Phases

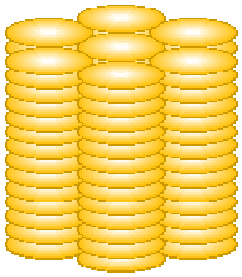


Fig. 12.29: Columnar liquid crystals

Columnar liquid crystals are shaped like disks instead of long rods and are stacked columns of molecules.

On the basis of what you have studied so far, answer the following SAQ.

SAQ 4

What are nematic liquid crystals?

12.7 SUMMARY

In this unit, we have briefly described X-rays diffraction and Bragg's Law along with structures of NaCl, ZnS and CsCl. Thereafter we have also dealt with defects in crystals and glasses and liquid crystals.

We summarize below what we have studied so far:

- Bragg's law was explained.
- the determination of crystal structure by X-ray diffraction method was described.
- how to determine the type of unit cell was explained.
- the defects in crystals were explained.
- glasses and liquid crystals were described.

12.8 TERMINAL QUESTIONS

1. What are vacancy defects?
2. In non-ionic solids, which defect result in increase in density of the substances?
3. How many net atoms are there in a fcc and bcc unit cell? Arrive at the conclusion by geometrical arguments.

4. Sodium crystallises in a ***bcc*** lattice with a cell-edge length of 4.23 X 10^{-10} m. Calculate the density of sodium metal.

5. The density and cell-edge length of sodium chloride are 2.163 X 10^{3} kg m^{-3} and 5.63X 10^{-10} m, respectively. Using these data, arrive at the number of formula units per unit cell of sodium chloride crystal.

6. What are smectic liquid crystals.

12.9 ANSWERS

Self Assessment Questions

1. (a) Using Eq. 12.1,
   $n\lambda = 2d \sin \theta$, 1x154 = 2x404sin θ,
   $\sin \theta = 0.191, \theta = \sin^{-1}(0.191) = 11$ degrees

   (b) XRD & crystallography helps to determine this

2. 1.936 x 10^{4} kg m^{-3}

3. (i) Any departure from perfectly ordered arrangement of constituent particles (atoms, molecules or ions) in crystal is called imperfection or defect.

   (ii) Comparison between Schottky and Frenkel defects

Schottky defect	**Frenkel defect**
Results from missing ions from their normal crystal sites.	Results from ions displaced from their normal sites and moving to interstitial sites.
Lowers the density of the crystal.	No effect on the density of the crystal.
Ionic solids having high coordination number and cations and anions of similar sizes, for example, NaCl, CsCl exhibit this.	Ionic solids having low coordination number and larger anions than cations. For example, AgCl, ZnS exhibit this.

4. Nematic liquid crystals constitute of molecules that have no positional order but tend to point in the same direction (along the director). Here the molecules are not arranged in planes and their orientation changes when electric field is applied. Thereby their optical properties changes which makes a nematic liquid crystal useful in LCD (liquid crystal display) watches and calculators.

Terminal Questions

1. When in crystalline substance, some of the lattice sites are vacant, the crystal is said to have vacancy defect. It result in the decrease in the density of the substance. This defect is shown by non- ionic solids.

2. When some constituent particles (atoms, molecules)are present in the interstitial sites, the crystals are said to have interstitial defect. This defect increases the density of substance(because mass increases but volume remains same). This defect is in non-ionic solids.

3. A bcc unit cell, total atoms are
8 corners × 1/8 per unit cell+1 body-centred atom= 2

In a fcc unit cell, total atoms are

8 corners atoms ×1/8 atom per unit cell + 6 face-centred atoms×1/2atom per unit cell = 4.

4. 1.01 x 10^3 kg m^{-3}.

v) Substituting the density (ρ), cell-edge length (a) and molar mass (w) of sodium chloride we get,

$$z = \frac{2.163 \text{ x } 103 \text{ kg m}^{-3} \text{ } (5.63 \text{ x } 10^{-10} \text{ m})^3 \text{ x } 6.022 \text{ x } 10^{23} \text{ mol}}{0.05845 \text{ kg mol}^{-1}}$$

= 4.

6. See section 12.6

Sources of Figures

Fig.12.3: Wikimedia

Further Reading

Physical Chemistry, Third Edition 1046pp/PB 3rd Edition (English, Paperback, G. W. Castellan)

A Textbook of Physical Chemistry, Volume 1, K L Kapoor, Macmillan, 1999.

ignou
THE PEOPLE'S
UNIVERSITY