
UNIT 1 UNITS AND DIMENSIONS

Structure

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1.1 INTRODUCTION

Problem-solving is an essential aspect of scientific study in general and of physical chemistry in particular. It is possible that some of us are 'afraid' of equations containing physical quantities. This fear is mainly due to the mathematical clothing of such equation. To dispel this fear, first of all, we have to understand how to represent one single physical quantity in terms of its magnitude and units. This will help us to handle with comfort and confidence, an equation containing many physical quantities. Here we shall study the principles of representing the units of the physical quantities.

Till recently in the scientific world, mainly two systems of units had been in common use. One is c.g.s. (centimetre, gram, second) which was more commonly used over the European Continent and the other is f.p.s. (foot, pound and second) prevalent in England. A common system of units helps in exchanging the scientific facts and ideas originating from different countries. It is better still if the system of units could be derived from the scientific formulae or **fundamental** constants. This long felt need for a common system of scientific units was realised at a meeting called General Conference on Weights and Measures in 1960. At this meeting, the international scientific community agreed to adopt common units of measurements known as International System of Units. This is abbreviated as SI units from the French name, *Systeme Internationale*.

In this unit, we shall first state the SI units for a few basic and derived quantities. Then we shall explain the prefixes used to change the order of magnitude of the SI units. Also we shall state the rules for representing the SI units and the procedure for converting non-SI units into SI units.

Objectives

After studying this unit, you should be able to :

- explain the need for SI units,
- state basic and derived SI units,
- derive the dimensions and the SI unit of a physical quantity using an appropriate equation,
- explain how the multiples and the submultiples of SI units can be obtained,
- describe the rules for writing SI units, and
- convert non-SI units into SI units.

1.2 BASIC UNITS

There are seven basic physical quantities, from which all other physical quantities can be derived. The units of these basic physical quantities are called basic units. The names of these quantities along with their symbols, SI units and the symbols of SI units are given in Table 1.1. Each of these seven quantities is regarded as having its own dimension. The dimensions of basic quantities are useful in defining the derived physical quantities, which we shall study in Sec. 1.3. We will be using the symbols given in column (ii) of Table 1.1 to refer to the dimensions of the basic quantities.

Table 1.1 : Basic Physical Quantities and Their SI Units

Physical Quantity (i)	Symbol of the quantity (ii)	Name of the SI Unit (iii)	Symbol of the SI Unit (iv)
Length	<i>l</i>	metre	m
Mass	<i>m</i>	kilogram	kg
Time	<i>t</i>	second	s
Electric current	<i>I</i>	ampere	A
Temperature	<i>T</i>	kelvin	K
Luminous intensity	<i>I_v</i>	candela	cd
Amount of substance	<i>n</i>	mole	mol

Note that *m* (italicised) is the symbol for mass of an object, while m (roman) is the symbol of SI unit, metre.

We are not going to define kilogram, metre etc., since our aim is to use these units and not to establish the basis of these units.

1.3 DERIVED UNITS

All other physical quantities are regarded as being derived from the above seven basic quantities by definitions involving multiplication, division, differentiation and integration. Such quantities and their units are called **derived physical quantities and derived units**, respectively.

In Tables 1.2 and 1.3, the derived SI units without and with special names are given. You will find it useful, throughout your study of chemistry, to refer to these tables whenever some physical quantities are to be expressed. The units of some magnetic and electrical quantities were discussed in Unit 6 of Atoms and Molecules course. Since electrochemistry will be studied in Block 4 of this course, a few useful electrical quantities are also included in Table 1.3.

Table 1.2 : Derived SI Units Without Special Names

Physical Quantity (i)	Definition (ii)	Dimensional formula (iii)	Name of the SI Unit (iv)	Symbol of the SI Unit (v)
Area*	Length \times length	l^2	square metre	m^2
Volume*	Length \times length \times length	l^3	cubic metre	m^3
Density	Mass/Volume	ml^{-3}	kilogram per cubic metre	$kg\ m^{-3}$
Velocity	Displacement/Time	lt^{-1}	metre per second	$m\ s^{-1}$
Acceleration	(Change in velocity)/Time	lt^{-2}	metre per second squared	$m\ s^{-2}$
Molar mass	Mass/Amount of the substance	mn^{-1}	kilogram per mole	$kg\ mol^{-1}$

* The definitions given for area and volume are of general type, although specific formulae are to be used depending on the geometry of a surface or an object.

Table 1.3 : Derived SI Units Having Special Names

Physical Quantity (i)	Definition (ii)	Dimensional formula (iii)	Name of the SI Unit (iv)	Symbol of the SI Unit (v)
Force	Mass \times acceleration	mlt^{-2}	newton	N or $kg\ m\ s^{-2}$
Pressure	$\frac{\text{Force}}{\text{Area}}$	$\frac{mlt^{-2}}{l^2}$ $= ml^{-1}t^{-2}$	pascal	Pa or $N\ m^{-2}$ or $kg\ m^{-1}\ s^{-2}$
Energy or Work	Force \times distance	ml^2t^{-2} $= ml^2t^{-2}$	joule	J or $N\ m$ or $Pa\ m^3$ or $kg\ m^2\ s^{-2}$
Electric charge	Electric current \times time	It	coulomb	C or A s
Electric potential difference	$\frac{\text{Electrical energy}}{\text{Electric charge}}$	$\frac{ml^2t^{-2}}{It}$ $= ml^2 I^{-1} t^{-3}$	volt	V or $J\ C^{-1}$ or $kg\ m^2\ A^{-1}\ s^{-3}$

Physical Quantity (i)	Definition (ii)	Dimensional formula (iii)	Name of the SI Unit (iv)	Symbol of the SI Unit (v)
Electric resistance	(Electric potential difference) Electric current	$\frac{ml^2 I^{-1} t^{-3}}{I}$ $= ml^2 I^{-2} t^{-3}$	ohm	Ω or $V A^{-1}$ or $kg m^2 A^{-2} s^{-3}$
Electric conductance	$\frac{1}{\text{(Electric resistance)}}$	$\frac{1}{ml^2 I^{-2} t^{-3}}$ $= I^2 t^3 m^{-1} I^{-2}$	siemens	S or $A V^{-1}$ or $A^2 s^3 kg^{-1} m^{-2}$
Frequency	$\frac{\text{(Number of waves or cycles)}}{\text{time}}$	$\frac{1}{t}$	hertz	Hz or s^{-1}

From Tables 1.1, 1.2 and 1.3, you can find a direct correspondence between the dimensions of a physical quantity and the symbol of its SI unit. For example, see how from the dimensions of acceleration, its SI unit has been worked out below :

Dimensions of acceleration = lt^{-2} [column (iii) of Table 1.2]

Units of acceleration = $m s^{-2}$ [columns (ii) and (iv) of Table 1.1]

Let us see how the dimensions and the units of a physical quantity can be obtained using Tables 1.1-1.3.

Deduction of the SI Unit of a Physical Quantity

We can derive the dimensions and the units of a physical quantity, provided a mathematical relationship is available between this physical quantity and other physical quantities of known dimensions. Suppose we want to find the dimensions and the units of the gas constant, R . The mathematical relationship to be used for this is the ideal gas equation (Eq. 1.1), which we will study in Unit 2.

$$\text{Pressure} \times \text{volume} = \text{Amount of the substance} \times \text{gas constant} \times \text{temperature} \quad \dots (1.1)$$

Rearranging this,

$$R = \frac{\text{Pressure} \times \text{volume}}{\text{Amount of the substance} \times \text{temperature}} \quad \dots (1.2)$$

The dimensions of the quantities in the right hand side of Eq. 1.2 are mentioned in Tables 1.1-1.3. We use the dimensions of these quantities to derive the dimensions and the units of R as shown below :

$$\begin{aligned} \text{Dimensions of } R &= \text{Dimensions of } \left[\frac{\text{Pressure} \times \text{volume}}{\text{Amount of the substance} \times \text{temperature}} \right] \\ &= \frac{ml^{-1}t^{-2}l^3}{n.T} = (ml^2t^{-2})(n^{-1})(T^{-1}) \end{aligned}$$

Hence, the units of $R = \text{joule mole}^{-1} \text{ kelvin}^{-1}$

(using the units corresponding to the dimensions mentioned in Tables 1.1-1.3).

Thus, R has the dimensions of (energy) (amount of the substance) $^{-1}$ (temperature) $^{-1}$ and the units, $J \text{ mol}^{-1} \text{ K}^{-1}$

In general, the following hints would be useful in the deduction of the unit of a quantity (which we name as test quantity) :

- Write an equation relating the test quantity to other quantities of known dimensions.
- Rearrange this equation such that only the test quantity is on the left hand side and others are on the right hand side.
- Substitute the dimensions of the quantities on the right hand side and simplify.
- Write down the units corresponding to the simplified dimensions, using Tables 1.1-1.3.

Use the above hints and work out the following SAQs.

SAQ 1

Derive the dimensions and the units of root mean square speed (u_{rms}) of a gas using the following equation :

$$u_{rms} = \sqrt{\frac{3 \times \text{gas constant} \times \text{temperature}}{\text{Molar mass}}}$$

The dimensions of molar mass are mn^{-1} .

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SAQ 2

From the equation, kinetic energy = $1/2 \times \text{mass} \times (\text{velocity})^2$, derive the units of kinetic energy.

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1.4 SI PREFIXES

We now discuss how to overcome the difficulty of expressing the units of physical quantities, which are either very large or small, as compared to the SI units. We add a prefix to the SI unit such that the magnitude of the physical quantity of a substance can be expressed as a convenient number.

For example, the bond distance in hydrogen molecule is 7.4×10^{-11} m. We express it conveniently as 74 pm where pico is the SI prefix and p is its symbol. The list of SI prefixes is given in Table 1.4 and it is possible to change the order of magnitude of any unit using this Table.

Prefixing of SI units helps in expressing a physical quantity, large or small, as a convenient number.

Example : 7.4×10^{-11} m
 $= 74 \times 10^{-12}$ m
 $= 74$ pm

Table 1.4 : SI Prefixes

Submultiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-1}	deci	d	10	deca	da
10^{-2}	centi	c	10^2	hecto	h
10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P
10^{-18}	atto	a	10^{18}	exa	E

More examples for usage of prefixes are given below :

10^3 m = 1 km; 10^{-9} s = 1 ns

The unit for mass is kg which is already prefixed. We do not add a second prefix but rather use a single prefix on the unit gram. Thus, to represent 10^{-9} gram, the symbol used is ng and not pkg. For 10^{-3} gram, mg is used and not μ kg.

SAQ 3

Write down the following with proper SI unit symbols and prefixes :

- (a) 10^{-9} metre (b) 10^{-12} second (c) 10^3 pascal
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-
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SAQ 4

Suggest a convenient SI unit to specify the diameters of atoms and molecules which are in the region of 10^{-10} m.

1.5 GRAMMATICAL RULES FOR REPRESENTING THE SI UNITS

The following rules would be of immense help to you while using SI units :

- i) The symbol of a unit is never to be used in plural form. Writing 10 kilogram as 10 kg is correct but not as 10 kgs
- ii) In normal usage, full stop is used to indicate the end of a sentence or the presence of an abbreviation. To denote SI unit as an abbreviation by means of a full stop after the symbol is incorrect; but if the SI unit is at the end of a sentence, then the full stop can be used.
- iii) When there is a combination of units, there should be a space between the symbols. If the units are written without leaving any space, the first letter is taken as a prefix. Thus, m s represents metre second whereas ms stands for millisecond.
- iv) Always leave a space between the magnitude and the unit symbol of a physical quantity. For example, writing 0.51 kg is correct but not 0.51 kg.
- v) Symbol of the unit derived from a proper name is represented using capital letters but not the name of the unit (Table 1.3). For example, writing 100 newton or 100 N is correct but not 100 Newton or 100 n.
- vi) For numbers less than unity, zero must be inserted to the left of the decimal point. Thus, writing 0.23 kg is correct but not .23 kg.
- vii) For larger numbers exceeding five figures, one space after every three digits (counting from the right end) must be left blank. Commas should not be used to space digits in numbers. For example 15 743 231 N is correct but not 15,743,231 N. It is preferable to use proper SI prefixes.
- viii) The degree sign is to be omitted before K while representing temperature. For example, 298 K is correct but not 298°K.
- ix) You should not mix words and symbols for representing SI units. For example, it is proper to write N m^{-2} or newton per square metre and not N per square metre.
- x) Exponents (or powers) operate on prefixes also. Let us derive the relationship between cm^3 and m^3 using the relation, $1 \text{ cm} = 10^{-2} \text{ m}$.
 $1 \text{ cm}^3 = (1 \text{ cm})^3 = (10^{-2} \text{ m}) \times (10^{-2} \text{ m}) \times (10^{-2} \text{ m}) = 10^{-6} \text{ m}^3$
Thus, 1 cm^3 is equal to 10^{-6} m^3 but not to 10^{-2} m^3 or 10^{-3} m^3 .
- xi) To show that a particular unit symbol has a negative exponent, one may be tempted to use the sign "/", known as solidus. It is better to avoid the usage of this sign and if used, no more than one should be employed. For example, representing pascal ($\text{kg m}^{-1} \text{ s}^{-2}$) as kg/m s^2 is allowed but not as kg/m/s^2 .

Three no's in SI units :

No plurals;

No full stops (except at the end of a sentence);

No dashes.

In cm unit, c (centi, 10^{-2}) is the prefix of the unit, m (metre).

So far, we studied some rules for writing SI units. Let us now discuss the dimensions of some mathematical functions which are useful in studying this course.

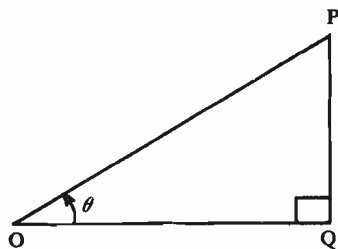
While representing the relationship among the physical quantities of substances, we often come across the mathematical functions like $\sin \theta$, e^x and $\ln x$. It is to be kept in mind that trigonometric ($\sin \theta$, $\cos \theta$, etc.), exponential (e^x or e^{-x}) and logarithmic functions ($\ln x$ or $\log x$) are dimensionless quantities and hence have no units.

You can understand the validity of this statement, once you recapitulate the definitions of these functions. We shall illustrate this for the functions, $\sin \theta$ and e^x .

From the right-angled triangle PQO,

$$\sin \theta = \frac{\text{length of PQ}}{\text{length of OP}}$$

Evidently $\sin \theta$ is dimensionless and has no unit. The same is true of other trigonometric functions also.



As an illustration for the exponential series, let us expand e^x .

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots$$

Since addition or subtraction must be done between quantities of same dimensions, $1, x, x^2, x^3, \dots$ etc., in the above series must all be of the same dimensions. This indicates that x and e^x are dimensionless and unitless. Again this is true of e^{-x} and $\ln x$ or $\log x$ also.

SAQ 5

In Unit 5 of this block, you will study that Bragg equation,

$$n\lambda = 2d \sin \theta$$

is useful in the diffraction studies of X-rays by crystals. Given that n is dimensionless and λ has the dimension of length, find the dimension and unit of d .

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1.6 CONVERSION OF NON-SI UNITS TO SI UNITS

Often in textbooks we see that the quantities are expressed in non-SI units such as c.g.s. and f.p.s. In such a situation, we must know how to convert non-SI units into SI units. There is a simple procedure available for this purpose. It is called **unit-factor method**. This method can be explained using the following example.

An important practical unit of pressure is atmosphere (atm). To be exact, at 298.2 K a column of mercury, 76 cm high ($h = 76 \text{ cm}$), exerts a pressure of 1 atm. (Fig. 1.1).

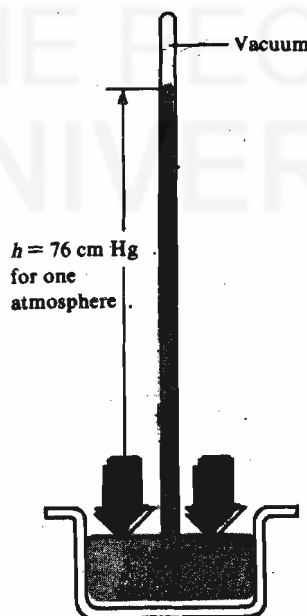


Fig. 1.1 : The pressure of a column of mercury 76 cm high inside the glass tube (black arrow) balances the pressure of air (red arrow) on the rest of the surfaces of mercury

The SI equivalent of 1 atm pressure can be obtained by substituting the values of h, g (acceleration due to gravity) and ρ (density of mercury) in SI units in the formula :

$$p = h g \rho \quad \dots (1.3)$$

The values of g and ρ in c.g.s. units are 980.66 cm s^{-2} and 13.595 g cm^{-3} , respectively. We have to convert the values of h, g and ρ into SI units, before substituting them in Eq. 1.3. To accomplish this, we must know how to construct a unit factor.

Construction of a Unit Factor

A unit factor is a ratio that is equal to 1. It states the relationship between the SI and the non-SI units of a physical quantity. It is constructed from the equivalence statement relating both these units. For example, for the conversion of the unit of h from c.g.s. into SI units, the equivalence statement is,

$$100 \text{ cm} = 1 \text{ m.}$$

From this equivalence statement, the unit factor for conversion can be constructed by dividing both sides by 100 cm (i.e. equivalent value in non-SI unit).

$$\frac{100 \text{ cm}}{100 \text{ cm}} = 1 = \frac{1 \text{ m}}{100 \text{ cm}} \quad \dots (1.4)$$

In general, the unit factor for conversion of a physical quantity into SI unit is given by the relationship :

$$\text{Unit factor} = \frac{\text{SI unit of a physical quantity}}{\text{Equivalent amount of the physical quantity in non-SI unit}}$$

Let us now see how the unit factor is useful in unit conversion.

Conversion into SI Unit

The unit factor is to be multiplied by the actual value of the physical quantity in non-SI unit to get the quantity in SI units. For example, the value of h (actual value = 76 cm) is to be multiplied by the unit factor, 1 m/100 cm to get it in metre unit.

$$h \text{ in SI unit} = 76 \text{ cm} \times \frac{1 \text{ m}}{100 \text{ cm}} = 0.76 \text{ m.}$$

The conversion of units of h , g and ρ into SI units is represented in Table 1.5.

Table 1.5 : Conversion of Units of h , g and ρ

Physical quantity	Symbol	Equivalence statement(s)	Unit factor	The actual value of the quantity in non-SI unit(s)	The quantity in SI unit(s)
(i)	(ii)	(iii)	(iv)	(v)	(vi) = (v) \times (iv)
Height of mercury column	h	100 cm = 1 m	$\frac{1 \text{ m}}{100 \text{ cm}}$	76 cm	$76 \text{ cm} \times \frac{1 \text{ m}}{100 \text{ cm}} = 0.76 \text{ m}$
Acceleration due to gravity	g	$100 \text{ cm s}^{-2} = 1 \text{ m s}^{-2}$	$\frac{1 \text{ m s}^{-2}}{100 \text{ cm s}^{-2}}$	980.66 cm s ⁻²	$980.66 \text{ cm s}^{-2} \times \frac{1 \text{ m s}^{-2}}{100 \text{ cm s}^{-2}} = 9.8066 \text{ m s}^{-2}$
Density of mercury	ρ	$10^3 \text{ g} = 1 \text{ kg}$ and $10^6 \text{ cm}^3 = 1 \text{ m}^3$ *	$\frac{(1 \text{ kg})}{(10^3 \text{ g})} \times \frac{(1 \text{ m}^3)**}{(10^6 \text{ cm}^3)}$ $= \frac{10^3 \text{ kg cm}^3}{1 \text{ g m}^3}$	13.595 g cm ⁻³	$13.595 \text{ g cm}^{-3} \times \frac{10^3 \text{ kg cm}^3}{(1 \text{ g m}^3)} = 1.3595 \times 10^4 \text{ kg m}^{-3}$ †

* $(10^2 \text{ cm})^3 = 10^6 \text{ cm}^3 = 1 \text{ m}^3$

** Density = Mass/Volume

$$\text{Unit factor for density conversion} = \frac{\text{Unit factor for mass conversion}}{\text{Unit factor for volume conversion}}$$

The values of h , g and ρ from the last column of Table 1.5 are to be substituted in Eq. 1.3 to get the SI equivalent of 1 atm pressure.

$$\text{i.e., } p = 0.76 \text{ m} \times 9.8066 \text{ m s}^{-2} \times 1.3595 \times 10^4 \text{ kg m}^{-3} \\ = 1.0132 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2} = 1.0132 \times 10^5 \text{ Pa.}$$

Hence, SI equivalent of 1 atm pressure is $1.0132 \times 10^5 \text{ Pa}$. Using the above illustration, we can sum up the steps for the conversion of non-SI units of a physical quantity into SI units as follows :

- (i) Obtain the equivalence statement relating the SI and the non-SI units.
- (ii) Construct the unit factor.

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

(iii) Multiply the actual amount of the physical quantity (in non-SI unit) by the unit factor.

Using the above procedure, attempt the following SAQ.

SAQ 6

The value of the gas constant R is often expressed as $1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$. Obtain its value in SI units ($\text{J mol}^{-1} \text{ K}^{-1}$). Given that $1 \text{ cal} = 4.184 \text{ J}$.

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1.7 SUMMARY

In the study of physical chemistry we come across many physical quantities. Confusion may arise in choosing the proper units for a particular quantity. We can overcome this difficulty by using SI units consistently. In this unit, we have discussed the basic and the derived units of SI system. The steps to be followed in deriving the dimensions and the units of physical quantities are explained with examples. The rules for representing the SI units of quantities, have also been stated. The method of converting non-SI units into SI units has been explained using an illustration.

1.8 TERMINAL QUESTIONS

- Examine the following statements and indicate their validity by writing T for true or F for false; if false, indicate the reason.
 - The SI unit of mass is gram.
 - The symbol of SI unit of temperature is k.
 - The SI unit of pressure is pascal.
 - $1 \text{ N} = 1 \text{ kg ms}^{-2}$.
 - $10^{-6} \text{ gram} = 1 \mu\text{g}$.
- If 25.3 g of a substance occupies a volume of 23 cm^3 , calculate its density in SI units.
- The molar mass (M_m) of an ideal gas is related to its pressure (p), density (ρ) and temperature (T), according to the equation,

$$M_m = \frac{\rho RT}{p}$$
 In this expression, R is the gas constant. Find the SI unit of molar mass.
- The reduced mass (μ) of two objects of masses m_1 and m_2 is given by the formula :

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)}$$
 What is the unit of reduced mass?
- Complete the following conversions :
 - $1 \text{ mg} = \dots\dots\dots \text{ kg} = \dots\dots\dots \text{ g}$
 - $1 \text{ s} = \dots\dots\dots \text{ ms} = \dots\dots\dots \text{ ns}$
 - $1 \text{ km} = \dots\dots\dots \text{ m} = \dots\dots\dots \text{ mm}$

1.9 ANSWERS

Self Assessment Questions

- Dimensions of u_{rms}

$$= \text{Dimensions of } \sqrt{\frac{\text{gas constant} \times \text{temperature}}{\text{Molar mass}}}$$

$$= \sqrt{\frac{\text{ml}^2 \text{t}^{-2} \text{n}^{-1} \text{T}^{-1} \text{T}}{\text{mn}^{-1}}}$$

$$= \sqrt{p t^2} = l t^{-1}$$

Hence u_{rms} has the dimensions, $l t^{-1}$ and the units, m s^{-1} .

- Kinetic energy has the unit, J.
- (a) nm (b) ps (c) kPa.
- $10^{-10} \text{ m} = 10^2 \text{ pm}$; hence pm unit can be used.
- Since n and $\sin \theta$ are dimensionless, d has the same dimension and unit as λ ; its dimension is l and its unit is metre (m).
- Value of R in SI unit = The value of R in non-SI unit \times unit factor

$$= 1.987 \text{ cal mol}^{-1} \text{ K}^{-1} \times \frac{4.184 \text{ J}}{1 \text{ cal}}$$

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

Terminal Questions

- F; (the SI unit of mass is kilogram)
 - F; (the symbol of SI unit of temperature is K)
 - T
 - F; $1 \text{ N} = 1 \text{ kg m s}^{-2}$ (a blank space needed between m and s^{-2})
 - T.

$$2. \text{ Mass in SI unit} = 25.3 \text{ g} \times \frac{1 \text{ kg}}{10^3 \text{ g}} = 2.53 \times 10^{-2} \text{ kg}$$

$$\text{Volume in SI unit} = 23 \text{ cm}^3 \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} = 2.3 \times 10^{-5} \text{ m}^3$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{2.53 \times 10^{-2} \text{ kg}}{2.3 \times 10^{-5} \text{ m}^3} = 1.1 \times 10^3 \text{ kg m}^{-3}$$

Dimensions of ρ , p , R and T are ml^{-3} , $ml^{-1}t^{-2}$, $ml^2t^{-2}n^{-1}T^{-1}$ and T , respectively.

$$\begin{aligned} \text{Dimensions of } M_m &= \text{Dimensions of } \frac{\rho RT}{p} \\ &= \frac{(ml^{-3})(ml^2t^{-2}n^{-1}T^{-1})T}{ml^{-1}t^{-2}} \\ &= mn^{-1} \end{aligned}$$

Hence, the dimensions and the symbol of the SI units of molar mass are mn^{-1} and kg mol^{-1} , respectively.

- The unit of reduced mass is kg.
- $1 \text{ mg} = 10^{-6} \text{ kg} = 10^{-3} \text{ g}$
 - $1 \text{ s} = 10^3 \text{ ms} = 10^9 \text{ ns}$
 - $1 \text{ km} = 10^3 \text{ m} = 10^6 \text{ mm}$.

UNIT 2 KINETIC THEORY OF GASES

Structure

- 2.1 Introduction
 - Objectives
- 2.2 Recapitulation of the Gas Laws
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 - Charles' Law
 - Avogadro's Law
- 2.3 Equation of State for Ideal Gases
- 2.4 Dalton's Law of Partial Pressures
- 2.5 Graham's Law of Effusion
- 2.6 Kinetic Theory of Gases
 - Resolution of Molecular Velocities
 - Mean Square Speed
- 2.7 Derivation of the Expression for Pressure
- 2.8 Ideal Gas Equation
 - Calculation of Average Kinetic Energy
 - Calculation of Number Density and Concentration
 - Calculation of Mean Square Speed and Root Mean Square Speed
- 2.9 Distribution of Molecular Speeds
- 2.10 Principle of Equipartition of Energy
- 2.11 Intermolecular Collisions
- 2.12 Mean Free Path
- 2.13 Summary
- 2.14 Terminal Questions
- 2.15 Answers

2.1 INTRODUCTION

Matter exists in solid, liquid or gaseous state depending on temperature and pressure. A familiar example is the compound H_2O , which can exist as ice, water or steam. The study of the gaseous state is the easiest as gas laws take a simple form at low pressure and high temperature. However, these laws are not valid at all temperatures and pressures. Also the range of validity depends on the nature of the substance itself. In a gas, the molecules on the average are separated by large intermolecular distances and at such distances, interactions between these molecules are very weak. This is not so in solids and liquids. Hence, the molecules in a gas have greater freedom of motion. As a result of this, they move about randomly and tend to occupy the maximum space available to them. Hence, gases have no particular shape or volume. Another consequence of their random motion is that each gas molecule collides with other molecules and also with the walls of the container. The constant bombardment against the walls of the container manifests itself as the pressure exerted by the gas.

This unit provides a molecular interpretation for the properties of gases. We shall start with a recapitulation of the gas laws. Then we shall explain the use of ideal gas equation in calculating the pressure, volume, temperature and amount of a gas. The postulates of the kinetic theory of gases will be explained and used in deriving an equation which is useful in calculating the parameters such as pressure, average kinetic energy etc. of the gas molecules. The principle of equipartition of energy will be described.

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 will be derived.*

In this unit, the behaviour of ideal gases shall be discussed. In the next unit, the deviation from ideal behaviour and the behaviour of real gases shall be taken up for discussion. Many of the expressions derived in this unit would be useful in studying the units on chemical equilibrium, solutions and chemical kinetics.

Objectives

After studying this unit, you shall be able to :

- state the gas laws and derive the ideal gas equation,
- 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 and Graham's law of effusion,
- 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,
- state and explain the principle of equipartition of energy,
- derive an expression to calculate the collision number between gas molecules, and
- calculate the mean free path of molecules.

2.2 RECAPITULATION OF THE GAS LAWS

Some of the earliest measurements on pressure, volume and temperature (p - V - T) were made on air at atmospheric pressure and room temperature. Fortunately, under these conditions air nearly behaves as 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. We shall recapitulate these gas laws after stating the units of pressure, volume and temperature.

Pressure : The SI unit of pressure is pascal (Pa). Its equivalence with other units of pressure are as follows :

$$\begin{aligned} 1 \text{ standard atmosphere} &= 1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} \\ &= 1.0132 \times 10^5 \text{ Pa} = 1.0132 \text{ bar.} \end{aligned}$$

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

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

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.

Let us now state the gas laws.

2.2.1 Boyle's Law

It states that at constant temperature, the volume, V , of a fixed mass of gas varies inversely as its pressure, p .

$$\text{i.e., } V \propto \frac{1}{p} \quad \dots (2.1)$$

$$\text{or } pV = K_1 \quad \dots (2.2)$$

Here K_1 is a constant at a given temperature for a fixed amount of the gas. This type of behaviour of a gas is shown in Fig. 2.1 at two different temperatures. Such a plot at constant temperature is called an isotherm and it resembles a hyperbola.

A gas that obeys Boyle's law is called an ideal gas.

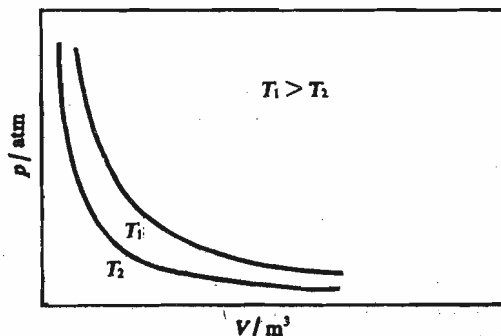


Fig. 2.1 : Isotherms at T_1 and T_2

2.2.2 Charles' Law

It states that for a certain amount of gas at a constant pressure, its volume (V) is directly proportional to its absolute temperature (T).

$$\text{i.e., } V \propto T \quad \dots (2.3)$$

$$\text{or } V = K_2 T \quad \dots (2.4)$$

where K_2 is a constant for a given pressure and amount of gas. This law is also known as Gay-Lussac's law. Fig. 2.2 depicts the variation of volume with temperature at constant pressure. Such a plot is a straight line and is known as an isobar.

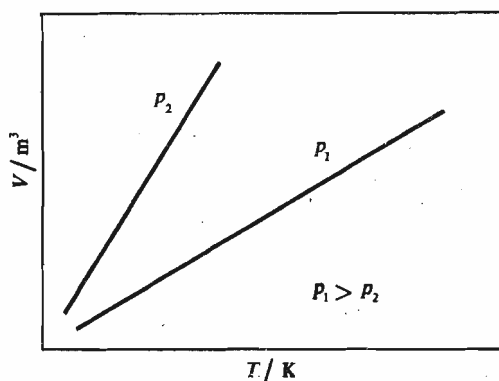


Fig. 2.2 : Isobars at p_1 and p_2

2.2.3 Avogadro's Law

It states that equal volumes of all the gases contain equal number of molecules under the same conditions of temperature and pressure. In other words,

$$V \propto N \quad \dots (2.5)$$

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

$$n = \frac{N}{N_A} \quad \dots (2.6)$$

where N_A is Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$). Using Eqs. 2.5 and 2.6, we can state that at constant temperature and pressure,

$$V \propto n \quad \dots (2.7)$$

That is, 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.

Using the above gas laws, we can arrive at the ideal gas equation.

2.3 EQUATION OF STATE FOR IDEAL GASES

By combining Eqs. 2.1, 2.3 and 2.7, we obtain the combined gas law i.e.,

$$V \propto \frac{nT}{p} \quad \dots (2.8)$$

$$\text{or } pV = nRT \quad \dots (2.9)$$

where R is the gas constant.

Eq. 2.9 is known as the equation of state for an ideal gas. The state of the gas is its condition at a given time. A particular state of a gas is described by its pressure, volume, temperature and the amount. Knowledge of any three of its properties is enough to define completely the state of the gas, since the fourth property can then be determined using Eq. 2.9.

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

Units of R

In Sec. 1.3 of Unit 1, you have studied that R has the dimensions of (energy) (amount of substance)⁻¹ (temperature)⁻¹. In SI units, the value of R is $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and we will be using this value throughout this course.

The values of R in different units are given below :

$$\begin{aligned} R &= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 8.314 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1} \\ &= 1.987 \text{ cal mol}^{-1} \text{ K}^{-1} \\ &= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \end{aligned}$$

Calculations Using Ideal Gas Equation

Eq. 2.9 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 calculating the volume occupied by 0.0660 kg of carbon dioxide gas at a temperature of 300.2 K and a pressure of $9.41 \times 10^4 \text{ Pa}$ assuming ideal behaviour.

$$\begin{aligned} \text{Number of moles of carbon dioxide } (n) &= \frac{\text{Mass of carbon dioxide}}{\text{Molar mass of carbon dioxide}} \\ &= \frac{0.0660 \text{ kg}}{0.044 \text{ kg mol}^{-1}} \end{aligned}$$

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

$$\begin{aligned} V &= \frac{nRT}{p} \\ &= \frac{\left(\frac{0.0660}{0.044} \text{ mol}\right) \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (300.2 \text{ K})}{9.41 \times 10^4 \text{ Pa}} \\ &= 0.0398 \text{ m}^3 \end{aligned}$$

$$\begin{aligned} \frac{1 \text{ J}}{1 \text{ Pa}} &= \frac{1 \text{ kg m}^2 \text{ s}^{-2}}{1 \text{ kg m}^{-1} \text{ s}^{-2}} \\ &= 1 \text{ m}^3 \\ \text{Also } \frac{1 \text{ J}}{1 \text{ m}^3} &= 1 \text{ Pa} \end{aligned}$$

Using the ideas developed above, attempt the following SAQ.

SAQ 1

Calculate the density of oxygen gas at 273.2 K and $1.013 \times 10^5 \text{ Pa}$, assuming ideal behaviour

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

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SAQ 2

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

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2.4 DALTON'S LAW OF PARTIAL PRESSURES

Dalton's law of partial pressures states that at constant temperature, the total pressure exerted by a mixture of 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 each gas be p_A , p_B and p_C , respectively when each of them is kept separately at a temperature T and volume V . Let us 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) is given by,

$$p_t = p_A + p_B + p_C \quad \dots (2.10)$$

Using Eq. 2.9 for each of the gases, we can write

$$p_A = \frac{n_A RT}{V} \quad \dots (2.11)$$

$$p_B = \frac{n_B RT}{V} \quad \dots (2.12)$$

$$\text{and } p_C = \frac{n_C RT}{V} \quad \dots (2.13)$$

Using Eqs. 2.10 to 2.13, we can write,

$$p_t = (n_A + n_B + n_C) \frac{RT}{V} = \frac{n_t RT}{V} \quad \dots (2.14)$$

where n_t = total number of moles in the mixture of gases = $n_A + n_B + n_C$

Dividing Eqs. 2.11 to 2.13 by Eq. 2.14 and rearranging we get,

$$p_A = \frac{n_A}{n_t} p_t \quad \dots (2.15)$$

$$p_B = \frac{n_B}{n_t} p_t \quad \dots (2.16)$$

$$\text{and } p_C = \frac{n_C}{n_t} p_t \quad \dots (2.17)$$

This law will be useful in studying the liquid-vapour equilibria discussed in the unit on solutions.

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 and are represented as x_A , x_B and x_C .

Thus the Eqs. 2.15 to 2.17 can be rewritten as,

$$p_A = x_A p_t \quad \dots (2.18)$$

$$p_B = x_B p_t \quad \dots (2.19)$$

$$p_C = x_C p_t \quad \dots (2.20)$$

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

Using the above principles, attempt the following SAQs.

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.

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SAQ 4

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

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2.5 GRAHAM'S LAW OF EFFUSION

Effusion is the passage of a gas through a small opening into an evacuated chamber. Graham's law states that the rates at which gases effuse are inversely proportional to the square root of their densities or molar masses under similar conditions of temperature and pressure.

If r , ρ and M_m are the rate of effusion, density and molar mass of a gas, then

$$\text{then } r \propto \frac{1}{\sqrt{\rho}} \quad \dots (2.21)$$

or

$$r \propto \frac{1}{\sqrt{M_m}} \quad \dots (2.22)$$

If two gases with molar masses M_{m1} and M_{m2} have densities ρ_1 and ρ_2 , then their rates of effusion r_1 and r_2 , under same conditions of temperature and pressure, are related as,

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_{m2}}{M_{m1}}} \quad \dots (2.23)$$

Using Eq. 2.23, answer the following SAQ.

SAQ 5

What is the ratio of effusion rate of hydrogen to oxygen?

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2.6 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) provides a theoretical explanation for the properties of gases. Let us first go through the following basic assumptions of the kinetic theory of gases.

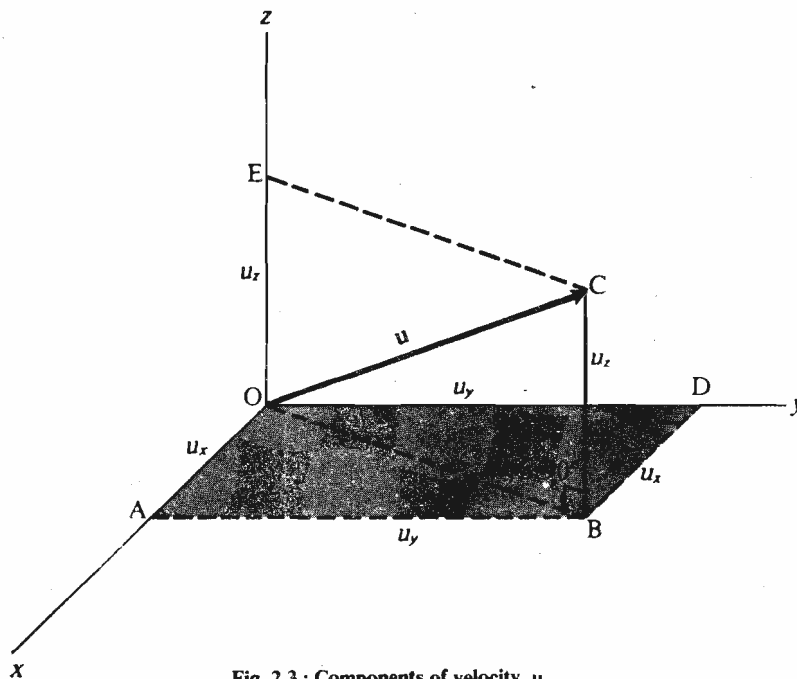
- 1) A gas is composed of a very large number of tiny molecules. The gas molecules are far apart from one another in comparison with their own dimensions. The gas molecules are considered as small hard spheres. Their volume is negligible compared to the total volume occupied by the gas.
- 2) The gas molecules are in a state of constant random 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 kinetic energy of the molecules before and after collision is 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 now discuss some of the features regarding molecular velocities which will be required for deriving the equation of state for the gases.

2.6.1 Resolution of Molecular Velocities

Velocity (\mathbf{u}) is a vector quantity. The components of \mathbf{u} in the x , y and z directions are u_x , u_y and u_z . The speed u is the magnitude of the vector \mathbf{u} and the latter is represented by OC (Fig. 2.3).

Some authors mention this law as the law of diffusion which is not quite exact, since diffusion is the transfer of material under a concentration difference.

Fig. 2.3 : Components of velocity, u

The lengths OA, OD and OE represent the velocity components u_x , u_y , and u_z . Hence, note that $OC = u$

$$OA = DB = u_x$$

$$OD = AB = u_y$$

$$OE = BC = u_z$$

BC is perpendicular to xy plane (shaded). Since OB is in xy plane, BC is perpendicular to OB. Hence, $\angle OBC = 90^\circ$

$$\text{From the right angled triangle OBC, } u^2 \doteq OC^2 = OB^2 + BC^2 = OB^2 + u_z^2.$$

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., $\angle ODB = 90^\circ$

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

$$\therefore u^2 = OB^2 + u_z^2 = u_x^2 + u_y^2 + u_z^2 \quad \dots (2.24)$$

It is important to note that u is a vector. The speed u and the velocity components u_x , u_y and u_z are scalars. A velocity component like 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 u must be by definition positive or zero.

2.6.2 Mean Square Speed

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

$$\bar{u}_x^2 = \frac{(u_{1x}^2 + u_{2x}^2 + u_{3x}^2 + \dots + u_{Nx}^2)}{N} \quad \dots (2.25)$$

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

For \bar{u}_y^2 and \bar{u}_z^2 also, the expressions similar to Eq. 2.25 can be written. Further, similar to Eq. 2.24, the average of the square of the molecular speeds, \bar{u}^2 , is related to \bar{u}_x^2 , \bar{u}_y^2 and \bar{u}_z^2 as,

$$\bar{u}^2 = \bar{u}_x^2 + \bar{u}_y^2 + \bar{u}_z^2 \quad \dots (2.26)$$

The quantity \bar{u}^2 is called the mean square speed. Since the gas molecules are in random motion, no particular direction is preferred. The quantities, \bar{u}_x^2 , \bar{u}_y^2 and \bar{u}_z^2 are equal. Hence,

$$\bar{u}_x^2 = \bar{u}_y^2 = \bar{u}_z^2 = \bar{u}^2/3 \quad \dots (2.27)$$

2.7 DERIVATION OF THE EXPRESSION FOR PRESSURE

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. 2.4). 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 $-mu_{1x}$.

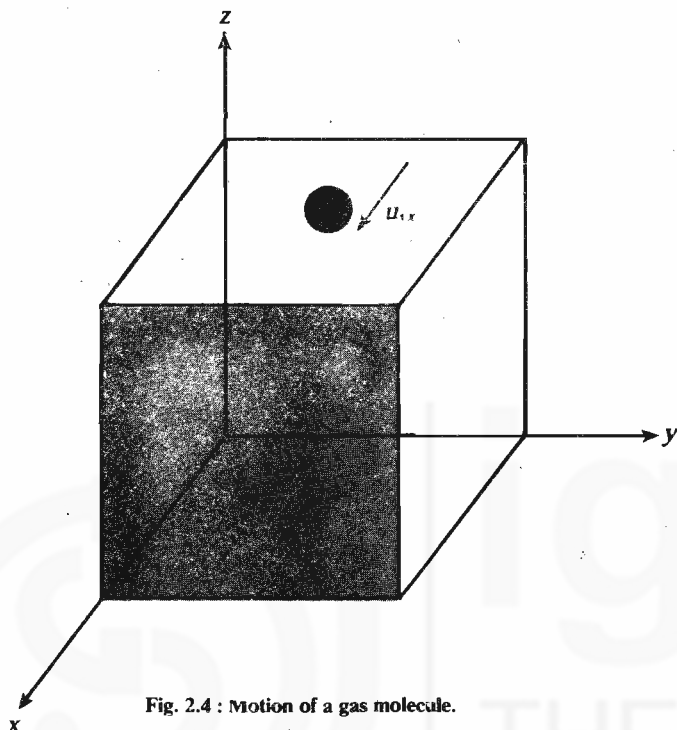


Fig. 2.4 : Motion of a gas molecule.

The change in momentum of the molecule in one collision is, $mu_{1x} - (-mu_{1x}) = 2mu_{1x}$. This molecule has to travel a distance of $2l$ before it collides with the shaded face again. 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 $2l/u_{1x}$ 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., $u_{1x}/2l$.

The change of momentum in one second (or rate of change of momentum) per molecule

$$\begin{aligned} &= \text{Change of momentum per molecule per collision} \times \text{number of collisions a molecule undergoes in one second} \\ &= 2mu_{1x} \times \frac{u_{1x}}{2l} \\ &= \frac{mu_{1x}^2}{l} \end{aligned}$$

As per Newton's second law of motion,
force = Rate of change of momentum

$$\text{Hence force due to collisions by one molecule} = \frac{mu_{1x}^2}{l} \quad \dots (2.28)$$

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:

$$F = \frac{m}{l} [u_{1x}^2 + u_{2x}^2 + u_{3x}^2 + \dots + u_{Nx}^2] \quad \dots (2.29)$$

$$= \frac{m}{l} N \bar{u}^2 \quad (\text{using Eq. 2.25})$$

Using Eq. 2.27,

$$F = \frac{mN\bar{u}^2}{3l}$$

But pressure (p) is force per unit area (A). The area of the shaded face is l^2

$$\therefore p = \frac{F}{A} = \frac{F}{l^2} = \frac{mN\bar{u}^2}{3l \cdot l^2} = \frac{mN\bar{u}^2}{3l^3}$$

Since for a cube, volume (V) = l^3 ,

$$p = \frac{mN\bar{u}^2}{3V} \quad \dots (2.30)$$

$$\therefore pV = \frac{1}{3} mN\bar{u}^2 \quad \dots (2.31)$$

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

2.8 IDEAL GAS EQUATION

Although all the gas laws could be derived from Eq. 2.31, we shall derive the ideal gas equation only and then proceed to calculate different molecular parameters.

Eq. 2.31 can be rewritten as,

$$pV = \frac{2}{3} N \left(\frac{1}{2} m \bar{u}^2 \right) \quad \dots (2.32)$$

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.,

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

$$\text{or } \frac{1}{2} m \bar{u}^2 = K_1 T \quad \dots (2.33)$$

where K_1 is a constant.

Substituting this in Eq. 2.32, we obtain,

$$pV = \frac{2}{3} NK_1 T \quad \dots (2.34)$$

This can be written as

$$pV = NkT \quad \dots (2.35)$$

Where k , known as Boltzmann constant is equal to $2/3 K_1$. The value of k is $1.38 \times 10^{-23} \text{ J K}^{-1}$. Eq. 2.35 is the ideal gas equation for N molecules. For a gas having n moles, the number of molecules N is given by,

$$N = nN_A \quad \dots (2.36)$$

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 $6.022 \times 10^{23} \text{ mol}^{-1}$. Hence the equation for n moles of the gas can be written by using Eqs. 2.35 and 2.36.

$$pV = nN_A k T = nRT \quad \dots (2.37)$$

where R is equal to $N_A k$. Eq. 2.37 is the same as Eq. 2.9 which has been derived in Sec. 2.3.

Let us now calculate some parameters of the gas molecules by the combined use of Eqs. 2.31, 2.33, 2.35 and 2.37.

2.8.1 Calculation of Average Kinetic Energy

Average kinetic energy per molecule can be calculated from Eq. 2.33, knowing that

$$K_1 = \frac{3}{2} k$$

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

$$\text{Average kinetic energy per molecule} = \frac{1}{2} m \bar{u}^2 = \frac{3}{2} kT \quad \dots (2.38)$$

$$\begin{aligned} \text{Similarly, average kinetic energy per mole} &= (N_A) \left(\frac{1}{2} m \bar{u}^2 \right) \\ &= (N_A) \left(\frac{3}{2} kT \right) \\ &= \frac{3}{2} N_A kT \\ &= \frac{3}{2} RT (\because R = N_A k) \quad \dots (2.39) \end{aligned}$$

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 illustrate the use of Eqs. 2.38 and 2.39 in calculating the average translational kinetic energy values of nitrogen molecules at 300 K.

$$\begin{aligned} \text{Using Eq. 2.38, the translational energy of nitrogen per molecule at 300 K} &= \frac{3}{2} kT \\ &= \frac{3}{2} \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 300 \text{ K} \\ &= 6.21 \times 10^{-21} \text{ J.} \end{aligned}$$

$$\begin{aligned} \text{Similarly using Eq. 2.39, the translational energy of nitrogen per mole at 300 K} &= \frac{3}{2} RT \\ &= \frac{3}{2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K} \\ &= 3.74 \times 10^3 \text{ J mol}^{-1}. \end{aligned}$$

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.

2.8.2 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. 2.35.

$$\text{Number density of a gas } (n_o) = \frac{N}{V} = \frac{p}{kT} \quad \dots (2.40)$$

Similarly, concentration (c), defined as the number of moles of a gas in unit volume, can be calculated by rearranging Eq. 2.37.

$$\text{Concentration of a gas } (c) = \frac{n}{V} = \frac{p}{RT} \quad \dots (2.41)$$

Let us apply Eqs. 2.40 and 2.41 in calculating the number density and concentration of nitrogen molecules at 298.2 K and 1.013×10^5 Pa.

$$\begin{aligned} \text{Number density } (n_o) \text{ of nitrogen molecules at 298.2 K} &= \frac{p}{kT} = \frac{1.013 \times 10^5 \text{ Pa}}{1.38 \times 10^{-23} \text{ J K}^{-1} \times 298.2 \text{ K}} \\ &= 2.462 \times 10^{25} \text{ m}^{-3} \end{aligned}$$

$$\begin{aligned} \text{Concentration } (c) \text{ of nitrogen at 298.2 K} &= \frac{p}{RT} = \frac{1.013 \times 10^5 \text{ Pa}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.2 \text{ K}} \\ &= 40.86 \text{ mol m}^{-3} \end{aligned}$$

Eq. 2.41 will be used in the unit on chemical equilibrium for the calculation of concentrations of reactants and products.

Note that the number density or the concentration of a gas is directly proportional to the gas pressure and inversely proportional to its temperature.

2.8.3 Calculation of Mean Square Speed and Root Mean Square Speed

In Subsec. 2.6.2, 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, combining Eqs. 2.31 and 2.37, we can write

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

$$\text{i.e., mean square speed } (\bar{u}^2) = \frac{3RT}{M_m} \quad \dots (2.42)$$

$$\text{Root mean square speed } (\sqrt{\bar{u}^2}) = u_{rms} = \sqrt{\frac{3RT}{M_m}} \quad \dots (2.43)$$

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

States of Matter

$$\begin{aligned} \sqrt{\frac{1 \text{ J}}{1 \text{ kg}}} &= \sqrt{\frac{1 \text{ kg m}^2 \text{ s}^{-2}}{1 \text{ kg}}} \\ &= \sqrt{1 \text{ m}^2 \text{ s}^{-2}} = 1 \text{ m s}^{-1} \end{aligned}$$

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

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 m s^{-1} (i.e., around two thirds of u_{rms} of air molecules).

Let us calculate u_{rms} of methane molecules at 515 K using Eq. 2.43.

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3RT}{M_m}} = \sqrt{\frac{3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 515 \text{ K}}{0.016 \text{ kg mol}}} \\ &= 8.96 \times 10^2 \text{ m s}^{-1}. \end{aligned}$$

Using the above example, answer the following SAQ.

SAQ 6

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

2.9 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 in nitrogen gas at 273 K is shown in Fig. 2.5. Here the relative probability of a particular speed occurring, 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. 2.5).

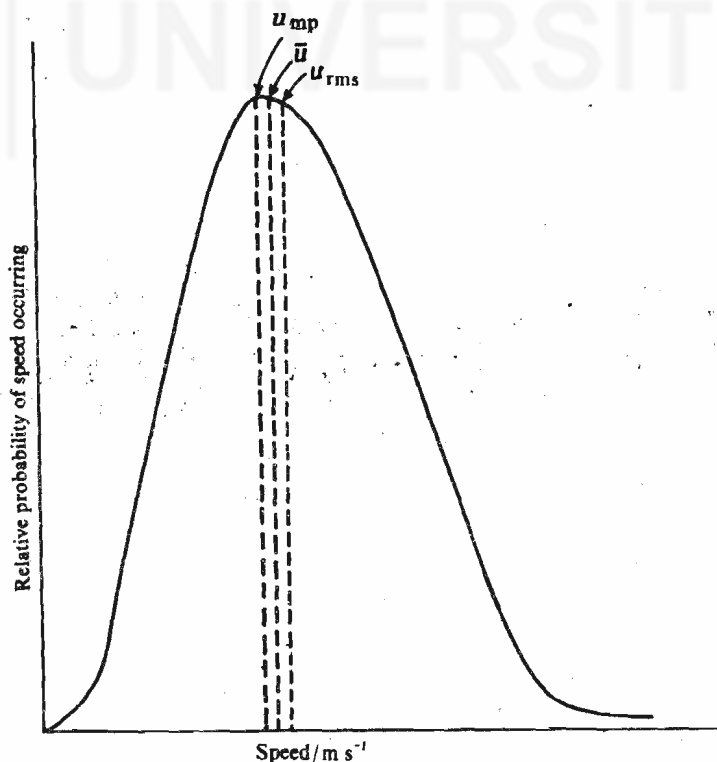


Fig. 2.5 : Distribution of speeds of nitrogen molecules at 273 K .

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

$$\bar{u} = \frac{1}{N} (u_1 + u_2 + u_3 + \dots + u_N) \quad \dots (2.44)$$

It is the arithmetic average of the speeds of the molecules 1 to N .

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

$$u_{rms} = \sqrt{\bar{u}^2} = \sqrt{\frac{1}{N} (u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2)} \quad \dots (2.45)$$

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 :

$$u_{mp} = \sqrt{\frac{2RT}{M_m}} \quad \dots (2.46)$$

$$\bar{u} = \sqrt{\frac{8RT}{\pi M_m}} \quad \dots (2.47)$$

$$u_{rms} = \sqrt{\frac{3RT}{M_m}} \quad \dots (2.48)$$

Let us calculate the average speed of nitrogen molecules at 298.2 K using Eq. 2.47.

$$\begin{aligned} \text{Average speed } (\bar{u}) \text{ of nitrogen molecules at } 298.2 \text{ K} &= \sqrt{\frac{8RT}{\pi M_m}} \\ &= \sqrt{\frac{8 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.2 \text{ K}}{3.142 \times 0.028 \text{ kg mol}^{-1}}} \\ \bar{u} &= 474.8 \text{ m s}^{-1} \end{aligned}$$

A change in temperature affects the molecular speed distribution curve. The distribution curves for nitrogen gas at temperatures of 273, 1273 and 2273 K are shown in Fig. 2.6.

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 SAQ.

SAQ 7

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?

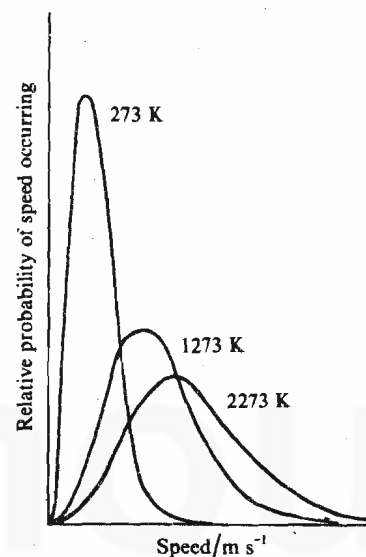


Fig. 2.6 : Distribution of speeds of nitrogen molecules at three different temperatures.

The importance of the temperature-molecular speed relationship on reaction rate will be discussed in the unit on chemical kinetics.

2.10 PRINCIPLE OF EQUIPARTITION OF ENERGY

In Subsec. 2.8.1, 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. Using this principle, the total energy (U) of the gaseous molecules can be calculated. From the U values at different temperatures, molar heat capacity values at constant volume (\bar{C}_v) and at constant pressure (\bar{C}_p) can be calculated using the following expressions (which we shall derive in Unit 6 of Block 2 of this course) :

$$\bar{C}_v = \left(\frac{\partial U}{\partial T} \right)_v$$

$$\bar{C}_p = \bar{C}_v + R$$

The contribution RT to energy due to each vibrational degree of freedom is significant only at high temperatures. At room temperature we need consider only contribution due to translational and rotational degrees of freedom. This is evident from the molar heat capacity values and \bar{C}_p/\bar{C}_v ratios of some gases at 298 K given in Table 2.1. Classical physics cannot explain as to why contribution to heat capacity values due to vibrational degrees of freedom is significant only at high temperatures. In Unit 1 of Atoms and Molecules course, we explained this using the principles of quantum mechanics.

Table 2.1 : \bar{C}_p and \bar{C}_v values at 298 K

Type of the molecule	Example	Degrees of freedom	U^* J mol ⁻¹	\bar{C}_v J mol ⁻¹ K ⁻¹	\bar{C}_p J mol ⁻¹ K ⁻¹	$\frac{\bar{C}_p}{\bar{C}_v}$	
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)	$\frac{3}{2} RT$	$\frac{5}{2} RT$	$\frac{5}{2} R$	$\frac{7}{2} R$	1.40
		2 (rotational)	$2 \times \frac{1}{2} RT$				
		1 (vibrational not active at 298 K)					
Non-linear triatomic molecule	Water	3 (translational)	$\frac{3}{2} RT$	$3RT$	$3R$	$4R$	1.33
		3 (rotational)	$3 \times \frac{1}{2} RT$				
		3 (vibrational not active at 298 K)					

SAQ 8

The specific heat 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 \bar{C}_p/\bar{C}_v ratio for the gas?

(Hint : \bar{C}_v = specific heat at constant volume \times molar mass)

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 \times specific heat

\bar{C}_p , \bar{C}_v , and R have the same units, viz., J mol⁻¹ K⁻¹

2.11 INTERMOLECULAR COLLISIONS

A cubic metre of nitrogen gas at room temperature and pressure contains about 2.462×10^{25} molecules (Subsec. 2.8.2) moving with an average speed of 474.8 m s^{-1} (Sec. 2.9). 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 in Fig. 2.7) to be within a twisted 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. 2.7 depicts the motion of a molecule and indicates the condition under which it hits or misses another molecule.

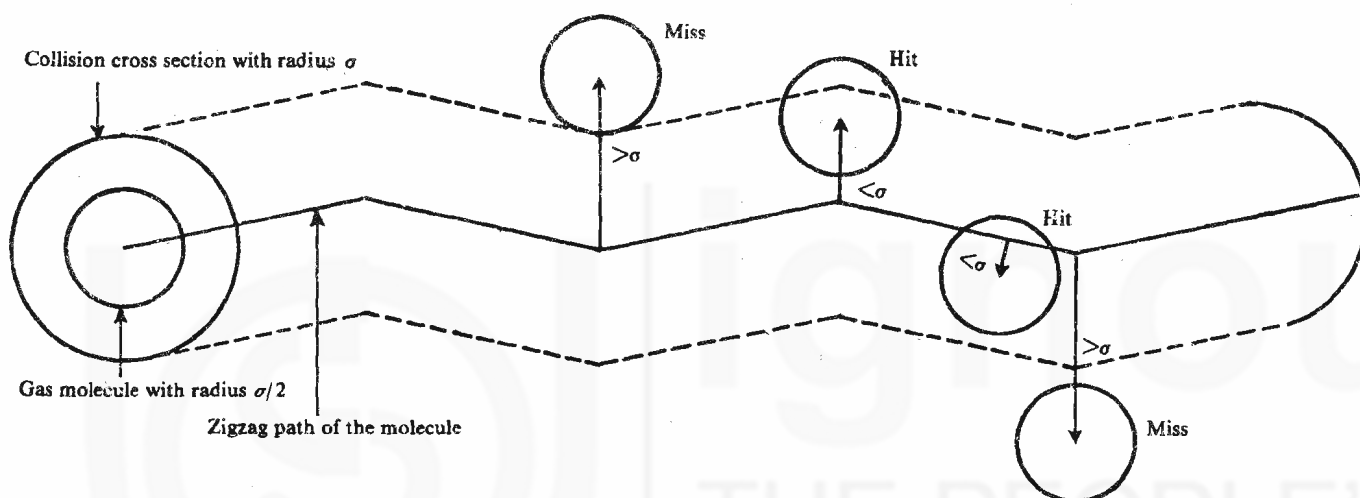


Fig. 2.7 : The zigzag motion of a molecule.

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 twisted cylinder with base equal to $\pi\sigma^2$ collide with the moving molecule. If there are not too many bends, then the volume of the cylinder is given by Eq. 2.49.

$$\begin{aligned} \text{Volume covered by the molecule in one second} &= \text{base of the cylinder} \times \text{height} \\ &= \pi\sigma^2\bar{u} \end{aligned} \quad \dots (2.49)$$

The number of molecules present per unit volume (number density) is n_0 . The collision frequency for a single molecule (z_{11}) 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.

$$z_{11} = \pi\sigma^2\bar{u}n_0 \quad \dots (2.50)$$

In the derivation of Eq. 2.50, 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. 2.50. Hence the collision frequency for a single molecule,

$$z_{11} = \sqrt{2} \pi\sigma^2\bar{u}n_0 \quad \dots (2.51)$$

Eq. 2.51 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, Z_{11}) is given by

$$Z_{11} = \frac{1}{2} z_{11}n_0 = \frac{1}{\sqrt{2}} \pi\sigma^2\bar{u}n_0^2 \quad \dots (2.52)$$

The factor $\frac{1}{2}$ has been introduced so that collision between any two molecules is not counted twice.

Total collision frequency is an important parameter in deciding the reaction rate. We shall study this in the unit on chemical kinetics.

Let us illustrate the calculation of total collision frequency of nitrogen at 298.2 K and 1.013×10^5 Pa using Eq. 2.52. The collision diameter of nitrogen is 3.740×10^{-10} m. The following steps are used in calculating the total collision frequency:

Step (i) : Calculation of number density (n_o) of nitrogen :

This has been already worked out in Subsec. 2.8.2.

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

Step (ii) : Calculation of average speed of nitrogen:

This has been worked out in Sec. 2.9.

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

Step (iii) : Calculation of total collision frequency :

Using Eq. 2.52,

$$\begin{aligned} Z_{11} &= \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{u} n_o^2 \\ &= \frac{1}{\sqrt{2}} \times 3.142 \times (3.740 \times 10^{-10} \text{ m})^2 \times 474.8 \text{ m s}^{-1} \times (2.462 \times 10^{25} \text{ m}^{-3})^2 \\ \therefore Z_{11} &= 8.945 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1} \end{aligned}$$

2.12 MEAN FREE PATH

An important quantity in the kinetic theory of gases is the mean free path, λ . This is 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 :

Distance travelled by a molecule in one second = \bar{u}

Number of collisions per molecule in one second = z_{11}

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

$$= \frac{\bar{u}}{z_{11}} \quad \dots (2.53)$$

$$= \frac{\bar{u}}{\sqrt{2} \pi \sigma^2 \bar{u} n_o} \quad (\text{using Eq. 2.51})$$

$$\text{i.e., } \lambda = \frac{1}{\sqrt{2} \pi \sigma^2 n_o} \quad \dots (2.54)$$

It can be seen that λ is inversely proportional to n_o and hence it should be inversely proportional to pressure (Subsec. 2.8.2). 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 9

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

.....

.....

.....

2.13 SUMMARY

In this unit, we have discussed some characteristic features of gases. Laws governing the behaviour 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 be 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 total collision frequency and the mean free path assuming hard sphere model for the molecules.

2.14 TERMINAL QUESTIONS

- 1) Calculate the molar mass of a gas for which density is $1.250 \times 10^3 \text{ kg m}^{-3}$ at 273.2 K and $1.013 \times 10^5 \text{ Pa}$.
- 2) $1.000 \times 10^{-3} \text{ m}^3$ of argon at a certain pressure and temperature took 151 s to effuse through a porous barrier. How long it will take for the same volume of oxygen to effuse under identical conditions?
[Hint : The time taken by a gas to effuse varies inversely as its rate of effusion.]
- 3) A mixture of $2.00 \times 10^{-3} \text{ kg}$ of H_2 and $2.00 \times 10^{-3} \text{ kg}$ of He exerts a pressure of $1.50 \times 10^5 \text{ Pa}$. What are the partial pressures of H_2 and He?
- 4) Calculate the ratio of mean square speeds of oxygen to nitrogen at 300 K.
- 5) Calculate the number density and concentration of oxygen at $1.013 \times 10^5 \text{ Pa}$ and 300 K.
- 6) What is the \bar{C}_p/\bar{C}_v value of a non-rigid diatomic gas?
[Hint : A non-rigid molecule has vibrational degree of freedom too.]

2.15 ANSWERS

Self Assessment Questions

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

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

$$= \frac{1.013 \times 10^5 \text{ Pa} \times 0.032 \text{ kg mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 273.2 \text{ K}}$$

$$= 1.427 \text{ kg m}^{-3}$$

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

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

$$2) 6.022 \times 10^{22} \text{ molecules.}$$

$$3) \text{ Total number of moles } (n_t)$$

$$= n_{\text{N}_2} + n_{\text{O}_2} + n_{\text{CH}_4} = 5.00 \text{ mol.}$$

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

$$= \frac{5.00 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 250.2 \text{ K}}{0.0600 \text{ m}^3}$$

$$= 1.73 \times 10^5 \text{ Pa}$$

$$p_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_t} p_t = \frac{2.00}{5.00} \times 1.73 \times 10^5 \text{ Pa}$$

$$= 6.92 \times 10^4 \text{ Pa}$$

$$\text{Similarly } p_{\text{O}_2} = 3.46 \times 10^4 \text{ Pa.}$$

$$\text{and } p_{\text{CH}_4} = 6.92 \times 10^4 \text{ Pa}$$

$$4) \text{ Nitrogen}$$

$$5) 4$$

$$\begin{aligned}
 6) \quad & \text{Root mean square speed of hydrogen at 500 K} \\
 & = \sqrt{\frac{3RT}{M_m}} = \sqrt{\frac{3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 500 \text{ K}}{0.002 \text{ kg mol}^{-1}}} \\
 & = 2.50 \times 10^3 \text{ m s}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 7) \quad & u_{mp} : \bar{u} : u_{rms} \\
 & = \sqrt{\frac{2RT}{M_m}} : \sqrt{\frac{8RT}{\pi M_m}} : \sqrt{\frac{3RT}{M_m}} \\
 & = 1.000 : 1.128 : 1.225 \text{ (Dividing by } \sqrt{\frac{2RT}{M_m}} \text{)}
 \end{aligned}$$

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

$$\begin{aligned}
 8) \quad & \bar{C}_v = 692 \text{ J kg}^{-1} \text{ K}^{-1} \times 0.018 \text{ kg mol}^{-1} \\
 & = 12.5 \text{ J mol}^{-1} \text{ K}^{-1} \\
 & \text{Since } \bar{C}_p = \bar{C}_v + R \\
 & \bar{C}_p = 20.8 \text{ J mol}^{-1} \text{ K}^{-1} \\
 & \frac{\bar{C}_p}{\bar{C}_v} = 1.66
 \end{aligned}$$

$$\begin{aligned}
 9) \quad & \lambda = \frac{1}{\sqrt{2} \pi \sigma^2 n_o} \\
 & \text{Using } n_o \text{ calculated in Subsec. 2.8.2,} \\
 & \lambda = \frac{1}{1.414 \times 3.142 \times (3.740 \times 10^{-10} \text{ m})^2 \times 2.462 \times 10^{25} \text{ m}^{-3}} \\
 & = 6.536 \times 10^{-8} \text{ m}
 \end{aligned}$$

Terminal Questions

- Molar mass of the gas = 28.02 kg mol⁻¹.
- The gas with the smaller molar mass effuses at the faster rate, which means that it takes less time for a given quantity of gas to effuse. That is, time (*t*) taken by a gas for effusion varies inversely as its rate of effusion (*r*).

$$\therefore t \propto \frac{1}{r}$$

$$\text{But according to Graham's law, } r \propto \frac{1}{\sqrt{\text{Molar mass}}}$$

$$\therefore t \propto \sqrt{\text{Molar mass}}$$

$$\begin{aligned}
 \frac{t_{\text{oxygen}}}{t_{\text{Argon}}} &= \sqrt{\frac{\text{Molar mass of oxygen}}{\text{Molar mass of argon}}} \\
 &= \sqrt{\frac{32}{40}}
 \end{aligned}$$

$$t_{\text{oxygen}} = t_{\text{Argon}} \times \sqrt{\frac{32}{40}} = 151 \times \sqrt{\frac{32}{40}} \text{ s} = 135 \text{ s}$$

$$3) \quad p_{\text{H}_2} = 1.00 \times 10^5 \text{ Pa}; p_{\text{He}} = 5.00 \times 10^4 \text{ Pa}$$

$$4) \quad \frac{\bar{u}_{\text{Oxygen}}^2}{\bar{u}_{\text{Nitrogen}}^2} = \frac{7}{8}$$

$$5) \quad \text{Number density} = 2.447 \times 10^{25} \text{ m}^{-3}; \\ \text{Concentration} = 40.61 \text{ mol m}^{-3}.$$

$$6) \quad U = (3 \times RT/2) + (2 \times RT/2) + (1 \times RT) \\ = 7/2 RT$$

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

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

UNIT 3 REAL GASES AND THEIR LIQUEFACTION

Structure

- 3.1 Introduction
 - Objectives
- 3.2 Deviation from Ideal Gas Behaviour
- 3.3 van der Waals Equation
- 3.4 Critical Phenomena
- 3.5 Critical Point and Critical Constants
 - Critical Constants and van der Waals Constants
 - Determination of Critical Constants
 - Test for van der Waals Equation
- 3.6 Equation of Corresponding States
- 3.7 Liquefaction of Gases
 - Linde's Method
 - Claude's Method
- 3.8 Intermolecular Forces
 - van der Waals Forces
 - Total Interaction Energy
 - Hydrogen Bonding
 - Effect of Molecular Interactions on Physical Properties
- 3.9 Summary
- 3.10 Terminal Questions
- 3.11 Answers

3.1 INTRODUCTION

The gas laws developed in Unit 2 are based on certain assumptions regarding molecules and their interaction with each other. Some of these assumptions are not valid under all conditions; the gases obey ideal gas laws only at low pressures and high temperatures. To start with, the deviation of the real gases from ideal gas behaviour will be discussed in this unit. The features of the isotherms at different temperatures will be explained. Afterwards, van der Waals equation will be deduced. This will be followed by a discussion on critical phenomena and critical constants. The relationships between critical constants and van der Waals constants will be derived. The principle of corresponding states will be explained. After this, the methods of liquefaction of gases will be outlined. Finally the nature of intermolecular forces and their effect on gases will be discussed. The study of intermolecular forces will help you understand the properties of liquids and solids which we will take up in units 4 and 5, respectively.

Objectives

After studying this unit, you should be able to :

- state the difference in behaviour between real and ideal gases,
- 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 liquefaction methods,
- explain the nature of intermolecular forces, and
- discuss the effect of intermolecular forces on the condensation of gases into liquids and solids.

3.2 DEVIATION FROM IDEAL GAS BEHAVIOUR

An ideal gas is a hypothetical concept. The real gases obey ideal gas laws only at low pressures and high temperatures. Before going into the reasons for the deviation from ideal gas behaviour, let us study the behaviour of gases at different pressures and temperatures.

States of Matter

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

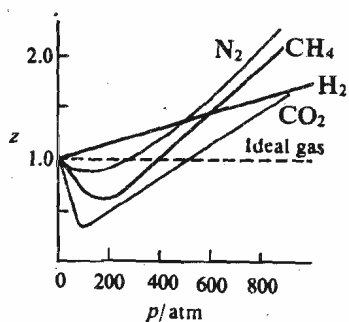


Fig. 3.1 : Plots of z against p for several gases.

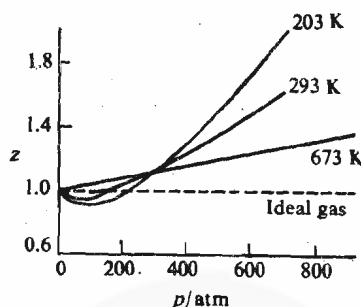


Fig. 3.2 : Plots of z against p for nitrogen gas at three temperatures.

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, $\text{m}^3 \text{mol}^{-1}$

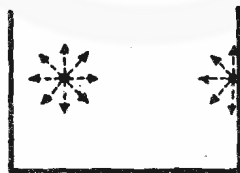


Fig. 3.3 : The attraction experienced by the molecules of a gas.

Liquefaction of gases (sec. 3.7) clearly indicates the presence of forces of attraction among gaseous molecules.

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

Behaviour of Real Gases

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. 3.1 must be equal to 1.

$$z = \frac{pV}{nRT} \quad \dots (3.1)$$

If z deviates from the value of unity, the gas is said to deviate from ideal behaviour. In Fig. 3.1, z is plotted against pressure for several 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, z is plotted against pressure for nitrogen gas at three temperatures in Fig. 3.2. 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. To sum up, the 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 gases. We shall study this in the next section.

3.3 VAN DER WAALS EQUATION

The origin of the deviations from ideal gas behaviour lies in two faulty assumptions of the kinetic theory of gases (discussed in Unit 2). Firstly, the volume of a molecule is by no means negligible and cannot be ignored under all conditions. Secondly, there certainly exists intermolecular interaction between molecules at close distances. van der Waals modified the ideal gas equation by taking into account the above shortcomings.

Volume Correction : van der Waals realised that the molecules of a real gas have definite volume. 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.

$$\text{Hence, corrected volume} = V_{\text{corr}} = V - nb \quad \dots (3.2)$$

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. 3.3).

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.

Each of the above factors is proportional to the concentration of the gas. i.e., $\Delta p \propto (\text{concentration})^2$

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

Hence, it can be written that,

$$\Delta p \propto \frac{n^2}{V^2}$$

$$\text{i.e., } \Delta p = \frac{n^2 a}{V^2} \quad \dots (3.3)$$

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

$$p_{\text{corr}} = p + \frac{n^2 a}{V^2} \quad \dots (3.4)$$

If the corrected pressure and the corrected volume of the gas are substituted in the ideal gas equation (Eq. 2.9), we obtain

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad \dots (3.5)$$

This 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. 3.5 becomes

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad \dots (3.6)$$

van der Waals equation (Eq. 3.5 or 3.6) is quite important and is applicable over a much wider range of $p-V-T$ data 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. 3.5. It may be pointed that ' b ' is a measure of the molecular size and ' a ' is related to the intermolecular interaction. Table 3.1 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 compressible gas. The values of the critical constants p_c , V_c and T_c are also given in Table 3.1 and their significance will be dealt with in Sec. 3.5.

Table 3.1 : van der Waals Parameters and Critical Constants of Some Gases

Gas	$a/\text{Pa m}^6 \text{mol}^{-2}$	$10^6 \times b/\text{m}^3 \text{mol}^{-1}$	$10^{-3} \times p_c/\text{Pa}$	$10^6 \times V_c/\text{m}^3 \text{mol}^{-1}$	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 ₂ O	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 use Table 3.1, the actual values of the parameters for methane are given below

$$\begin{aligned} a &= 0.2283 \text{ Pa m}^6 \text{mol}^{-2} \\ b &= 42.78 \times 10^{-6} \text{ m}^3 \text{mol}^{-1} \\ p_c &= 46.41 \times 10^5 \text{ Pa} \\ V_c &= 99.0 \times 10^{-6} \text{ m}^3 \text{mol}^{-1} \\ T_c &= 191.1 \text{ K} \end{aligned}$$

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 negligible

If ' b ' is very small, then Eq. 3.6 becomes,

$$\left(p + \frac{a}{V_m^2}\right)V_m = RT \quad \dots (3.7)$$

$$\text{i.e., } pV_m = RT - \frac{a}{V_m}$$

$$\text{or } z = \frac{pV_m}{RT} = 1 - \frac{a}{RTV_m} \quad \dots (3.8)$$

This shows that under these conditions, pV_m will be less than RT or z will be less than unity. Eq. 3.8 will be valid for substances like water vapour for which ' a ' is large and ' b ' is comparatively small (See Table 3.1). Also for gases such as N₂, CH₄ and CO₂ (Fig. 3.1) at moderately low pressures, V_m is large such that $(V_m - b)$ is nearly equal to V_m . Hence, Eq. 3.8 is applicable for such gases at moderately low pressures.

When ' a ' is negligible

If ' a ' is negligible, we have

$$p(V_m - b) = RT \quad \dots (3.9)$$

$$\text{i.e., } pV_m = RT + pb$$

$$\text{or } z = \frac{pV_m}{RT} = 1 + \frac{pb}{RT} \quad \dots (3.10)$$

Hence, pV_m will be greater than RT or z will be greater than unity. Particularly this is true for hydrogen (Fig. 3.1) and noble gases for which the value of ' a ' is small. This is also true

for all the gases at high pressures; since then $\frac{a}{V_m^2}$ is negligible in comparison to p .

When a and b are both 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 are both negligible in comparison to p and V_m .

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

Let us now illustrate the use of Eq. 3.5 in the calculation of pressure of 2.000 mol of methane at 1.000×10^3 K occupying a volume of $5.000 \times 10^{-2} \text{ m}^3$

Rearranging Eq. 3.5 we can write,

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

From Table 3.1, $a = 0.2283 \text{ Pa m}^6 \text{ mol}^{-2}$

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

substituting the values of the parameters we get,

$$p = \frac{2.000 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 1.000 \times 10^3 \text{ K}}{(5.000 \times 10^{-2} \text{ m}^3 - 2.000 \text{ mol} \times 42.78 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})} - \frac{(2.000 \text{ mol})^2 \times (0.2283 \text{ Pa m}^6 \text{ mol}^{-2})}{(5.000 \times 10^{-2} \text{ m}^3)^2}$$

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

Applying van der Waals equation to methane at 1.000×10^3 K, the pressure calculated is $3.328 \times 10^5 \text{ Pa}$.

Let us also calculate the pressure of methane using the same values of n , T and V but assuming ideal behaviour.

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

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

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

A number of attempts have been made to propose equation of state for real gases. These are supposed to represent the $p - V - T$ data over as wide range as possible. However, from practical consideration, it is desirable that the equation of state should have only a few adjustable parameters. 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 :

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

The coefficients $B(T)$, $C(T)$... are known as virial coefficients. It may be noted that these depend on temperature. By having sufficient number of terms in this equation, $p - V - T$ data can be represented to desired accuracy.

In the next section, we introduce the critical phenomena and then study the relationship between van der Waals constants and critical constants. Before that, work out the following SAQ.

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.

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3.4 CRITICAL PHENOMENA

Andrews performed a series of experiments and obtained isotherms (p against V plots at constant temperature) for carbon dioxide. The results obtained by him are shown in Fig. 3.4.

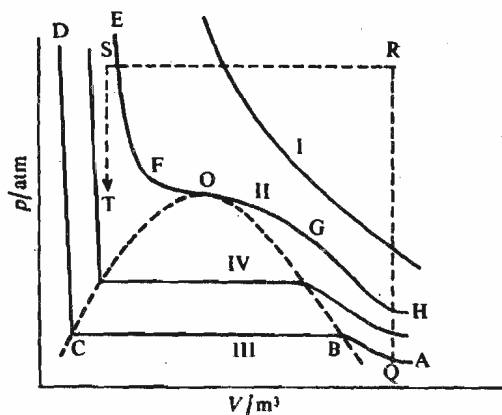


Fig. 3.4 · Isotherms of carbon dioxide.

At high temperature, the isotherm is a hyperbola (curve I) in accordance with Boyle's law (Unit 2). At low temperatures, the isotherms (the curves II, III and IV) show considerable deviation from ideal gas behaviour. The isotherm at 304.2 K (curve II) remains horizontal for a certain value of pressure. The two falling portions, EFO and OGH, of curve II 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 state. Note that the molecules 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 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 and IV) are joined, a bell shaped curve is obtained with crest at O. This is the area of discontinuity in which liquid and vapour coexist. Outside this area, there is either only gas (or 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 bell-shaped area, BOC. First of all 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 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. This is called the continuity of state. That is, the gas and the liquid are the combination of the same state and it is not necessary to pass through both the states simultaneously in their interconversion. The gaseous and liquid states are collectively known as fluids.

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.

3.5 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 vapour 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.

3.5.1 Critical Constants and van der Waals Constants

The van der Waals equation (Eq. 3.6) can be made the basis of a theoretical consideration. The curves in Fig. 3.5, known as van der Waals isotherms, show the isotherms calculated on the basis of this equation.

Expanding Eq. 3.6 we get,

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

$$\text{i.e., } pV_m - pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT \quad \dots (3.11)$$

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

$$V_m^3 - bV_m^2 + \frac{aV_m}{p} - \frac{ab}{p} = \frac{RTV_m^2}{p} \quad \dots (3.12)$$

$$\text{i.e., } V_m^3 - V_m^2\left(b + \frac{RT}{p}\right) + \frac{a}{p}V_m - \frac{ab}{p} = 0 \quad \dots (3.13)$$

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 complex conjugates. Isotherms 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 perturbation, then portions BC and EF are realisable; these portions represent the supersaturated vapour and superheated liquid, respectively.

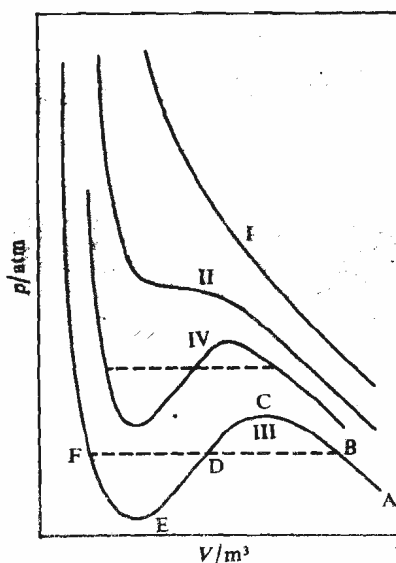


Fig. 3.5 : van der Waals isotherms.

The wave like portion decreases as temperature increases. At the critical temperature, it is reduced to a point which means that all the three roots of Eq. 3.13 are identical and equal to the critical volume, V_c .

$$\text{i.e., } V_m = V_c \text{ or } V_m - V_c = 0$$

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

$$(V_m - V_c)^3 = 0 \quad \dots (3.14)$$

$$\text{or } V_m^3 - 3V_cV_m^2 + 3V_c^2V_m - V_c^3 = 0 \quad \dots (3.15)$$

This equation should be identical with the expanded form of van der Waals equation (Eq. 3.13) at critical temperature and pressure

$$V_m^3 - V_m^2\left(b + \frac{RT_c}{p_c}\right) + \frac{a}{p_c}V_m - \frac{ab}{p_c} = 0 \quad \dots (3.16)$$

Now comparing the coefficients of equal powers of V_m in Eqs 3.15 and 3.16, we obtain

$$-3V_c = -\left(b + \frac{RT_c}{p_c}\right) \text{ or } 3V_c = b + \frac{RT_c}{p_c} \quad \dots (3.17)$$

$$3V_c^2 = \frac{a}{p_c} \quad \dots (3.18)$$

$$\text{and } -V_c^3 = -\frac{ab}{p_c} \text{ or } V_c^3 = \frac{ab}{p_c} \quad \dots (3.19)$$

From Eqs. 3.18 and 3.19, we obtain

$$\frac{V_c}{3} = b \text{ or } V_c = 3b \quad \dots (3.20)$$

Substituting the value of V_c in Eq. 3.18,

$$p_c = \frac{a}{27b^2} \quad \dots (3.21)$$

From Eqs 3.17 and 3.20, we get

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

$$\text{or } T_c = 8b \cdot \frac{p_c}{R}$$

$$= 8b \cdot \frac{a}{27b^2} \cdot \frac{1}{R} \text{ (using Eq. 3.21)}$$

$$= \frac{8a}{27Rb} \quad \dots (3.22)$$

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

3.5.2 Determination of Critical Constants

Let us study the experimental method of determination of critical constants.

Critical Temperature

A capillary tube capable of standing high pressure is evacuated and filled with the liquid and sealed. This is placed in an aluminium block having a window. The system is then heated and the meniscus of the liquid is kept under observation through the window.

Initially, the liquid is in equilibrium with the vapours and a distinct boundary can be seen.

As soon as the critical temperature is reached, the boundary disappears. The experiment is repeated a number of times by varying the temperature in both directions. The mean is then taken as the experimental value of critical temperature.

Critical Pressure

The gas under observation is taken in a high pressure vessel at the critical temperature.

Initially the gas pressure is kept low. Slowly the gas is compressed at constant temperature.

As soon as the vessel inside is covered with mist, it indicates the formation of some liquid and this pressure corresponds to p_c . Since the pressure is generally much higher than what an ordinary manometer can measure, special pressure gauges are to be used.

Critical Volume

Critical volume is determined indirectly based on the findings of Cailletet and Mathies. According to them, a plot of the mean values of the densities of a liquid and its saturated vapour against temperature is a straight line (Fig. 3.6).

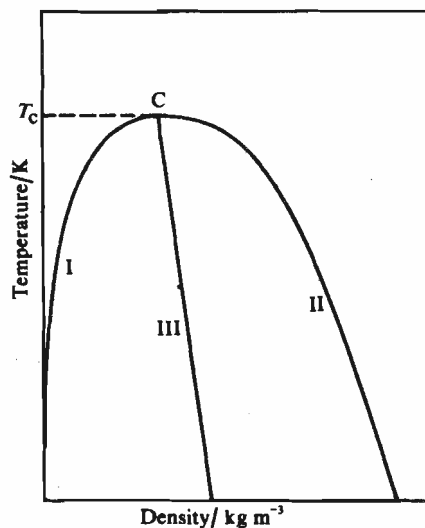


Fig. 3.6 : Plot of densities of vapour (I), liquid (II) and their mean values (III) against temperature.

It is clear that the density of the vapour (curve I) increases with the increase in temperature because the evaporation is higher at higher temperature. But the density of the liquid decreases as temperature increases (curve II). At the critical temperature, the two densities must be equal. However, due to fluctuations it is very difficult to measure the density at T_c . Hence, the two curves, I and II are extrapolated to give a continuous curve. The mean density is now plotted to get curve III and extrapolated to intersect the combined curves I and II at C. The density at C, known as critical density, represents the density at T_c . From this, the critical volume is calculated using the relationship,

$$V_c = \frac{\text{Molar mass}}{\text{Critical density}}$$

Some of the experimental values of the critical constants are already given in Table 3.1.

3.5.3 Test for van der Waals Equation

The calculation of the compressibility factor at the critical point (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 :

$$\begin{aligned} z_c &= \frac{p_c V_c}{RT_c} \quad \dots (3.23) \\ &= \left(\frac{a}{27b^2}\right) \cdot (3b) \cdot \frac{1}{R} \cdot \frac{1}{8a/27Rb} \\ &= \frac{3}{8} = 0.375 \end{aligned}$$

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 SAQs?

SAQ 2

Indane gas supplied for household use is mostly a mixture of propane and butane. Are the critical temperatures of these two gases higher than 298 K?

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SAQ 3

Using p_c , V_c and T_c values of methane from Table 3.1, calculate the value of z_c . Does methane obey van der Waals equation at the critical point?

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3.6 EQUATION OF CORRESPONDING STATES

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

$$\text{Thus, reduced pressure} = \pi = \frac{p}{p_c} \text{ or } p = \pi p_c \quad \dots (3.24)$$

$$\text{Reduced volume} = \phi = \frac{V_m}{V_c} \text{ or } V_m = \phi V_c \quad \dots (3.25)$$

$$\text{Reduced temperature} = \theta = \frac{T}{T_c} \text{ or } T = \theta T_c \quad \dots (3.26)$$

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. 3.6, 3.24, 3.25 and 3.26 we obtain,

$$\left(\pi p_c + \frac{a}{\phi^2 V_c^2}\right) (\phi V_c - b) = R\theta T_c \quad \dots (3.27)$$

Now substituting the values of p_c , V_c , and T_c from Eqs. 3.20-3.22,

$$\left(\pi \cdot \frac{a}{27b^2} + \frac{a}{\phi^2 9b^2}\right) (3\phi b - b) = R\theta \frac{8a}{27Rb} \quad \dots (3.28)$$

$$\frac{a}{27b^2} \left(\pi + \frac{3}{\phi^2}\right) (3\phi - 1) b = \frac{8\theta a}{27b} \quad \dots (3.29)$$

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

$$\text{or } \left(\pi + \frac{3}{\phi^2}\right) (3\phi - 1) = 8\theta \quad \dots (3.30)$$

This is known as the equation of the corresponding states. 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 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. 3.30, work out the following SAQ.

SAQ 4

Using the values of p_c and V_c for methane from Table 3.1, calculate its reduced temperature if it occupies $5.000 \times 10^{-2} \text{ m}^3$ space at $3.328 \times 10^5 \text{ pa}$.

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The superconducting materials conduct electricity without offering 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.

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

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

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

3.7 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 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.

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.

3.7.1 Linde's Method

This method is based on the principle known as Joule-Thomson effect. According to this effect, 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.

The schematic diagram of the equipment used is shown in Fig. 3.7.

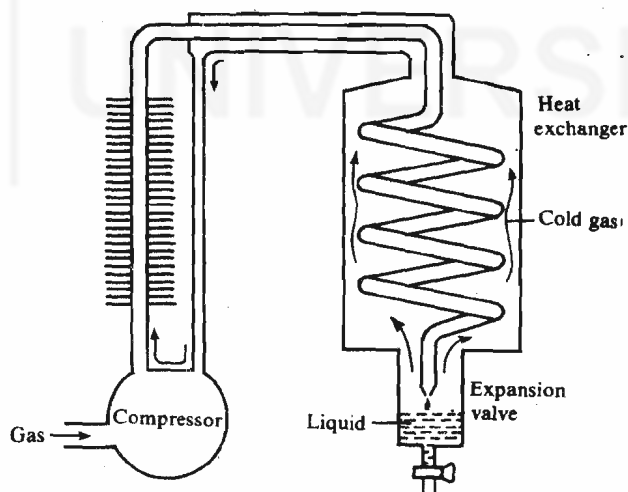


Fig. 3.7 : Liquefaction using Linde's method

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.

3.7.2 Claude's Method

Claude's method (Fig. 3.8), 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

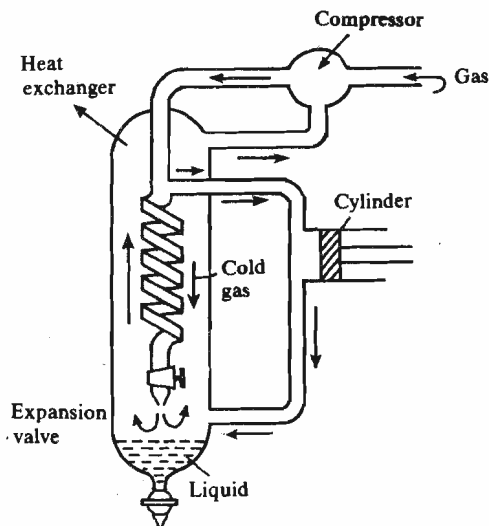


Fig. 3.8 : Liquefaction using Claude's method.

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.

piston in a cylinder and partly expanded through a valve. 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.

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3.8 INTERMOLECULAR FORCES

In Sec. 3.3, we have studied that the real gases deviate from the ideal gas behaviour because of the presence of intermolecular forces. The intermolecular forces are also responsible for the conversion of gases into liquids and solids. van der Waals not only derived an equation to explain the behaviour of real gases but also tried to develop a model that would explain the behaviour of liquids. In recognition of his work, the weak intermolecular forces in liquids and solids are often called **van der Waals forces**.

Attractive forces between uncharged atoms or molecules are known as van der Waals forces.

3.8.1 van der Waals Forces

van der Waals forces include :

- i) Dipole-dipole interactions
- ii) Dipole-induced dipole interactions
- iii) London or dispersion forces

Let us study them in detail.

Dipole-Dipole Forces

Polar molecules can attract each other electrostatically. During this attraction the positive end of one molecule is close to the negative end of the adjacent molecule, as shown in Fig. 3.9.

Such an attraction is called **dipole-dipole interaction**. 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.

The interaction energy ($V_{\mu\mu}$) 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

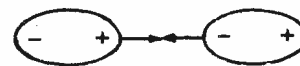


Fig. 3.9 : The electrostatic interaction of two polar molecules; - - shows attraction.

The dipole-dipole interaction between two HCl molecules is 130 times weaker than the bond energy of HCl molecule.

- inversely proportional to temperature
- inversely proportional to r^6

$$\text{(i.e., } V_{\mu\mu} \propto \frac{1}{r^6}\text{)}$$

Dipole-Induced Dipole Interaction

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 polarisable atom or molecule. Let us explain, the terms 'polarisable' and 'polarisability'. An atom or molecule is said to be polarisable, if its electron cloud can be distorted. The ability of a species to undergo electronic distortion is described in terms of polarisability. 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 larger distance

So a larger atom has a higher polarisability than a smaller atom. For example, argon has higher polarisability than helium. Similarly larger molecules (due to greater number of electrons) have higher polarisability than smaller molecules. For example, ethane is more polarisable than methane; propane is more polarisable than ethane, and so on.

The **dipole-induced dipole interaction** between a polar molecule and a neighbouring polarisable molecule (in which dipole is induced) causes a lowering of energy. That is, such an attractive interaction adds to the stability. The interaction energy ($V_{\mu d}$) 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 polarisability of the molecule (in which dipole is induced),
- inversely proportional to the sixth power of r

$$\text{(i.e., } V_{\mu d} \propto \frac{1}{r^6}\text{)}$$

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

Induced Dipole-Induced Dipole or London or Dispersion Interaction

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**. These forces are called **dispersion forces** since the oscillations producing the attractive forces are also responsible for the dispersion of light by the molecules.

To understand the origin of this interaction, let us consider a pair of helium atoms. On the average the charge cloud around a helium atom is symmetrical. But the electrons surrounding the nucleus of the helium atom are in constant motion. Because of this, the helium atom can develop a momentary nonsymmetrical electron distribution. This results in a temporary dipolar arrangement of charge, otherwise known as **instantaneous polarity**. This helium atom which has instantaneous polarity can then induce a dipole in the neighbouring helium atom, Fig. 3.10.

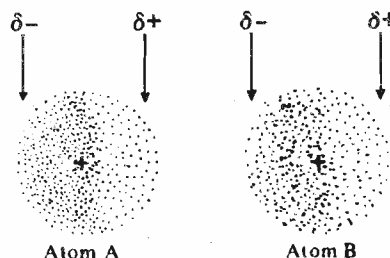


Fig. 3.10 : Instantaneous dipole on atom A induces a dipole on atom B. δ^+ and δ^- refer to dipolar charges and + stands for the nucleus.

London forces are the only attractive forces between nonpolar molecules. Polar molecules have dipole-dipole, dipole-induced dipole and also London forces.

The resultant **induced dipole-induced dipole** attraction is both weak and short-lived. But this can be very significant for large atoms (or molecules) which have high polarisability. 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 (V_{dis}) between two noble gas atoms or two nonpolar molecules separated by a distance r is

- directly proportional to the product of the polarisabilities of the two species
- inversely proportional to the sixth power of r ,

$$\text{i.e., } V_{dis} \propto \frac{1}{r^6}$$

3.8.2 Total Interaction Energy

All the three types of interactions explained above are attractive in nature and can account for the cohesive forces responsible for liquefaction of gases. It must be remembered that repulsive forces also operate when molecules are brought too close. It has been estimated that the interaction energy due to repulsion (V_{rep}) is inversely proportional to twelfth power of r .

$$\text{i.e., } V_{rep} \propto \frac{1}{r^{12}}$$

The sum of attractive and repulsive energies, is the total interaction energy (V_i).

$$V_i = V_{\mu\mu} + V_{\mu d} + V_{dis} + V_{rep} \quad \dots (3.31)$$

This equation can also be written as

$$V_i = \frac{p}{r^{12}} - \frac{q}{r^6} \quad \dots (3.32)$$

Where the first term in the right hand side stands for repulsive interaction V_{rep} (+ve sign); and the second term for the sum of all attractive interactions, viz., $V_{\mu\mu}$, $V_{\mu d}$ and V_{dis} (-ve sign). The terms p and q are characteristic of the molecules under study. Eq. 3.32 implies that the molecules have attractive forces (proportional to r^{-6}) and repulsive forces (proportional to r^{-12}).

The effect of attractive and repulsive interactions on the energy of a system can be understood by a plot of V_i against r (Fig. 3.11) drawn for methane molecules. By convention, the total interaction energy of the two methane molecules separated by infinite distance (represented by the point A) is zero. When the two molecules are brought closer, they begin to attract one another and there is decrease in the total interaction energy. This is indicated by the falling portion ABC of the curve. At C, the two molecules have the lowest energy. If the two molecules are brought still closer, repulsive forces overtake the attractive forces and the total interaction energy starts increasing. This is indicated by the rising portion CD of the curve. Note that the decrease in V_i due to attractive forces (along ABC) is gradual but the increase in V_i due to repulsive forces (along CD) is very steep (Guess the reason!).

Cohesive force is responsible for the condensation of a gas into a liquid or solid. van der Waals forces mentioned in Sec. 3.8.1 are cohesive in nature.

Attractive forces cause decrease in interaction energy. Repulsive forces result in increase of interaction energy.

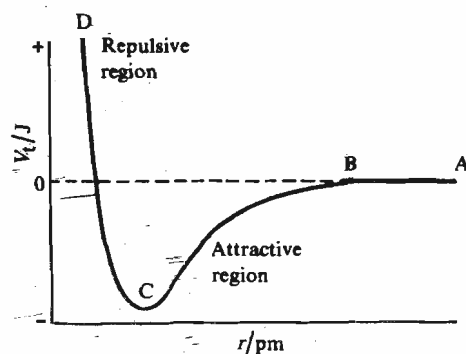


Fig. 3.11 : Total interaction energy as a function of intermolecular distance.

3.8.3 Hydrogen Bonding

The strength of hydrogen bonding is of the order of $10\text{--}40 \text{ kJ mol}^{-1}$

There are several specific types of interactions encountered between various types of molecules. Of these, metallic bonding and hydrogen bonding are very significant. We shall study metallic bonding in Unit 5. Here let us study hydrogen bonding in detail. When a hydrogen atom is covalently bonded to a 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 a 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. In water, for example, hydrogen bonding arises between hydrogen atom (positive end of the dipole) of one water molecule and the oxygen atom (negative end of the dipole) of the other. (Fig. 3.12a). Hydrogen fluoride is another molecule having hydrogen bonding. (Fig. 3.12b).

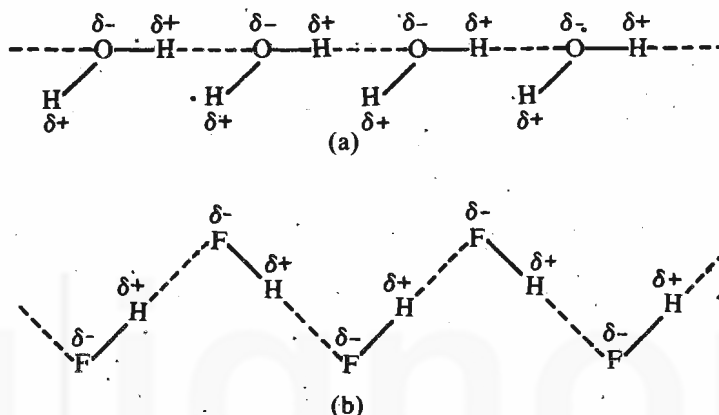


Fig. 3.12 : Hydrogen bonding : (a) in water (b) in hydrogen fluoride.

Hydrogen bonding is strong in HF, H_2O and NH_3 as compared to many hydrides due to the higher electronegativity of fluorine, oxygen and nitrogen. Strong hydrogen bonding in these compounds results in enhanced attractive interactions between the molecules.

Let us study the effect of the above interactions on the physical properties of the compounds.

3.8.4 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. Some of these aspects will be studied in Unit 4. But here we consider the effect of intermolecular forces on melting and boiling points only, since these two concern change of state.

- 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, dipolar interactions are also present. In general, larger the dipole moment, the higher the melting and boiling points. See some illustrative data in Table 3.2.

Table 3.2 : 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

In Unit 6 of Atoms and Molecules course, you have studied that the unit of dipole moment is C m.

- Among the noble gases, the boiling point increases with atomic number (Table 3.3). As explained earlier, the London forces are more in large atoms due to higher polarisability.

- iii) Among a series of similar nonpolar molecules such as hydrocarbons, boiling point increases with the molecular size (Table 3.3). Again, the reason is that a larger molecule has higher polarisability 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 3.3 : 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

Relative molecular mass is more commonly known as molecular weight.

- 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. 3.13) 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. 3.14)

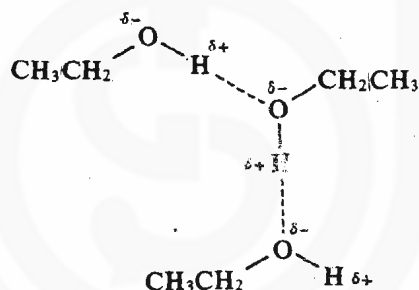


Fig. 3.13 : Hydrogen bonding in ethanol.

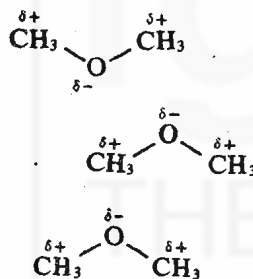


Fig. 3.14 : Dipole-dipole interaction in dimethyl ether.

- 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. 3.15a and b).

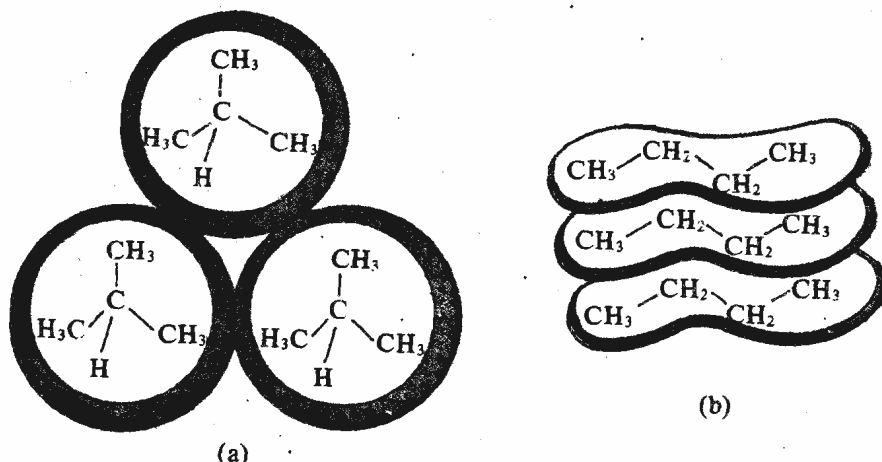


Fig. 3.15 : (a) Interactions among nearly spherical molecules of 2-methylpropane
(b) Interactions among distorted rod-like molecules of butane.

For a given volume, a sphere has the smallest surface area as compared to other geometrical shapes.

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 6

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

3.9 SUMMARY

In this unit, we have discussed the behaviour of real gases. Their deviation from ideal gas behaviour has been explained in terms of intermolecular forces. van der Waals equation has been derived and used in explaining the deviation from ideal gas behaviour. The necessary conditions for liquefaction of gases have been discussed. The critical constants have been defined. Their relationships with van der Waals parameters have been established. The principle of corresponding states has been stated and explained. The methods for liquefaction of gases are outlined. The nature of intermolecular forces, their types and their effect on physical properties of substances are discussed.

3.10 TERMINAL QUESTIONS

- Using the van der Waals parameters of nitrogen given in Table 3.1, estimate its critical constants and compare with the actual values given in Table 3.1.
- 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.
 $a = 0.5536 \text{ Pa} \cdot \text{m}^6 \text{ mol}^{-2}$ and
 $b = 3.049 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$
- Which of the substances listed in Table 3.1 can be liquefied at 298 K?
- State the principle of corresponding states in as many ways as you can.
- Why is the liquefaction of gases easier at low temperatures and high pressures?
- Ethanol has higher boiling point than butane although the latter has higher relative molecular mass. Explain.
- A vessel of $1.000 \times 10^{-3} \text{ m}^3$ volume contains 0.0180 kg of argon at 300.0 K. Calculate its pressure using ideal gas and van der Waals equations. Use Table 3.1.
- Calculate the reduced pressure and reduced temperature for oxygen gas at 273.2 K and $1.013 \times 10^5 \text{ Pa}$. Use Table 3.1.

3.11 ANSWERS**Self Assessment Questions**

- As a van der Waals gas :

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

$$= 9.898 \times 10^4 \text{ Pa}$$

As an ideal gas :

$p = 9.917 \times 10^4 \text{ Pa}$. Thus, the values of pressure calculated from van der Waals equation and ideal gas equation are slightly different.

2. The indane gas is in the liquid state inside the cylinder; hence, the critical temperatures 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 3.1,
 $z_c = 0.2892$
 Substituting the expressions for p_c , V_c and T_c from Eqs. 3.20—3.22, in Eq. 3.23,
 $z_c = 0.375$
 Hence, at the critical point, methane deviates from van der Waals equation.
4. $\pi = \frac{p}{p_c} = 7.171 \times 10^{-2}$
 $\phi = \frac{V}{V_c} = 50.51$
 Substituting these quantities in Eq. 3.30, 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 main intermolecular interactions in Cl_2 , Br_2 and I_2 are London forces. Since the polarisability and hence, London forces increases with relative molecular mass, the melting points are in that order.

Terminal Questions

1. Critical constant calculated as per Eqs. 3.20-3.22:
 $V_c = 1.174 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$
 $p_c = 3.400 \times 10^6 \text{ Pa}$
 $T_c = 128.2 \text{ K}$
2. Using van der Waals equation, the pressure values at $5.000 \times 10^2 \text{ K}$ and $1.000 \times 10^3 \text{ K}$ are $2.752 \times 10^5 \text{ Pa}$ and $5.530 \times 10^5 \text{ Pa}$. The pressure change is
 $(5.530 - 2.752) \times 10^5 \text{ Pa} = 2.778 \times 10^5 \text{ Pa}$.
3. CO_2 , H_2O and NH_3 can be liquefied at 298 K since their critical temperatures are higher than 298 K.
4. As given in Sec. 3.6.
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 pressures when distances between molecules are smaller on the average and hence, the attractive interactions are higher.
6. Apart from London forces, ethanol molecules have strong hydrogen bonding too. But in butane, only London forces are present. Because of stronger intermolecular forces, ethanol has higher boiling point than butane.
7. According to van der Waals equation, pressure calculated is $2.440 \times 10^6 \text{ Pa}$, whereas as per ideal gas equation, it is $2.494 \times 10^6 \text{ Pa}$.
8. $\theta = 1.765$; $\pi = 1.996 \times 10^{-2}$.

UNIT 4. LIQUIDS

Structure

- 4.1 Introduction
 - Objectives
- 4.2 Comparison of Liquids with Gases and Solids
- 4.3 Structure of Liquids
- 4.4 Surface Tension and Viscosity
- 4.5 Vaporization
 - Vapour Pressure
 - Boiling Point
- 4.6 Trouton's Rule
- 4.7 Liquid Crystals
- 4.8 Summary
- 4.9 Terminal Questions
- 4.10 Answers

4.1 INTRODUCTION

In Unit 2, we discussed the characteristics of ideal gases. We assumed that there is no attractive or repulsive interaction between the individual molecules. In Unit 3, this treatment was modified to account for the behaviour 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 recognised. In Unit 5, 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. Our aim is not to list the properties of liquids but to correlate these to the intermolecular interactions.

We will describe the features of a model proposed for the structure of liquids. We shall explain the correlation between the intermolecular forces and the properties of liquids such as surface tension, viscosity, vapour pressure, boiling point and molar enthalpy of vaporization. Finally we will briefly study liquid crystals, their types and their applications.

Objectives

After studying this unit, you should be able to :

- explain the structure of liquids,
- state the significance of surface tension and viscosity of liquids,
- discuss the qualitative dependence of vapour pressure, boiling point and molar enthalpy of vaporization of liquids on the molecular interactions,
- state and explain Trouton's rule, and
- discuss the types of liquid crystals and their applications.

4.2 COMPARISON OF LIQUIDS WITH GASES AND SOLIDS

We can obtain a liquid by heating a solid or by cooling a gas under certain conditions. Therefore, liquid state is in between solid and gaseous states. In a solid, the particles have only vibrational motion about their equilibrium positions. The strong intermolecular forces present in a solid crystal are responsible for the restricted motion of the particles and their orderly arrangement.

As a result, a solid has a definite shape. 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 characteristics of a liquid lie between the extremes of a gas and a solid. 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. Let us now examine the structural aspects of liquids.

4.3 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

A pure solid melts to give a liquid at a sharp temperature. This process is called fusion. It is generally seen that during fusion, volume increases by 10%. This implies that a substance retains its orderliness to a considerable extent during fusion. On the contrary, in the conversion of a liquid into vapour at its boiling point (known as vaporization), the volume increases 100-1000 fold. This large increase in volume during vaporization indicates that the particles are changed into a more disorganised state.

Molar Enthalpies 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 (ΔH_{fus}^0). 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 (ΔH_{vap}^0). The values of ΔH_{fus}^0 , ΔH_{vap}^0 and boiling points (BP) are given in Table 4.1 for some substances. It is seen that ΔH_{vap}^0 is larger than ΔH_{fus}^0 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 heat absorption during change of state is associated with increase in disorder. On this assumption, we can think that a liquid has considerable measure of orderly arrangement as compared to a gas.

Table 4.1 : Molar Enthalpies of Fusion (ΔH_{fus}^0) and Vaporization (ΔH_{vap}^0) and Boiling Points (BP) of the Substances

Substance	$\Delta H_{\text{fus}}^0/\text{kJ mol}^{-1}$	$\Delta H_{\text{vap}}^0/\text{kJ mol}^{-1}$	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	59.2	630
Silver	12.2	259	2430
Aluminium	10.9	292	2720

X-Ray Diffraction by Liquids

In the next unit, we shall study that the X-ray diffraction by a solid crystal gives rise to sharp diffraction pattern. The sharpness of diffraction pattern 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). The diffuse diffraction pattern makes it clear 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; 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. 4.1.

The main aspects of this model are summarised 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.

Water and a few other substances are exceptional in having a lower volume per unit mass (and higher density) in liquid state than in solid state. We shall discuss this aspect in the unit on phase equilibria.

The state of a substance under 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.

Heat absorbed by a substance at constant pressure at its melting or boiling point is used, not to increase the temperature but to increase its disorderliness. In the language of thermodynamics, such heat absorption during change of state increases the entropy of the substance. We shall discuss this in Unit 8. Some correlations regarding ΔH_{vap}^0 are given in Secs. 4.5 and 4.6.

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

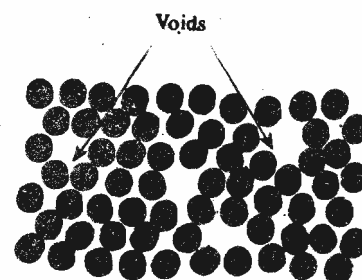


Fig. 4.1 : A model for the structure of liquids

- 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 1

Liquids are less compressible than gases. State the reason.

.....

.....

.....

4.4 SURFACE TENSION AND VISCOSITY

Having discussed the structure of liquids, we now take up the study of the properties of liquids. Three of the characteristic properties of liquids are :

- Possession of a sharply defined surface
- Ability to flow
- Tendency to vaporize into space above the surface and to exert vapour pressure.

These properties are related to the strength of intermolecular forces in liquids. We now discuss surface tension and viscosity of liquids.

Surface Tension

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.

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. This fascinating phenomenon is one of the reasons for the spherical shape of earth, sun, moon, etc. Let us explain the origin of forces operating to minimise surface area.

A molecule in the interior of a liquid is attracted by all the molecules surrounding it. It is pulled equally in all directions. But a molecule at the surface of a liquid is attracted only by molecules below it (Fig. 4.2).

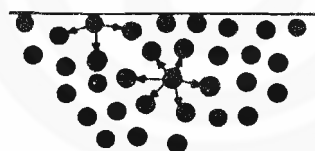


Fig. 4.2 : Molecules in the bulk and on the surface of liquid being attracted by neighbours.

Therefore, the molecules on the surface of the liquid are drawn inwards trying to minimise 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 energy required to increase the surface area by one unit by moving the molecules from the interior of the liquid to the surface. It is also defined as the force per unit length perpendicular to a liquid surface. Corresponding to these two definitions, SI units of surface tension are J m^{-2} and N m^{-1} (which are, of course, equivalent). 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 4.2.

Table 4.2 : Values of Surface Tension (γ) of Some Liquids at 293 K

Liquid	$10^2 \times \gamma / \text{N m}^{-1}$
Water	7.28
Benzene	2.89
Carbon tetrachloride	2.64
Chloroform	2.67
Mercury	46.5

The values of surface tension given in Table 4.2 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.

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.

Intermolecular forces give rise to **capillary action**. It is the rise of liquids through a capillary (narrow glass) tube (Fig. 4.3a). 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 as discussed in Unit 3. 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 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 cohesive forces (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. 4.3b) 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.



Fig. 4.3 (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.

Viscosity

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 viscosities of a few liquids are given in Table 4.3.

Table 4.3 : Viscosity (η) of some liquids at 298 K

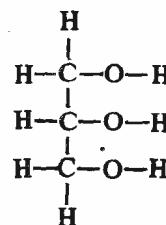
Liquid	η /Pa s
Water	8.90×10^{-4}
Benzene	6.0×10^{-4}
Glycerol	0.945
Chloroform	4.7×10^{-4}

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

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.



Glycerol

Liquids with larger intermolecular forces flow slowly and are called viscous liquids. Hydrogen bonding is particularly important in this respect because it can bind neighbouring

molecules together much strongly. This accounts for the fact that water has higher viscosity than benzene and chloroform, which have no hydrogen bonding. Glycerol has very high viscosity, mainly due to numerous hydrogen bonds it can form.

Molecular arrangement also could cause high viscosity: Heavy hydrocarbon oils and grease are not hydrogen bonded but are highly viscous. Their viscosity arises partly from London forces between molecules and partly because the long chainlike molecules become entangled with each other (Fig. 4.4) like cooked noodles served in a plate.



Fig. 4.4 : The molecules in the heavy hydrocarbon oil entangled together.

Viscosity measurements help in evaluating relative molecular masses of polymers.

Use the above discussion on surface tension and viscosity to answer the following SAQs.

SAQ 2

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

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

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SAQ 3

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?

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4.5 VAPORIZATION

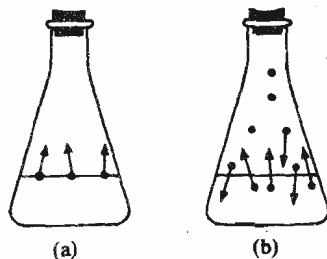


Fig. 4.5 : (a) Initially molecules are transferred from the liquid to the vapour phase; (b) at equilibrium the rate of vaporization is equal to the rate of condensation.

The escape of molecules from the liquid surface to form the vapour is called the vaporization or evaporation. To have an understanding of this process, we must know how vapour pressure, boiling point and molar enthalpy of vaporization are connected among themselves and also to the intermolecular forces.

4.5.1 Vapour Pressure

The molecules in a liquid move constantly. During this motion, the molecules with sufficient kinetic energy can jump out into the space above the liquid as vapour. If the liquid is kept in an open vessel, the molecules escape into the atmosphere and the liquid keeps on evaporating. However, if the liquid is kept in a closed vessel, the number of molecules in the vapour state increases at first (Fig. 4.5 a). They also start returning to the liquid surface which is called condensation. The condensation rate keeps on changing till it is equal to the rate of vaporization and the space above the liquid is saturated with vapour (Fig. 4.5 b). The pressure exerted by a vapour in contact with its liquid at a given temperature is called its vapour pressure.

Vapour pressure of a liquid is commonly measured by introducing a liquid into a container; the container is closed and connected to a U-tube containing mercury (Fig. 4.6)

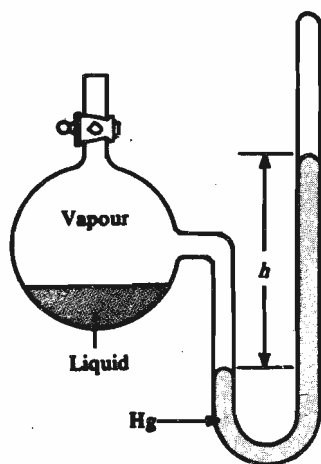


Fig. 4.6 : Vapour pressure measurement.

The difference in the heights of mercury columns (h) is measured in mm of Hg unit. The vapour pressure in SI units can be calculated using the following equivalence statement :

$$760 \text{ mm of Hg} = 1.013 \times 10^5 \text{ Pa}$$

(Recapitulate the unit conversions discussed in Sec. 1.6 of Unit 1).

The addition of a nonvolatile solute to a solvent causes lowering of vapour pressure. This, and the related effects would be discussed in the unit on colligative properties.

The vapour pressure of some liquids are given in Table 4.4.

Table 4.4 : Vapour Pressures of Some Liquids at 298 K

Substance	Vapour pressure/Pa
Mercury	0.227
Water	3.17×10^3
Ethanol	7.85×10^3
Diethyl ether	5.90×10^4
Benzene	1.26×10^4

From Table 4.4, it can be inferred that the liquids having strong intermolecular forces do not vaporize easily and their vapour pressures are low. Water, due to strong hydrogen bonding has lower vapour pressure than ethanol and, the latter has lower vapour pressure than diethyl ether. Metallic bonding signifies strong interaction among the atoms; as a result of this, mercury has low vapour pressure.

As the temperature of a liquid increases, the average kinetic energy of the molecules also increases. The number of molecules escaping as vapour also increases. Hence, the vapour pressure increases with temperature. To illustrate this, the vapour pressures of water are given at different temperatures in Table 4.5.

A molecule of water is capable of forming four hydrogen bonds; two with the (two lone pairs of) oxygen atom and two with two hydrogen atoms. A molecule of ethanol can form only three hydrogen bonds, two with oxygen atom and one with hydrogen atom. Water has stronger hydrogen bonding than ethanol.

Table 4.5 : Vapour Pressures of Water at Different Temperatures

Temperature/K	Vapour pressure/Pa
283	1.226×10^3
293	2.330×10^3
323	1.233×10^4
348	3.850×10^4
373	1.013×10^5

There is a quantitative relationship, known as Clausius-Clapeyron equation, between the vapour pressure of a liquid and its temperature. We will discuss this in Unit 9. Let us now define the boiling point of a liquid.

4.5.2 Boiling Point

The temperature at which the vapour pressure of a liquid equals the external pressure is called its boiling point. At this temperature, the vapour produced in the interior of the

Distillation is a procedure to separate pure substances from a solution using vaporization and condensation.

liquid results in continuous bubble formation that is characteristic of boiling. The temperature of a boiling liquid (even with the absorption of heat) remains constant until all the liquid has been vaporized.

The boiling point of a liquid at 1.013×10^5 Pa (1 atm) pressure is called its normal boiling point. The boiling points mentioned in this course are normal boiling points. A less volatile liquid (i.e., a liquid which has low vapour pressure at room temperature) is to be heated to a higher temperature so that its vapour pressure equals atmospheric pressure. That is a **less volatile liquid has a high boiling point**. On the contrary, a more volatile liquid (i.e., a liquid having high vapour pressure at room temperature) needs to be heated less to make it attain atmospheric pressure and it has a low boiling point. A glance at the boiling points (Table 4.1) and vapour pressure (Table 4.4) of water and diethyl ether indicates that water is less volatile and has higher boiling point; whereas diethyl ether is more volatile and has a lower boiling point.

Let us now study the effect of external pressure on boiling point. The boiling point increases as external pressure increases and the boiling point decreases as external pressure decreases. This principle is made use of in **distillation under reduced pressure** (Fig. 4.7). It means making a liquid boil at a pressure lower than atmospheric pressure. If a liquid has a high boiling point and decomposes when heated, it can be made to boil at a lower temperature by reducing the pressure. For reducing the pressure, a vacuum suction pump is used.

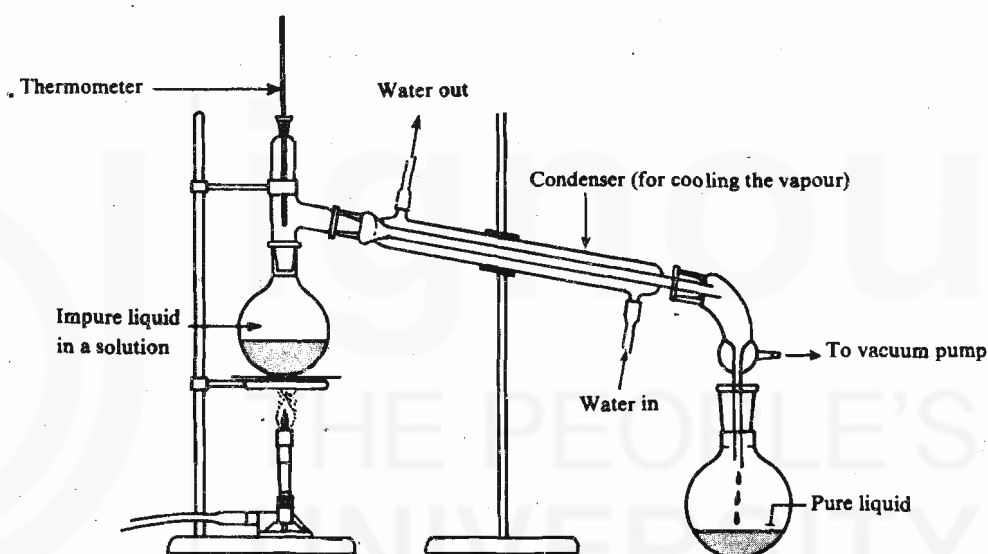


Fig. 4.7 : Reduced pressure distillation.

Distillation under reduced pressure is often used in the separation and purification of organic and inorganic compounds. A commercial application is that excess water content is removed from many food products by boiling under reduced pressure. An alternate way of looking at Table 4.5 is that it gives boiling points of water at different external pressures. Thus, at a reduced pressure of 1.226×10^3 Pa (0.0121 atm), water boils at 283 K; the boiling point of water is lowered by 90 K at this pressure.

Water has many abnormal but useful characteristics. Most strikingly, its large enthalpy of vaporization enables water to function as an effective coolant for our planet as well as for our body. Interestingly, the surface of the earth and human body have both around 70% water content.

In Unit 3, we learnt about the correlation between boiling points and intermolecular forces. It is interesting to note that intermolecular forces have similar effect on the boiling points and the molar enthalpies of vaporization, if comparisons are restricted to similar compounds. Let us examine Table 4.1 from this angle. Water has stronger hydrogen bonding than ethanol; the boiling point and molar enthalpy of vaporization of water are more than those of ethanol. Increasing intensity of London forces increases the boiling point and molar enthalpy of vaporization among the alkanes. Effect of metallic bonding is clearly seen in the high values of boiling points and molar enthalpies of vaporization of mercury, silver and aluminium.

The parallel between the molar enthalpies of vaporization and the boiling points of liquids led Trouton to suggest a relationship between the two quantities. Before studying Trouton's rule, organise your thoughts by answering the following SAQs.

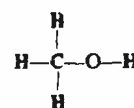
SAQ 4

The vapour pressure of methanol is higher than that of ethanol at 300 K. Suggest a reason.

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Methanol

SAQ 5

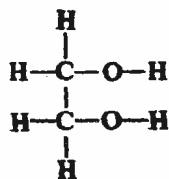
Arrange the following compounds in the increasing order of boiling points:

Ethanol, glycerol and ethylene glycol.

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Ethylene glycol

4.6 TROUTON'S RULE

Trouton's rule can be stated as follows:

The ratio of molar enthalpy of vaporization of a liquid to its boiling point is approximately $85 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$\text{i.e., } \frac{\Delta H_{\text{vap}}^0}{\text{BP}} = 85 \text{ J mol}^{-1} \text{ K}^{-1} \quad \dots (4.1)$$

Trouton's rule holds good for liquids in which hydrogen bonding is **absent**. The ratio, $\Delta H_{\text{vap}}^0/\text{BP}$ is also known as entropy of vaporization. It is a measure of disorderliness gained by a substance due to vaporization. During vaporization, a hydrogen bonded liquid gains more disorderliness as compared to a nonhydrogen bonded liquid; hence $\Delta H_{\text{vap}}^0/\text{BP}$ is more than $85 \text{ J mol}^{-1} \text{ K}^{-1}$ for hydrogen bonded liquids. For example, the values of $\Delta H_{\text{vap}}^0/\text{BP}$ for water and ethyl alcohol are 109 and $112 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

A hydrogen bonded liquid is more orderly in its molecular arrangement than a nonhydrogen bonded liquid. During vaporization, the increase in disorderliness is more in a hydrogen bonded liquid than in a nonhydrogen bonded liquid.

For nonpolar liquids, Eq. 4.1 is useful in calculating the boiling point or molar enthalpy of vaporization, if either is known. Let us calculate the molar enthalpy of vaporization of benzene; its boiling point is 353 K. Using Eq. 4.1.

$$\begin{aligned} \Delta H_{\text{vap}}^0 &= 353 \text{ K} \times 85 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 30 \text{ kJ mol}^{-1} \end{aligned}$$

The experimental value as given in Table 4.1 is 31.1 kJ mol^{-1} .

So far, we have studied the characteristics of liquids. There is a class of compounds, known as liquid crystals, which flow like liquids and have structural similarity to solids. We take up the study of liquid crystals in the next section; before going through the next section, it is better you try the following SAQ.

SAQ 6

Calculate the molar enthalpy of vaporization of carbon tetrachloride which boils at 350 K.

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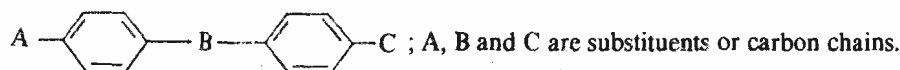
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4.7 LIQUID CRYSTALS

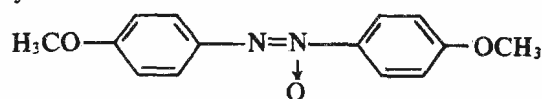
Gases and liquids are **isotropic**. This means for any gas or liquid, the value of any of the physical properties such as refractive index, coefficient of thermal expansion, electrical conductivity, speed of sound etc., is same in **all directions**. In contrast to this, a crystalline solid when examined as an individual crystal (or a single crystal) behaves in a different way. Depending upon the direction in which the crystal is kept during measurement, it may have a different value for its physical properties mentioned above. Such a single crystal is **anisotropic**. In some cases different faces of a crystal may show different catalytic activity. Another class of compounds which are anisotropic are liquid crystals. Let us first define the term 'liquid crystal' and then see how its anisotropy gives rise to interesting applications.

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 larger than 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 have molecules arranged in parallel layers or planes. These planes are at equal distances. The molecules in all the planes point to the same direction. That is, the molecules have same orientation. The only difference between a solid crystal (Fig. 4.8a) and a smectic liquid crystal (Fig. 4.8b) is that in the former, the particles are arranged at regular intervals within a plane; whereas in the latter it is not so.

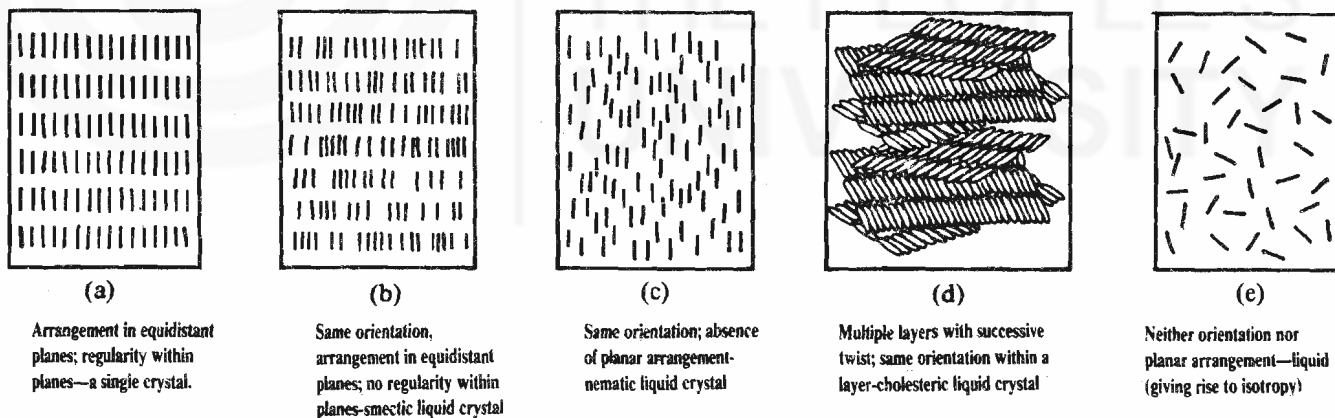


Fig. 4.8 : Structure of a single crystal, liquid crystals and liquid.

The optical (opaque or transparent) nature of a nematic liquid crystal depends on the way the molecules are oriented.

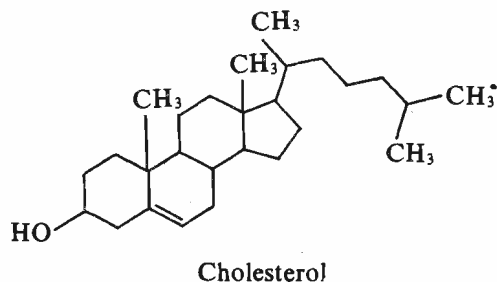
Nematic liquid crystals have all the molecules with the same orientation (Fig. 4.8c). Unlike in smectic type, the molecules are not arranged in planes in nematic liquid crystals. Application of an electric field causes a change in the orientation of the molecules in a nematic liquid crystal. A change in molecular orientation, causes a change in optical properties. It is this anisotropic character that makes a nematic liquid crystal useful in LCD (liquid crystal display) watches and calculators.

Cholesteric liquid crystals have a multiple layer structure, but each successive layer is inclined or twisted slightly. Fig. 4.8d illustrates the cholesteric liquid crystal structure. For comparison, the typical disorderly arrangement of molecules (accounting for isotropy) in a liquid is shown in Fig. 4.8e.

The successive twist in structure makes the cholesteric liquid crystals coloured. A minute change in temperature causes a change in the amount of twisting. It results in reflection of

different wavelength of visible light; that is, the colour changes with temperature. 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. This class of liquid crystals received their name from the fact that many derivatives of cholesterol pertain to this type.

The colour of a cholesteric liquid crystal changes with the change in twist-pattern of layers in its structure.



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. On the basis of what you have studied so far, answer the following SAQ.

SAQ 7

In what way, an isotropic substance is different from an anisotropic substance?

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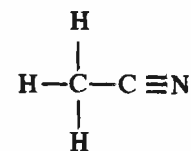
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4.8 SUMMARY

In this unit we studied the characteristics of liquids. The model proposed for the structure of liquid was discussed. Surface tension and viscosity of liquids were explained and the dependence of these characteristics on intermolecular forces was brought out. We discussed the properties of liquids such as vapour pressure, molar enthalpy of vaporization and boiling point. Trouton's rule was stated and explained. The terms isotropy and anisotropy were defined. The applications of anisotropic character of liquid crystals were illustrated.

4.9 TERMINAL QUESTIONS

- (1) Comment on the fact that the densities of solid, liquid and gaseous nitrogen are 1.026, 0.8081 and $1.251 \times 10^{-3} \text{ kg dm}^{-3}$, respectively.
- (2) In a polythene tube, water meniscus is convex. Explain.
- (3) Explain the reason for the anisotropy in the optical properties of nematic and cholesteric liquid crystals.
- (4) Molar enthalpies of vaporization of benzene and naphthalene are 31.1 and 44 kJ mol^{-1} . Explain.
- (5) At room temperature, among water, methyl cyanide and methanol, which is expected to have the highest surface tension? State the reason.
- (6) Why the viscosity of water at 373 K is one-sixth of its viscosity at 273 K?
- (7) The molar enthalpy of vaporization and boiling point of ammonia are 23.3 kJ mol^{-1} and 240 K, respectively. Does it obey Trouton's rule?



Methyl cyanide

4.10 ANSWERS

Self Assessment Questions

- (1) Gases have more free space than liquids; hence, it is easier for gases to be compressed or expanded.
- (2) 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.
- (3) Decane is expected to have the highest viscosity due to increased London forces with chain length.
- (4) Although methanol and ethanol are hydrogen bonded, the latter has higher London forces due to higher molar mass. The larger intermolecular forces in ethanol account for its lower vapour pressure than that of methanol.
- (5) The boiling points increase in the following order due to increasing hydrogen bond strength and London forces;

Ethanol < ethylene glycol < glycerol
- (6) $\Delta H_{\text{vap}}^0 = 29.75 \text{ kJ mol}^{-1}$
- (7) In an isotropic substance, the molecular arrangement is disorderly; the value for any physical property is same, irrespective of direction. In an anisotropic substance, the molecular arrangement is orderly and the values of some physical properties depend on the direction.

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) In nematic and cholesteric liquid crystals, there is some orderliness in the arrangement of molecules. The optical characteristics depend on a particular mode of arrangement of molecules. Any disturbance in the form of temperature or electricity, affects the arrangement pattern in the liquid crystal and causes a change in its optical characteristics.
- (4) Naphthalene has higher molar mass than benzene and hence, has greater London forces; this is reflected in its higher ΔH_{vap}^0 value.
- (5) Due to strong hydrogen bonding, water must have the highest surface tension among the three liquids.
- (6) With temperature increase, the number of voids increases. The molecules can move easily leading to an increase in the flow rate; the viscosity decreases.
- (7) The value of $\Delta H_{\text{vap}}^0 / \text{BP} = 97.1 \text{ J mol}^{-1} \text{ K}^{-1}$ for ammonia; it doesn't obey Trouton's rule due to hydrogen bonding.

UNIT 5 SOLID STATE

Structure

- 5.1 Introduction
 - Objectives
- 5.2 Definition of Terms Used in Crystal Systems
 - Lattice
 - Basis
 - Unit Cell
- 5.3 Bravais Lattices and Crystal Systems
 - Cubic System Geometry
 - Bravais Lattice
- 5.4 Crystal Planes and Miller Indices
- 5.5 X-rays and Crystal Structure
 - Principles of Diffraction
 - Bragg Law and Bragg Equation
- 5.6 Experimental Method for the Determination of Crystal Structure
 - Powder Method
 - Some Experimental Findings
- 5.7 Determination of Unit Cell
 - Number of Net Atoms in a Cubic Unit Cell
 - Density Calculation
 - Experimental Method
- 5.8 Nature of Bonds in Solids
- 5.9 Ionic, Covalent and Molecular Crystals
 - Ionic Crystals
 - Covalent Crystals
 - Molecular Crystals
- 5.10 Commonly Encountered Metallic Structures
- 5.11 Semiconductors
 - Intrinsic Semiconductors
 - Extrinsic Semiconductors
- 5.12 Summary
- 5.13 Terminal Questions
- 5.14 Answers

5.1 INTRODUCTION

In the earlier units, we had drawn a comparison amongst the three states of matter—solid, liquid and gas. These states of matter were described in terms of a few physical properties like “solids are denser than liquids and gases” or “it takes enormous pressure to compress a solid even by a fraction of its volume”, etc. However, instead of defining the states of matter in terms of the physical properties, it is much more useful to think in terms of the binding forces (ionic, covalent, van der Waals, etc.,) involved in a particular state imparting different properties to solids, liquids and gases. Thus, solid state could be defined as a state of a substance in which the neighbouring particles (molecules, atoms or ions) are close enough for van der Waals forces to operate. As a consequence, the motion of the molecules is restricted with respect to its neighbours.

The solids can be of two types — **crystalline** and **amorphous**. Let us explain what a crystalline solid is. Those solids which are formed due to regular repetition of identical building blocks are called crystals. It is like having a collection of identical bricks which could be arranged in some regular fashion to construct a wall. On the other hand, there are solids which do not appear to have any regular internal arrangement in every part and thus do not show regular shape; these are called amorphous solids. Amorphous solid means a solid without regular form. Glass, polyethylene as in plastic bags, etc., are common examples of amorphous substances. Though the study of amorphous substances is also quite useful and interesting, we shall confine ourselves to the study of the crystalline solids in this unit.

Different crystalline structures are associated with different physical properties. Hence, we discuss crystal forms and crystal structure determination method in this unit. Further, the theories of metallic bonding and semiconductors are also explained with particular reference to electrical conduction. The information obtained from crystal structure studies could help us in understanding the physical and chemical properties of solids.

Objectives

After studying this unit, you should be able to:

- define lattice, basis, unit cell, primitive and nonprimitive cells,
- describe the seven crystal systems and the fourteen Bravais lattices,
- identify the face, corner, edge, face-centre and body-centre in a cube,
- state the crystal planes in terms of Miller indices,
- state Bragg law,
- describe the determination of crystal structure by X-ray diffraction method,
- determine the type of unit cell based on experimental and calculated values of density,
- explain the types of bonds in solids,
- discuss the structures of some ionic, covalent and metallic crystals, and,
- describe the types of semiconductors.

5.2 DEFINITION OF TERMS USED IN CRYSTAL SYSTEMS

Atom is used in general sense in this unit; it stands for an atom or an ion or a molecule.

We have already seen that a crystal is defined in terms of a regular and repetitive arrangement of particles (atoms/molecules/ions) in space. In order to understand crystals and their structures, we encounter a few new terms. These terms form a kind of crystallographic language. Let us now look at the definitions of some of these terms.

5.2.1 Lattice

A parallel net-like arrangement of points in space is known as lattice.

Lattice is defined as an arrangement of geometrical points in a definite pattern in space (Fig. 5.1a). It resembles a scaffold (a framework) erected for the construction of a building. Putting it in a simpler way, one can define a lattice as a regular periodic arrangement of points in space.

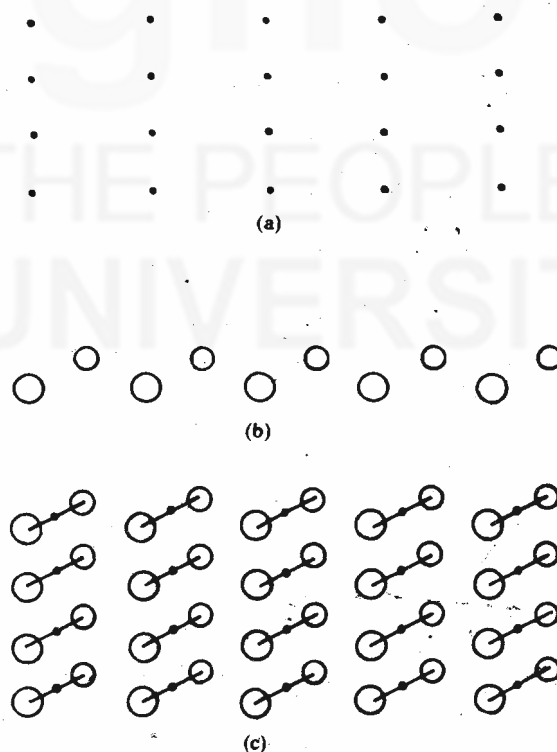


Fig. 5.1 : Representation of a) lattice in two dimensions, b) basis (with two atoms), c) crystal structure, showing the basis of two atoms in relation to lattice points.

5.2.2 Basis

Whenever there is a group of atoms around a lattice point, then the basis is defined.

When atoms are attached regularly to each lattice point, it forms a crystal. However, instead of an atom, we can have a group of atoms attached to each lattice point. The group is called a basis (Fig. 5.1b). The basis consists of the atoms, their spacings and internal bond angles. Every basis is identical in composition, arrangement and orientation. Fig. 5.1c shows the

crystal structure where you can recognise the basis and imagine the lattice. For a large number of crystals, the basis has only a small number of atoms but in a few instances, the basis exceeds 1000 atoms. For example, the basis in iodine crystal is I_2 molecule whereas in the ice crystal, H_2O molecule is the basis.

5.2.3 Unit Cell

The unit cell is the fundamental unit in a crystal. The repetitive arrangement of unit cells in three dimensions produces a crystal just as a wall is built from identical bricks. In other words, a unit cell is the smallest unit of a crystal which on translational displacement in three dimensions will produce the crystal. A unit cell chosen to represent the crystal may be quite different in size and shape from another unit cell which may represent the crystal equally well. The main point is that whatever the unit cell may be, it should be the simplest representation and, when repeated in three dimensions, it should produce the crystal.

Identical repetition of basis about each lattice point in three dimensions gives a crystal structure.

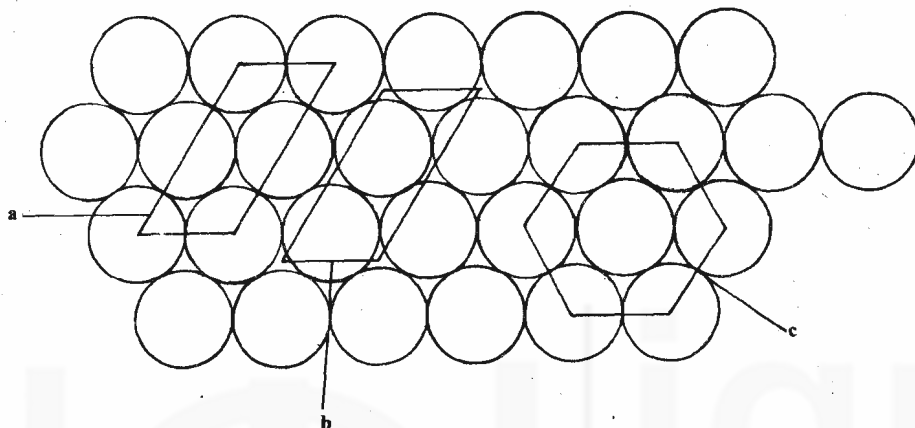


Fig. 5.2 : Choice of unit cell.

Fig. 5.2 shows four rows of spheres—representing atoms—in a closely packed structure in two dimensions. If we join the centres or any other points, say, gaps between the spheres, of different atoms in successive three 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. 5.2. 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. Does 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—

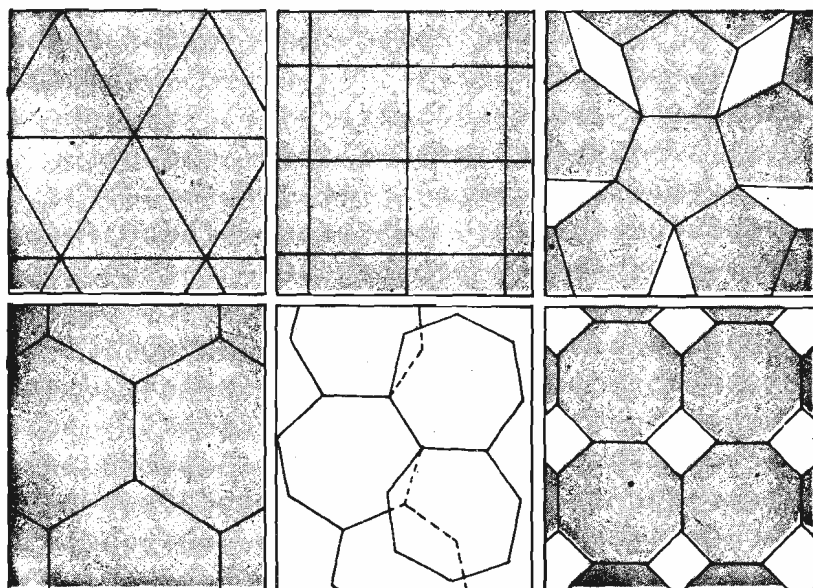


Fig. 5.3 : Of all the regular polygons, only triangles, squares and hexagons can fill a floor space without gap. Filled-in space is denoted by grey area.

triangular, square, pentagonal, hexagonal, heptagonal or octagonal? Against the answer is no. You can cover the floor space completely with triangular, square or hexagonal tiles but not with pentagonal, heptagonal or octagonal tiles (Fig. 5.3). Note the gaps in the interior floor space when pentagonal, heptagonal or octagonal tiles are used.

Just as tiles with specific shapes are useful in covering the floor space completely, unit cells with specific symmetry properties constitute the crystal lattice. The course on Spectroscopy deals with symmetry properties in detail.

SAQ 1

What is the essential characteristic of a unit cell?

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.....

.....

5.3 BRAVAIS LATTICES AND CRYSTAL SYSTEMS

A parallelepiped is a three dimensional model of a parallelogram.

The cell-edge lengths (a , b and c) are the repeat distances in a unit cell. Any point in a unit cell can be represented by coordinates which are fractions of a , b and c .

The basic shape of a unit cell is described by a parallelepiped. (Fig. 5.4a).

A unit cell has three coordinate axes, \mathbf{a} , \mathbf{b} and \mathbf{c} (note the bold letters). The cell-edge lengths in the three axes are a , b and c (note the italicised letters), respectively (Fig. 5.4b). The angles between \mathbf{a} and \mathbf{b} axes, \mathbf{b} and \mathbf{c} axes and \mathbf{c} and \mathbf{a} axes are γ , α and β , respectively. The quantities a , b and c are called lattice parameters or unit cell parameters.

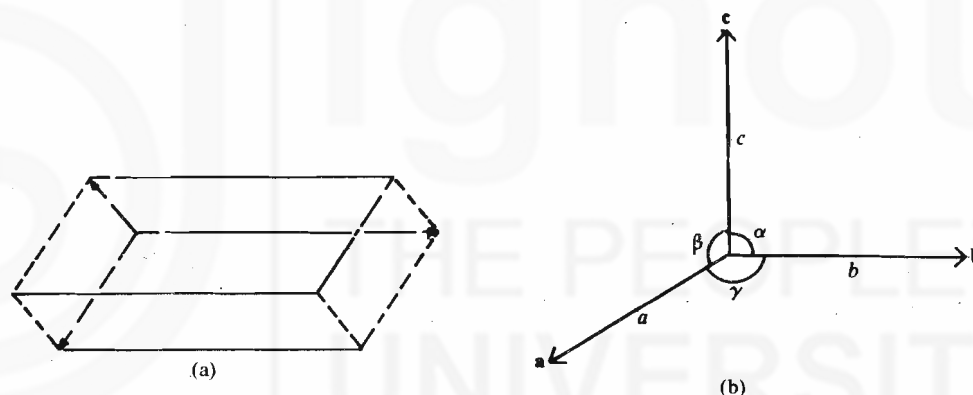


Fig. 5.4 : a) parallelepiped; b) three coordinate axes, cell-edge lengths and the angles between axes.

Based on the relationships among the axial angles and the edge-lengths, there are seven crystal systems as given in Table 5.1.

Table 5.1 : The Seven Crystal Systems

Systems	Axes	Angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, CsCl
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	TiO ₂ (rutile)
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	CdSO ₄ , HgBr ₂
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	CaCO ₃ (calcite)
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	SiO ₂
Monoöcnic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	KIO ₃ , NaHCO ₃
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$	NaHSO ₄ , CuF ₂

5.3.1 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 ($a = b = c$). We must understand the geometry of a cube. For this purpose, 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. You can consider the ceiling and the floor as horizontal walls!

Each point where three faces of a cube (or three walls in your room) meet is called a corner. A cube has eight corners and these are indicated by A to H in Fig. 5.5a.

Each face has four corners. By joining the corners of a face diagonally, two face diagonals are obtained. For example, in Fig. 5.5b, 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. 5.5b.

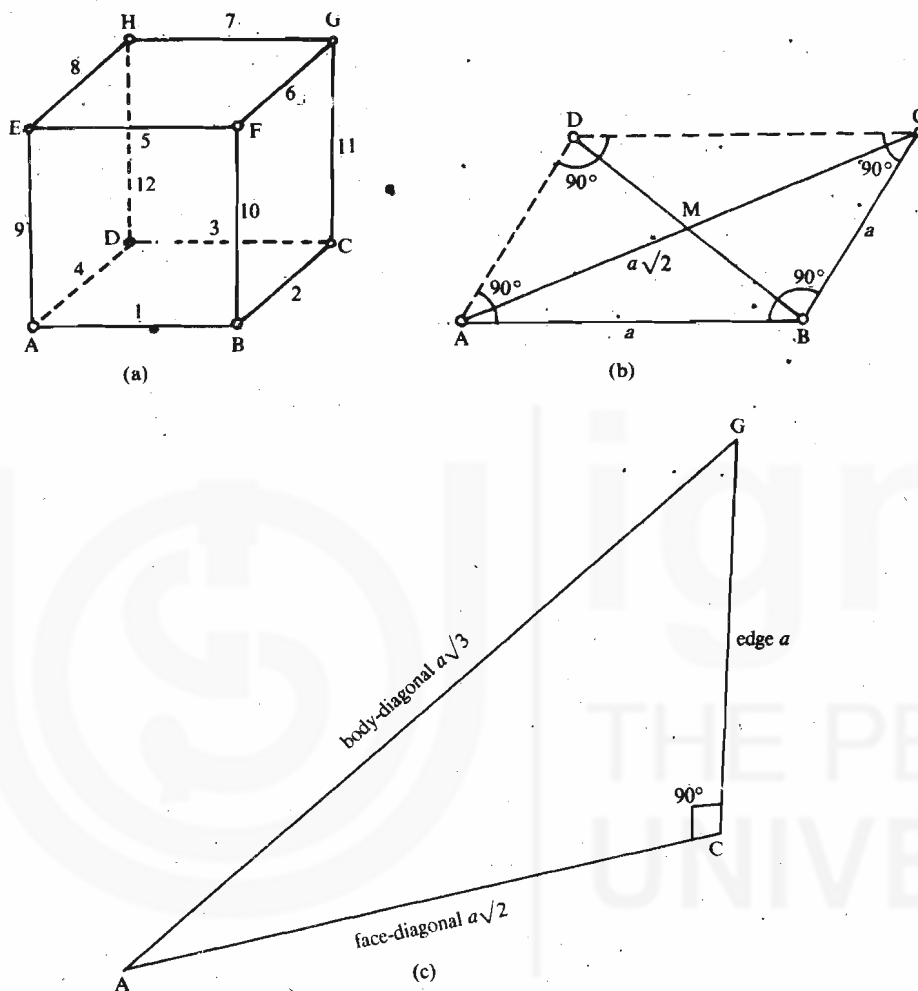


Fig. 5.5 : a) Eight corners in a cube indicated by letters A to H—each corner is marked by red dot; twelve edges indicated by number 1 to 12; b) bottom face ABCD of the cube shown; AC and BD are the face diagonals and M is face-centre; c) The right-angled $\triangle ACG$.

By joining any two 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. 5.5a. All the body diagonals meet at the body-centre. The definitions of face, corner, edge, face-centre and body-centre apply to other crystal systems also.

5.3.2 Bravais Lattice

Some crystal systems, may have one or more types of lattices depending on the number of lattice points. If there are lattice points only at the eight corners of a unit cell, it is called a simple or primitive (*P*) 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 a body-centred (*I*) cell. The unit cells of the type *F*, *C* and *I* are called nonprimitive cells. Based on the presence of lattice points in the seven crystal systems, there are fourteen Bravais lattices; these are given in Fig. 5.6.

For a cubic crystal, the cell-edge lengths are the same along the three axes and are represented as a .

$$\text{In } \triangle ABC, \angle ABC = 90^\circ$$

$$\begin{aligned} \text{Length of face diagonal, AC} \\ &= \sqrt{AB^2 + BC^2} \\ &= a\sqrt{2} \end{aligned}$$

$$\text{In } \triangle ACG, \angle ACG = 90^\circ.$$

$$\begin{aligned} \text{(See Fig. 5.5c)} \\ \text{Length of the body diagonal, AG} \\ &= \sqrt{AC^2 + CG^2} \\ &= \sqrt{2a^2 + a^2} \\ &= a\sqrt{3} \end{aligned}$$

A non-Bravais lattice structure is composed of two or more sublattices.

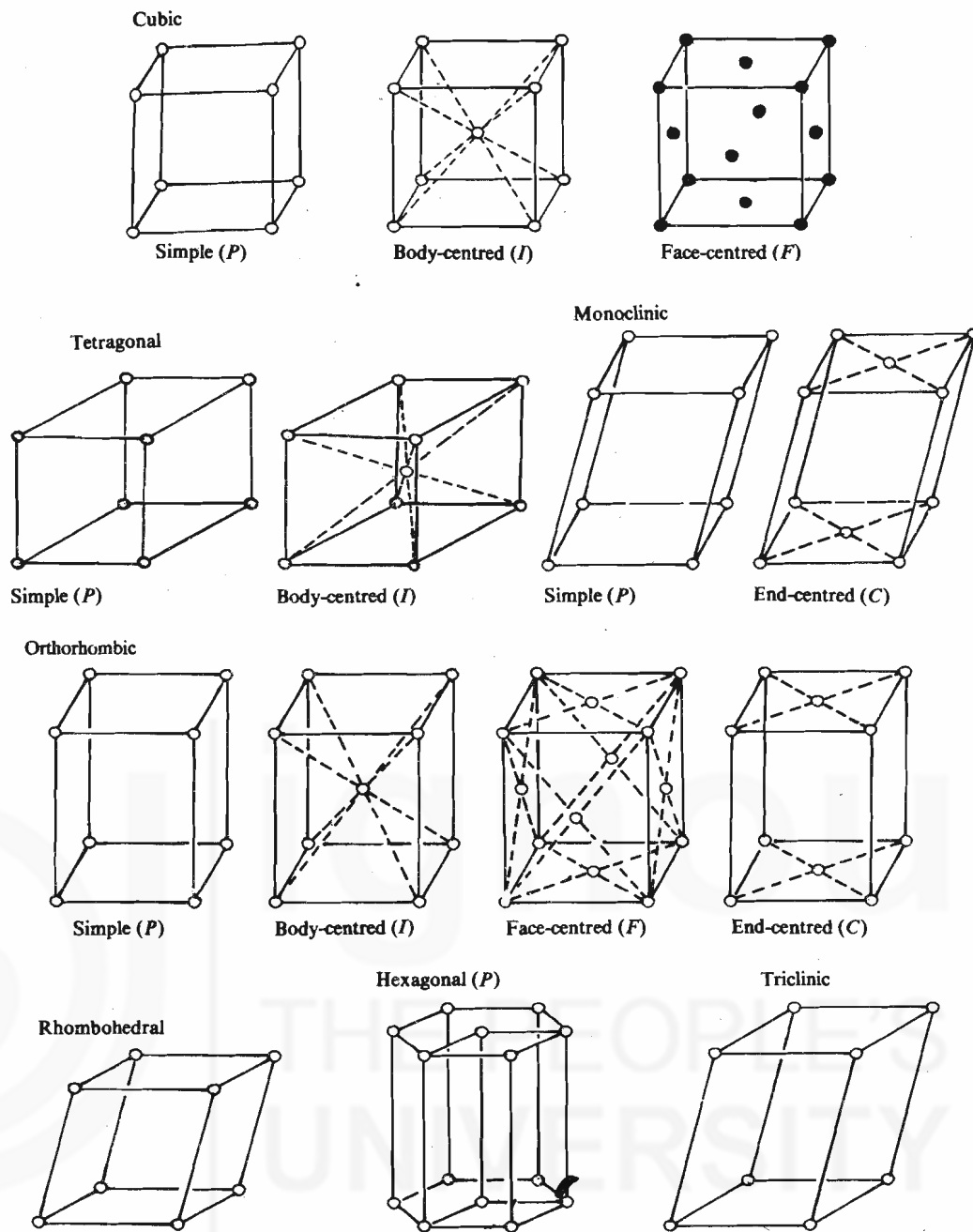


Fig. 5.6 : Fourteen Bravais Lattices.

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.

SAQ 2

Describe the following : simple cubic, body-centred cubic and face-centred cubic crystals.

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5.4 CRYSTAL PLANES AND MILLER INDICES

Crystal planes are represented by certain numbers known as Miller indices. These indices are determined in the following way :

- i) Find the intercepts of a crystal plane on the axes, *a*, *b* and *c* in terms of cell-edge lengths *a*, *b* and *c*. Suppose that a crystal plane makes intercepts $3a$, $2b$, $2c$ as shown in Fig. 5.7.

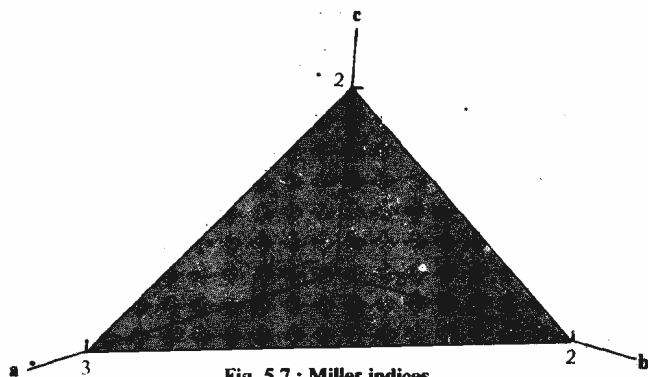


Fig. 5.7 : Miller indices.

- ii) Divide the intercepts by the respective cell-edge lengths (a , b and c). For the crystal plane in Fig. 5.7, this step gives $\frac{3a}{a}$, $\frac{2b}{b}$, $\frac{2c}{c}$, i.e., 3, 2, 2 as the answer.
- iii) Take the reciprocal of the above numbers. Corresponding to Fig. 5.7, this step gives $\frac{1}{3}$, $\frac{1}{2}$, $\frac{1}{2}$ as the answer.
- iv) Finally reduce the above fractions to the smallest integers having the same ratio. Write these numbers enclosed in parentheses without comma signs; these are the Miller indices of the given crystal plane. For the illustration in Fig. 5.7, the Miller indices are (233); this is to be pronounced as two three three plane.

Miller indices are generally represented as (hkl) . You will notice that the Miller indices are defined in such a way that all equivalent and parallel planes are represented by the same set of Miller indices. Thus, planes whose intercepts are $3a$, $2b$, $2c$ or a , $\frac{2b}{3}$, $\frac{2c}{3}$ or $9a$, $6b$, $6c$, etc. are all represented by a set of Miller indices (233).

If a face is parallel to an axis, theoretically the corresponding intercept is equal to ∞ . To illustrate this, 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. 5.8a. The (100) plane is indicated in Fig. 5.8b. 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. 5.8 c and d, respectively.

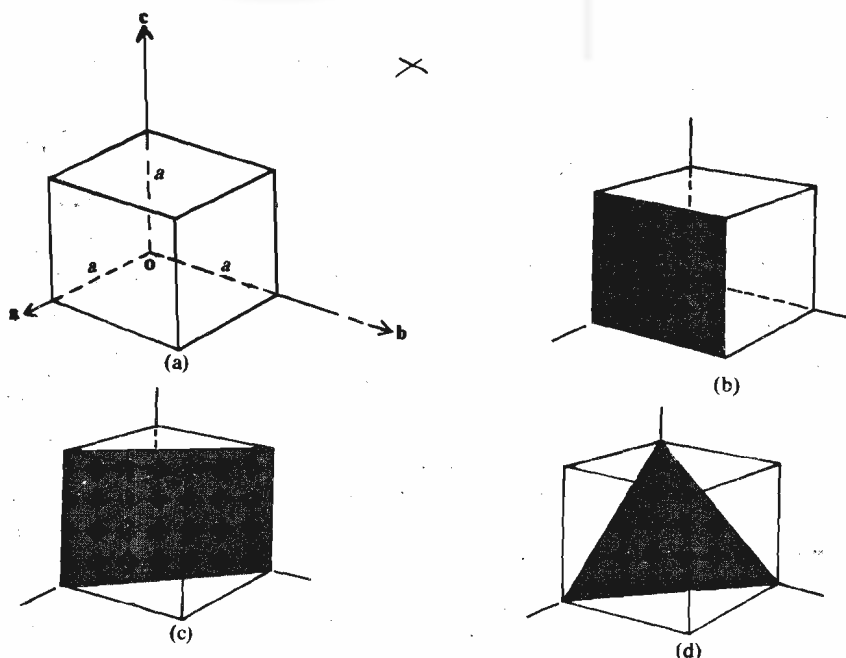


Fig. 5.8 : a) The origin, O, the axes and the cell-length a in a cubic cell; b) (100) plane; c) (110) plane; d) (111) plane.

We can calculate the distance between the adjacent planes labelled 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,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \dots (5.1)$$

where a is the cell-edge length of the cell and (hkl) are the Miller indices. Thus, in sodium chloride crystal, the cell-edge length is 5.63×10^{-10} m. The distance between (111) planes is given by Eq. 5.1,

$$d_{111} = \frac{5.63 \times 10^{-10} \text{ m}}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{5.63 \times 10^{-10} \text{ m}}{\sqrt{3}} = 3.25 \times 10^{-10} \text{ m}$$

Eq. 5.1 could be used only for cubic crystals. For an orthorhombic cell, the equation for d_{hkl} turns out to be,

$$\frac{1}{d_{hkl}^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2 \quad \dots (5.2)$$

Using Eq. 5.2, work out the following SAQ.

SAQ 3

An orthorhombic crystal has the following parameters:

$$a = 8.2 \times 10^{-10} \text{ m}; b = 9.4 \times 10^{-10} \text{ m}; c = 7.5 \times 10^{-10} \text{ m}.$$

What is the distance between (123) planes?

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5.5 X-RAYS AND CRYSTAL STRUCTURE

Crystal structures are usually determined with the help of X-rays. In addition to X-rays, other forms of radiations having similar properties—like a beam of neutrons or electrons—could also be used. However, our discussion will be limited to the use of X-rays only. We know that X-rays are electromagnetic radiations of wavelengths much shorter than either visible or ultraviolet light. In 1911, Ewall showed that whenever the wavelength of radiation is of the same order of magnitude as the size of the particle in a material, the radiation would be diffracted by the particle. In 1912, Laue 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. Let us explain the principle of diffraction, in general, and the diffraction of X-rays by crystals, in particular.

5.5.1 Principles of Diffraction

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. 5.9a); when they are out of phase (known as destructive interference), the intensity is decreased (Fig. 5.9b). If there are two waves starting from a common source, their **phase difference** will be directly proportional to their path difference.

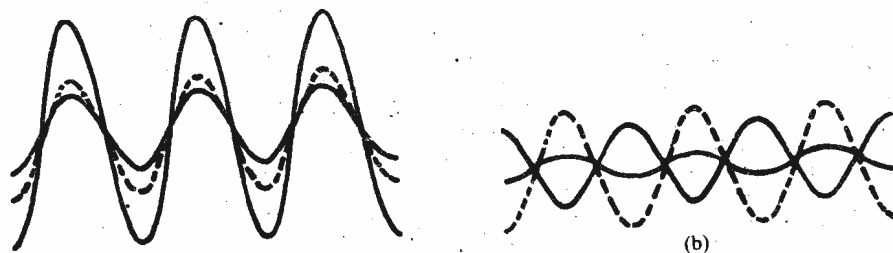


Fig. 5.9 : Two waves (shown by dotted and solid lines) giving rise to a resultant (shown by red colour) : a) constructive interference (in-phase wave—greater amplitude); b) destructive interference (out-of-phase wave—smaller amplitude).

The amplitude is directly related to the intensity of the beam.

The bending of light round 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. 5.10). 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.

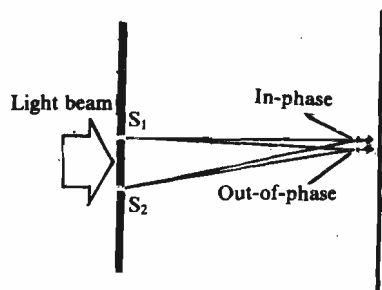


Fig. 5.10 : In-phase and out-of-phase waves.

5.5.2 Bragg Law and Bragg Equation

If the path difference between the two rays is an integral multiple ($n = 1, 2, 3, \dots$) 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). This is called **Bragg law**. Stated mathematically, for a bright diffraction pattern,

$$\text{path difference} = n \lambda \quad \dots (5.3)$$

Bragg derived an equation (Eq. 5.9) for X-ray diffraction of crystals. This equation is named after him. Some of the assumptions made by Bragg in deriving Eq. 5.9 are given below :

- The incident waves are reflected by parallel planes of atoms in a crystal such that the angle of incidence is equal to the angle of reflection. This is called specular (mirror-like) reflection.
- Each plane reflects only a fraction of incident radiation.
- When the reflections from parallel planes interfere constructively, the diffraction pattern arises.
- The wavelength of the X-rays is not changed on reflection; i.e., X-rays undergo elastic scattering on the lattice planes. Using geometric considerations, Bragg equation can be derived easily.

Two parallel beams PA and QC are incident at an angle θ on the parallel planes EF and GH (Fig. 5.11). The perpendicular distance (AC) between the two planes is d . The beams are reflected along AR and CS at an angle θ . The path difference between the two sets of incident and reflected beams (PAR and QCS) is the extra distance travelled by QCS as compared to PAR. To calculate the path difference, draw $AB \perp QC$ and $AD \perp CS$.

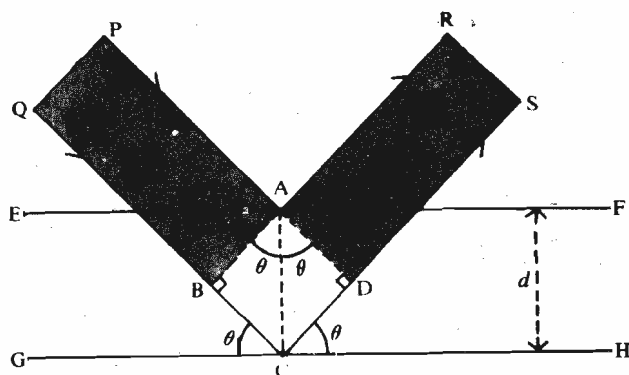


Fig. 5.11 : The incident and the reflected beams and the two parallel lattice planes.

The bright and dark spots which appear on a photographic film are called diffraction pattern; it should not be confused with diffraction phenomenon which is just the bending of light around the edges of an obstacle.

$$\begin{aligned}
 \text{Path difference} &= (QC + CS) - (PA + AR) \\
 &= (QB + BC) + (CD + DS) - (PA + AR) \\
 &= BC + CD \quad \dots (5.4) \\
 &[\because QB = PA \text{ and } DS = AR, \text{ being opposite sides of the rectangles shown} \\
 &\text{by the shaded portions in Fig. 5.11].}
 \end{aligned}$$

$$\text{Since } AC \perp GH, \angle ACG = 90^\circ = \angle ACB + \angle BCG = \angle ACB + \theta$$

$$[\because \angle QCG \text{ and } \angle BCG \text{ are same as } \theta]$$

$$\angle ACB = 90^\circ - \theta \quad \dots (5.5)$$

$$\text{In the right-angled } \triangle ABC, \angle BAC + \angle ACB + \angle CBA = 180^\circ$$

$$\text{Using Eq. 5.5, } \angle BAC + (90^\circ - \theta) + 90^\circ = 180^\circ$$

$$\angle BAC = 180^\circ - (180^\circ - \theta) = \theta$$

$$\text{Also, } \frac{BC}{AC} = \sin \theta \text{ or } BC = AC \sin \theta$$

$$\text{Since, } AC = d, BC = d \sin \theta \quad \dots (5.6)$$

$$\text{Similarly, we can prove that } CD = d \sin \theta \quad \dots (5.7)$$

Using Eqs. 5.4, 5.6 and 5.7,

$$\text{path difference} = 2d \sin \theta \quad \dots (5.8)$$

Again substituting in Eq. 5.3, we get,

$$n\lambda = 2d \sin \theta \quad \dots (5.9)$$

Bragg equation assumes that incident X-rays are reflected specularly (mirrorlike) such that the angle of incidence is equal to the angle of reflection. This assumption is convincing only because it explains the experimental results.

Eq. 5.9 is known as Bragg 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 4

If the separation between the lattice layers in a crystal is 404 pm and the wavelength of X-rays used is 154 pm, what would be the angle of incidence at which reflection would occur? Assume $n = 1$.

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15.6 EXPERIMENTAL METHODS FOR THE DETERMINATION OF CRYSTAL STRUCTURE

In any method of crystal structure determination, we must find out θ as well as the intensity of the diffracted beam. There are basically three methods—Laue, powder and the rotating crystal—which are used for the determination of the above quantities. In this section we shall discuss the outline of powder method only.

5.6.1 Powder Method

In this method, we use a powdered sample containing microcrystals which are randomly oriented. There are enough of microcrystals which will have the proper orientation for diffraction. The diffraction beam corresponding to each scattering fans out in the form of a cone, the axis of which lies along the incident beam as shown in Fig. 5.12. This gives rise to bright rings on a circular photographic film and is known as powder pattern. The X-ray

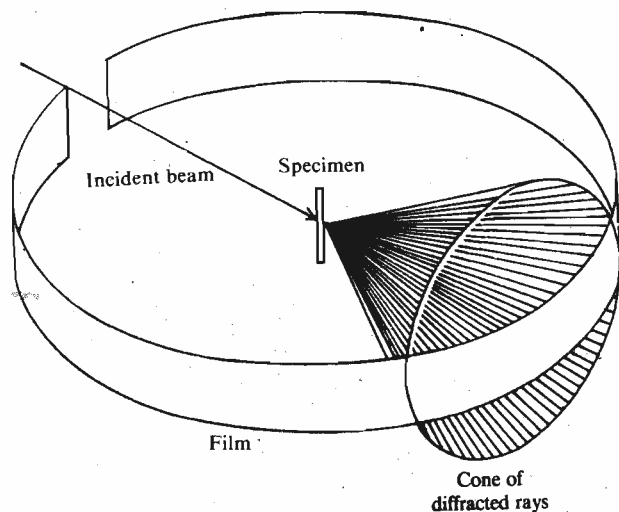


Fig. 5.12 : Powder method.

powder pattern for sodium chloride is shown in Fig. 5.13. Using powder method, the interplanar spacing can be found out since both λ and θ are known.

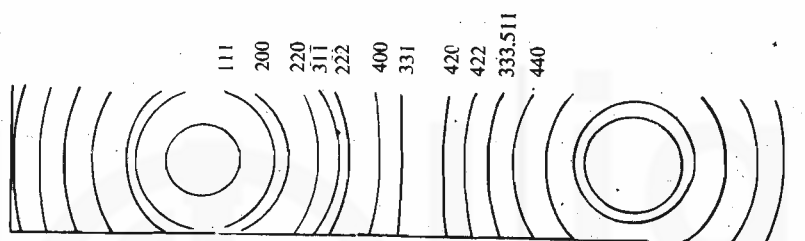


Fig. 5.13 : X-ray powder pattern for sodium chloride.

5.6.2 Some Experimental Findings

Some noteworthy features in crystal structure determination by X-ray diffraction are given below:

- It appears that a set of planes is reflecting the X-ray beam.
- The reflection takes place only for certain values of θ ; these values of θ must satisfy Bragg equation (Eq. 5.9).
- It is a common practice to set $n = 1$ in Eq. 5.9, unless specified otherwise. Higher order reflections ($n > 1$) are weak.

The X-ray diffraction method leads us to the value of cell-edge length which can be used to determine the density of the crystal.

5.7 DETERMINATION OF UNIT CELL

The comparison between the experimental and the theoretical values of density could help us in determining the cubic cell type. First let us calculate the number of atoms belonging to a unit cell in each type of cubic cell.

5.7.1 Number of Net Atoms in a Cubic Unit Cell

An atom at the body-centre of a unit cell belongs to that cell only (Fig. 5.14a). An atom on the face-centre of a unit cell is shared by two unit cells (Fig. 5.14b) and thus, only half of such an atom belongs to one unit cell. An atom at the edge-centre of a unit cell is shared by four unit cells (Fig. 5.14c); one-fourth of an atom in the edge-centre belongs to one unit cell. But an atom at the corner of a unit cell will be shared by eight unit cells as shown in Fig. 5.14d. Hence, we can say that one eighth of an atom in a corner belongs to a particular unit-cell. Using this background, let us calculate the number of net atoms present per unit cell for a simple cubic, face-centered cubic or body-centred cubic structure.

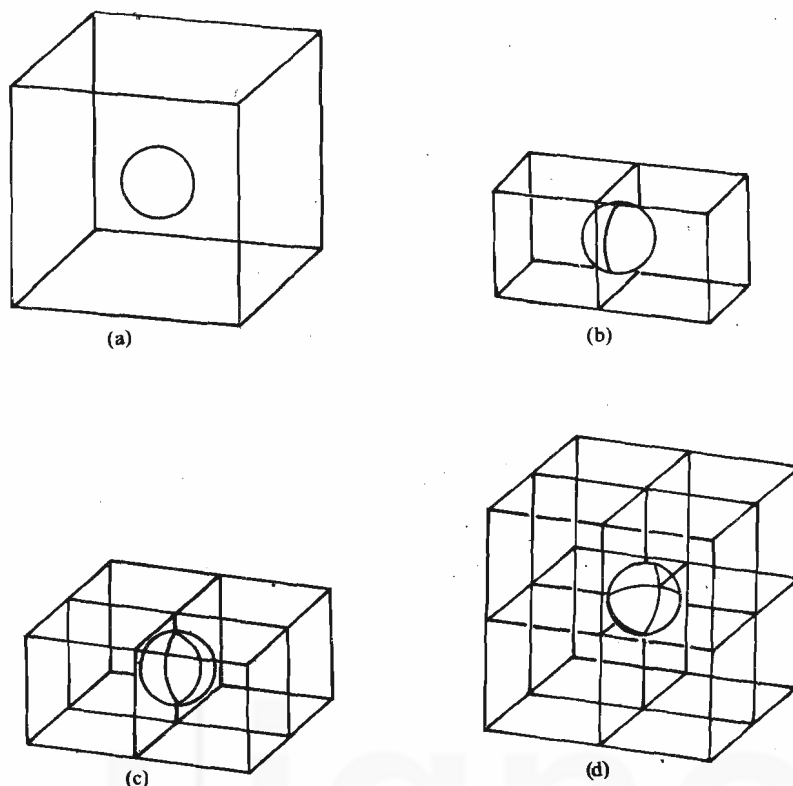


Fig. 5.14 : a) An atom at the body-centre of a unit cell; b) An atom at the face-centre shared by two unit cells; c) An atom at the edge-centre shared by four unit cells; d) An atom in the corner shared by eight unit cells.

The number of net atoms per unit cell are one, two and four in simple cubic, *bcc* and *fcc* structures.

- In a simple cubic cell, there are atoms only at the eight corners; and hence, a simple cubic structure has only one net atom ($8 \times \frac{1}{8} = 1$) per unit cell.
- On the other hand, in a *bcc* structure, there are atoms in the eight corners and the centre of the cell; hence, there are two net atoms [$(8 \times \frac{1}{8}) + 1 = 2$] per unit cell of a *bcc* structure.
- Finally, for a *fcc* structure, there are atoms in the eight corners and six face centres. That is, a *fcc* structure has four net atoms [$(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 1 + 3 = 4$] per unit cell.

The density of a crystal depends on the number of atoms, their mass and the volume of the unit cell. Let us now see the calculation of the densities of these three types of unit cells.

5.7.2 Density Calculation

$$\text{It is known that density} = \frac{\text{Mass}}{\text{Volume}} \quad \dots (5.10)$$

In this unit, the cell-edge lengths and the distance between the planes are given in m or pm units; but it is

usual to state such data in Å unit also.
 $1 \text{ Å} = 10^{-10} \text{ m}$.

X-ray measurements give us the cell-edge length. If the cell-edge length is a m, (i.e., a metre) then the volume of the unit cell = $a^3 \text{ m}^3$... (5.11)

The mass of an atom of the substance is obtained by dividing the mass of one mole atoms [i.e., atomic mass (w) in kg mol^{-1}] by Avogadro constant (N_A , which is equal to $6.022 \times 10^{23} \text{ mol}^{-1}$).

$$\text{Mass of one atom} = \frac{w \text{ kg mol}^{-1}}{N_A \text{ mol}^{-1}} = \frac{w}{N_A} \text{ kg} \quad \dots (5.12)$$

A simple cubic structure has only one atom per unit cell; hence, mass of unit cell of a simple cubic crystal is given by Eq. 5.12. Substituting the proper values from Eqs 5.11 and 5.12 in Eq. 5.10, we get,

$$\left. \begin{array}{l} \text{the density} \\ \text{of a simple} \\ \text{cubic cell} \end{array} \right\} = \frac{w}{N_A a^3} \text{ kg m}^{-3} \quad \dots (5.13)$$

Since, simple cubic, *bcc* and *fcc* unit cells have one, two and four atoms per unit cell, the densities of *bcc* and *fcc* are given by :

$$\text{Density of a } bcc \text{ cell} = \frac{2w}{N_A a^3} \text{ kg m}^{-3} \quad \dots (5.14)$$

$$\text{Density of a } fcc \text{ cell} = \frac{4w}{N_A a^3} \text{ kg m}^{-3} \quad \dots (5.15)$$

$$\text{In general, the density of a cubic unit cell } (\rho) = \frac{n w}{N_A a^3} \text{ kg m}^{-3} \quad \dots (5.16)$$

where n is the number of net atoms per unit cell.

Rearranging Eq. 5.16, we get,

$$n = \frac{\rho N_A a^3}{w} \quad \dots (5.17)$$

5.7.3 Experimental Method

The cell-edge length (a) and the density (ρ) of a crystal are experimentally determined. These values are substituted in Eq. 5.17 and n is calculated. Depending on whether $n = 1$ or 2 or 4, the unit cell is simple cubic or *bcc* or *fcc*. Let us work out an example.

Nickel metal packs in a cubic unit cell with a cell-edge length (a) of 3.524×10^{-10} m. The density (ρ) of nickel is 8.90×10^3 kg m⁻³. Let us find out the unit cell type for nickel. Since atomic mass of nickel is 58.7, $w = 0.0587$ kg mol⁻¹.

First we have to calculate n using Eq. 5.17

$$\begin{aligned} n &= \frac{\rho N_A a^3}{w} \\ &= \frac{8.90 \times 10^3 \text{ kg m}^{-3} \times 6.022 \times 10^{23} \text{ mol}^{-1} \times (3.524 \times 10^{-10} \text{ m})^3}{0.0587 \text{ kg mol}^{-1}} \\ &= 4 \text{ (rounded to the nearest whole number).} \end{aligned}$$

Since there are four atoms per unit cell, nickel has a *fcc* lattice.

In the following section, we shall study the nature of bonds responsible for holding the solid together. Before that attempt the following SAQ.

SAQ 5

Tungsten forms *bcc* crystals. Its cell-edge length is 3.16×10^{-10} m. Find the density of tungsten:

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5.8 NATURE OF BONDS IN SOLIDS

There are basically two theories or models to explain the nature of bonds in solids. One is known as bond model and the other as band model. These two names may sound new; however, they are the same two approaches that we have already studied (in Units 4 and 5 of **Atoms and Molecules** course) in connection with the formation of a molecule by the combination of two or more atoms. Thus the bond model is the same as the valence bond approach. Here we consider a crystal as a three dimensional arrangement of atoms and each of these atoms has valence electrons which can form normal chemical bonds with neighbouring atoms. These bonds may be ionic, covalent or van der Waals in character. In the other approach, which is called the band model, we follow the molecular orbital treatment. All the nuclei with their core electrons are considered as a fixed periodic array

over which the valence electrons are spread out. It is like pouring of electron cement over a fixed arrangement of nuclear bricks. We have already read about ionic bond, covalent bond, hydrogen bond, etc., in Unit 3 of **Atoms and Molecules** course. We shall now study metallic bonding in terms of the above two models.

Metallic Bonding

According to the bond theory, the metallic solids can be considered as having simple covalent bonds between adjacent atoms. However, in these cases, the number of electron pairs available for bond formation is less than the number of orbitals available. Hence, when such substances are placed under an applied electric field, the electrons from the filled orbitals can easily flow into the vacant orbitals, thus making them highly conducting.

In the band theory of metals, a crystalline metallic solid is considered as a single giant molecule. Linear combination of atomic orbitals on all the atoms is taken to give molecular orbitals of the solid just as in the case of simple diatomic molecule. It is also assumed that there is negligible overlap of inner shell atomic orbitals and the energies of these remain practically the same as atomic orbitals on isolated atoms. However, the outer orbitals do combine to give molecular orbitals of bonding and antibonding character. Suppose that a crystal of sodium contains N atoms, where N is of the order of 10^{23} . Neglecting the inner orbitals, there are N number of $3s$ orbitals on all the atoms in the crystal which can combine to give N molecular orbitals or delocalised crystal orbitals. Since each molecular orbital can hold 2 electrons, the total number of electrons which these orbitals can hold is $2N$. The actual number of electrons is however only N , since each atom is contributing only one $3s$ electron. Hence, only half of the molecular orbitals will be occupied by the electrons and half will remain vacant. Further, since there are N molecular orbitals and the total energy difference between the highest and the lowest orbital is very small, the energy separation between the adjacent molecular orbitals would be very small. For all practical purposes we can consider these molecular orbitals as forming a continuous band of energy rather than separate energy levels. Thus we have a situation where a band of vacant energy levels lie very near to a band of occupied energy levels. Therefore, the electrons present in the occupied lower energy levels can easily move out to vacant band. This is the reason given for metals being good conductors of electricity. In the next section, we shall study the structures of ionic, covalent and molecular crystals.

5.9 IONIC, COVALENT AND MOLECULAR CRYSTALS

In this section we shall consider the structures of some crystals, which have either ionic or covalent bonds; examples are also given for crystals having covalent bonding with van der Waals attraction or hydrogen bonding.

5.9.1 Ionic Crystals

As examples for ionic crystals, we shall consider caesium chloride and sodium chloride which have *bcc* and *fcc* structures, respectively.

bcc Structure

The structure of a *bcc* crystal can be defined in terms of unit cell-edge length and two unique positions in the cell. Consider a crystal like CsCl which has *bcc* structure and has two different ions in lattice positions. Suppose the centre of a cube is occupied by Cs^+ ion; then, this is one of the unique positions of the crystal. It is unique because there is no other point within the cell which is one cell-edge length away and which can be occupied by another Cs^+ ion. Now if one of the corners of the cube is occupied by a chloride ion, then all the eight corners of the cube must be occupied by chloride ions. This is so because each of the corners is one unit cell-edge length away from its nearest neighbours and if one corner is occupied by Cl^- ion, its immediate neighbours which are unit cell-edge length away must also be occupied by chloride ions. We can say that any one corner position is unique in the sense that once you associate an atom with this position, then all the other corners automatically get associated with the similar atoms. Thus, once these two positions are defined, the whole crystal gets defined (Fig. 5.15).

Unit cell-edge length must connect equivalent points. If there is an atom at the corner of a unit-cell, similar atoms must be present at all the corners. If there is an atom at a face-centre, the opposite face-centre also must have the similar atom.

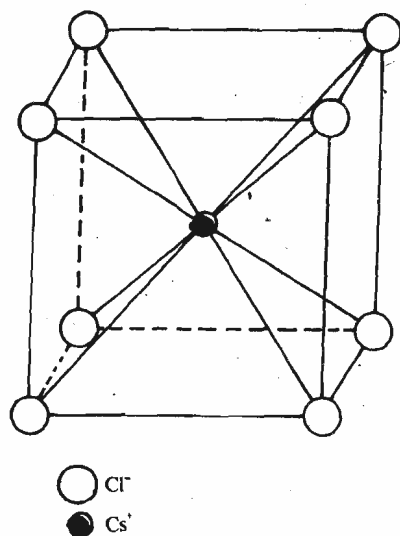


Fig. 5.15 : CsCl structure

Since CsCl crystal has one Cs^+ ion at the centre and eight Cl^- ions at the corners, it has one Cs^+ ion and one Cl^- ion ($8 \times \frac{1}{8} = 1$) belonging to one unit cell as per discussion in

Subsec. 5.7.1. That is, each CsCl unit cell has one formula unit.

fcc Structure

In a *fcc* structure, there are four unique positions; once these positions are defined, the rest of the crystal gets completely described. These are the centres of three adjacent faces and one corner. Once one corner is occupied by an atom, all other corners will have similar atoms. Further, if one atom occupies the centre of one face, the centre of the opposite face would also be occupied by similar atom. Thus, by describing the atoms which occupy the centres of adjacent three faces, we know the atoms occupying the centres of all the six faces. Similarly, all the eight corners are described, once we know the atom occupying one of the corner positions. Thus, the whole crystal is described. Sodium chloride is one such example. It can be considered to be composed of two interpenetrating *fcc* lattices, one made up of sodium ions and the other made up of chloride ions (Fig. 5.16).

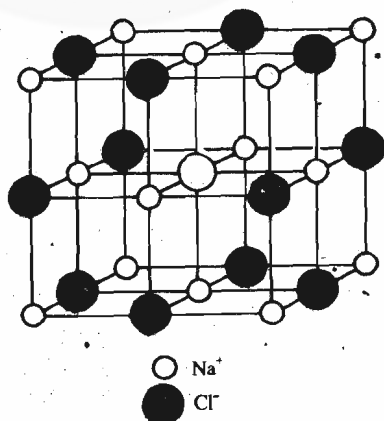


Fig. 5.16 : Structure of sodium chloride.

The sodium ion lattice is shifted in all the three dimensions by half cell-edge length from the chloride ion lattice. A unit cell of NaCl contains four formula units.

5.9.2 Covalent Crystals

In covalent crystals, definite covalent bonds join all the atoms in the crystal. The structure of a covalent crystal is related to the number of valence electrons, the nature of orbitals involved in bond formation and their orientation. One of the most commonly cited

A unit cell of sodium chloride can be considered to be made up of

- one *fcc* unit cell of sodium ions and
- one *fcc* unit cell of chloride ions.

Since each such *fcc* unit cell has four atoms (or ions), sodium chloride crystal has four NaCl formula units per unit cell.

examples is that of diamond (Fig. 5.17). Each carbon atom in diamond is tetrahedrally bonded to four neighbouring carbon atoms. This is so since each carbon has four sp^3 hybridised orbitals pointing towards the corners of a regular tetrahedron. These orbitals overlap with the similar set of orbitals on the neighbouring atoms. Crystals thus formed are hard and unreactive.

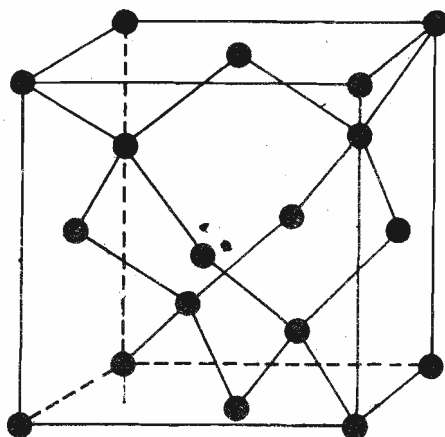


Fig. 5.17 : Structure of diamond.

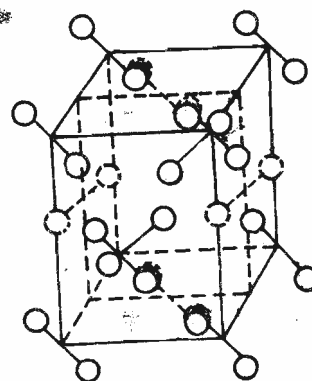


Fig. 5.18 : Structure of iodine crystal—the basis is I_2 molecule.

Let us now see another type of covalent crystals known as molecular crystals.

5.9.3 Molecular Crystals

In molecular crystals, the molecules are held together due to van der Waals interaction. These crystals acquire the structure which has the minimum energy maintaining the original shape of the discrete molecules. Iodine (Fig. 5.18) and carbon dioxide crystals are examples of this type.

There is a class of crystals which have hydrogen bonding between the molecules. An example of this type is ice. In ice, each oxygen atom is tetrahedrally surrounded by four hydrogen atoms, two being linked through covalent bonds in the same molecule and the other two through hydrogen bonds to different water molecules. In the next section, we shall illustrate the four main types of crystal structures in metals.

SAQ 6

The density of potassium bromide is $2.826 \times 10^3 \text{ kg m}^{-3}$. Its cell edge-length is $6.54 \times 10^{-10} \text{ m}$. It has a cubic structure. Find out whether it has CsCl or NaCl type of structure.

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5.10 COMMONLY ENCOUNTERED METALLIC STRUCTURES

Most of the metals crystallise in one of the four basic structures—simple cubic, body-centred cubic (*bcc*), hexagonal closest packed (*hcp*) and face-centred cubic (or cubic closest packed—*ccp*). Simple cubic structure is not very common except perhaps for polonium metal which packs in this structure. Alkali metals, Ba, V, Cr, Mo, etc., crystallise in *bcc* structure. The number of nearest neighbours (coordination number) is 8 in *bcc* arrangement.

Each atom in *hcp* and *ccp* arrangements touches three atoms in the plane above, three in the plane below and six in the same plane. Thus, in both the cases, the coordination number is

In *hcp* and *ccp* structures, each layer of atoms is closely packed as the name suggests.

The unit cell with *ccp* arrangement is called *fcc* unit cell.

12. Further, in *ccp* and *hcp* structures, 74% of the total space is filled with atoms. The difference between the *hcp* and *ccp* structures (Figs. 5.19 a and b) is in the arrangement of the third layer of atoms with respect to the first layer. Metals like Be, Mg, Co, Zn pack in the *hcp* structure, whereas those like Ag, Au, Cu, Ni crystallise in *ccp* arrangement.

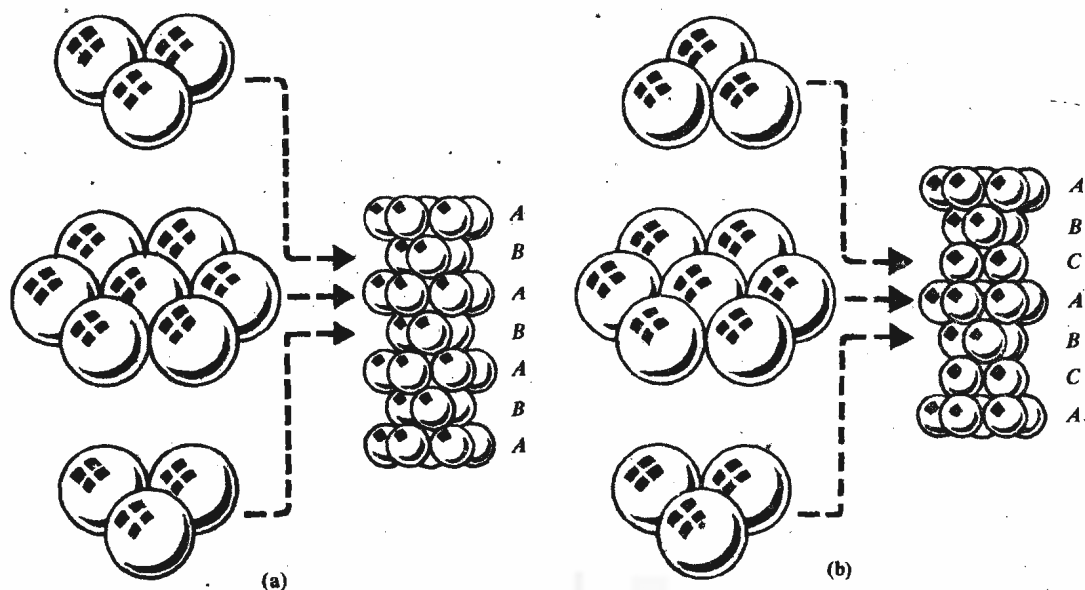


Fig. 5.19 : a) *hcp* arrangement—the atoms in the third layer are straight above those in the first layer—called ABAB arrangement; b) *ccp* arrangement—the atoms in the third layer arranged differently from those in the first—called ABCABC arrangement.

5.11 SEMICONDUCTORS

Semiconductors are solids which are insulators under normal conditions but become conductors when heated or doped with impurities. The electrical conductivity of a semiconductor increases with temperature. The semiconductors can be broadly classified into two types. Let us consider them one by one.

The addition of impurities to a semiconductor is called doping.

5.11.1 Intrinsic Semiconductors

Intrinsic semiconductors are pure substances which conduct electricity when heated. In an intrinsic semiconductor, the energy gap between the highest filled band and the next empty one is very small. Pure germanium, pure grey tin, etc., are intrinsic semiconductors. At absolute zero, they are insulators. But increase in temperature promotes some electrons from filled to next higher band across the gap; so they become conductors. The number of excited electrons increases as the temperature increases; so their conductivity increases with increase in temperature.

5.11.2 Extrinsic Semiconductors

Semiconductors with impurities are called extrinsic semiconductors. They can further be classified into *n*-type and *p*-type semiconductors.

n-type Semiconductors

When a semiconductor is doped with an impurity having more valence electrons than those in the semiconductor, a *n*-type semiconductor is produced. Such an impurity can donate electron(s) to the valence band of the semiconductor, and is called a donor. Phosphorus, arsenic or antimony (each having five valence electrons) are examples of donor impurities added to germanium or silicon (each semiconductor having four valence electrons). The addition of donor impurity to the semiconductor provides additional energy levels and if they are rightly related to the bands of the semiconductor, conductivity may result. That is, if the impurity contains a full energy level just below that of an empty band in the semiconductor, the electrons from the impurity go to empty band in the semiconductor; hence, it becomes negatively charged (*n*-type). Upto certain temperature, the conductivity of a *n*-type semiconductor increases with increase in temperature.

p-type Semiconductors

When the impurity used for doping has less valence electrons than the semiconductor, the impurity can accept electron(s) from the valence band of the semiconductor. Such an impurity is called acceptor. The addition of boron, aluminium, gallium or indium (each having three valence electrons) to silicon or germanium (each semiconductor having four valence electrons) is an example of this type. The essential feature is that the impurity must contain an empty energy level just above a full band in the semiconductor; the electrons from the full band in the semiconductor will pass to the empty level of the impurity. Passage of electrons from the semiconductor to impurity makes the former positively charged (*p*-type). The effect of temperature on the conductivity of a *p*-type semiconductor is similar to that of *n*-type semiconductor.

The combination of *p*-type and *n*-type semiconductor is called *p-n* junction. The *p-n* junctions are used as rectifiers, solar cells, light emitting diodes and other electronic devices.

SAQ 7

Differentiate between intrinsic and extrinsic semiconductors.

5.12 SUMMARY

In this unit, we have briefly described those solid substances which can be classified as crystals. We have also given a hint at the potential usefulness of crystal studies. We summarise below what we have studied so far :

- The terms—lattice, basis and unit cell—were explained.
- Seven crystal systems and fourteen Bravais lattices were discussed.
- Diffraction method and its utility in crystal structure determination were emphasised; an experimental technique was then discussed.
- The nature of bonding in crystals with special reference to metallic bonding was discussed briefly.
- Types of semiconductors were stated and defined.

5.13 TERMINAL QUESTIONS

- 1) 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.,
 $\text{radius} = \frac{a}{2}$).
- 2) In the following cases, mark '✓' for correct statement and '×' for wrong statement :
 - i) The Miller indices of a crystal plane which makes intercepts $2a$, $3b$, $2c$ 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 .
- 3) 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?
- 4) How many net atoms are there in a *fcc* and *bcc* unit cell? Arrive at the conclusion by geometrical arguments.
- 5) 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

- 6) Sodium crystallises in a *bcc* lattice with a cell-edge length of 4.23×10^{-10} m. Calculate the density of sodium metal.
- 7) The density and cell-edge length of sodium chloride are $2.163 \times 10^3 \text{ kg m}^{-3}$ and 5.63×10^{-10} m, respectively. Using these data, arrive at the number of formula units per unit cell of sodium chloride crystal.

5.14 ANSWERS

Self Assessment Questions

- 1) A unit cell is the smallest unit chosen which repeats itself in three dimensions.
- 2) 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.
- 3) $d_{123} = 2.132 \times 10^{-10}$ m.
- 4) Using Eq. 5.9,
 $\sin \theta = 0.191$
 $\therefore \theta = \sin^{-1} 0.191$
 $= 11^\circ$
- 5) Using Eq. 5.14, density of tungsten = $1.936 \times 10^4 \text{ kg m}^{-3}$
- 6) Let us find out the number of formula units of KBr present in a unit cell using Eq. 5.17.
 $w = \text{Molar mass of KBr} = 0.119 \text{ kg mol}^{-1}$

$$n = \frac{\rho a^3 N_A}{w}$$

$$= \frac{2.826 \times 10^3 \text{ kg m}^{-3} \times (6.54 \times 10^{-10} \text{ m})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}{0.119 \text{ kg mol}^{-1}}$$

$$= 4$$
 Since it has four formula units per unit cell, it has NaCl structure and not CsCl structure.
- 7) The conductivity of an intrinsic semiconductor is due to the existence of a vacant conduction band separated by a small energy gap from the filled valence band. An extrinsic semiconductor owes its electrical conductivity largely to the presence of an impurity with appropriate energy levels.

Terminal Questions

- 1) Since the spheres touch along the edge, the cell-edge length (a) is twice the radius of a sphere (r), i.e., $r = \frac{a}{2}$.
- The volume of a sphere = $\frac{4\pi r^3}{3} = \frac{\pi a^3}{6}$
- A simple cubic lattice has one net sphere only per unit cell (Subsec. 5.7.1). Hence,
 volume occupied in a unit cell = $\frac{\pi a^3}{6}$
- But the volume of the unit cell = a^3
- \therefore Fraction of the volume filled = $\frac{\text{Volume occupied}}{\text{unit cell volume}}$
- $$= \frac{\pi a^3}{6 \times a^3} = 0.52$$
- 2) (i) \times (ii) \checkmark (iii) \checkmark (iv) \times .
- 3) 2.49×10^{-10} m; 1.76×10^{-10} m and 4.32×10^{-10} m.
- 4) A *fcc* unit cell has four net atoms while a *bcc* unit cell has two net atoms (see subsec. 5.7.1).

- 5) i) Covalent bonding
ii) Electrostatic forces (ionic bonding)
iii) Metallic bonding
iv) van der waals interaction.
- 6) $1.01 \times 10^3 \text{ kg m}^{-3}$.
- 7) Substituting the density (ρ), cell-edge length (a) and molar mass (w) of sodium chloride in Eq. 5.17, we get,

$$n = \frac{2.163 \times 10^3 \text{ kg m}^{-3} \times (5.63 \times 10^{-10} \text{ m})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}{0.05845 \text{ kg mol}^{-1}}$$
$$= 4.$$

Further Reading

- 1) *Principles of Physical Chemistry*, Samuel H. Maron and Carl F. Prutton, Oxford and IBH Publishing Co., New Delhi, 4th ed., 1985.
- 2) *Physical Chemistry*, Gilbert W. Castellan, Narosa Publishing House, Addison—Wesley/Narosa (Indian Student Edition), Delhi, 3rd ed., 1983.
- 3) *Physical Chemistry*, P.C. Rakshit, Sarat Book House, Calcutta, 5th ed., 1988.
- 4) *Physical-Chemistry through Problems*, S.K. Dogra and S. Dogra, Wiley Eastern Ltd., New Delhi, 1984.
- 5) *Physical Chemistry—Principles and Problems*, D.V.S. Jain and P. Jauhar, Tata McGraw-Hill Pub. Company Ltd., New Delhi, 1990.