स्वाध्याय स्वमन्थन स्वावलम्बन

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UGCHE-04
Physical Chemistry

FIRST BLOCK : States of Matter

SECOND BLOCK : Chemical Thermodynamics

THIRD BLOCK : Solutions & Phase Rool

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UGCHE-04
Physical Chemistry

Block

1

STATES OF MATTER

STATES OF MATTER

Matter generally exists in one of the three states, namely, gas, liquid and solid. These are referred to as states of matter. In this block, we discuss the main characteristics of the three states of matter.

The first unit discusses the use of SI units. This unit material will help you to express the physical quantities in SI units. In the second unit, we discuss the gas laws based on the experiments performed by Boyle, Charles and Dalton. Furthermore, the assumptions of the kinetic theory of gases are explained and used in deriving an equation giving relationship between pressure, volume and temperature. This unit brings out how experimental and theoretical aspects of the properties of gases go hand in hand. In the third unit, the reasons for the deviation of gases from ideal behaviour are explained. **van der Waals** equation of state is derived and used in calculating critical constants. The methods of liquefaction of gases and the types of intermolecular forces are described.

The fourth unit is on liquids. It gives a glimpse of the structure and the properties of liquids. There is a discussion on the types and the importance of liquid crystals. The last unit is on solid state. It deals with the crystal geometry and gives an elementary account of X-ray diffraction of crystals.

After studying this block, you should be able to :

- state the SI units of basic and derived quantities,
- explain the gas laws,
- discuss the kinetic theory of gases,
- list the reasons for the deviation of the gases from ideal behaviour,
- derive van der Waals equation of state,
- discuss the principles of methods for liquefaction of gases,
- state the types of intermolecular forces,
- explain the characteristics of liquids,
- state the types and the applications of liquid crystals, and
- discuss the elements of crystal structure determination using X-ray diffraction.

Study Guide

Although you may be familiar with some fundamental aspects of chemistry, background material is provided in this block wherever possible. Thus, the material provided in the first two units may help you in recapitulating what you have studied earlier. The SI units have been used throughout. You are advised to study carefully Unit 1 of this course and also the appendix to Unit 6 (Block 2) of Atoms and Molecules Course, where we have discussed the SI units of some electrical and magnetic quantities. This will help you in the choice of proper SI units for a particular quantity.

An elementary knowledge of calculus would help you to study the material without much difficulty. In this connection, you are advised to choose the course on Mathematical Methods as one of your electives. However, the derivations of equations have been done in a step-wise manner. This is done particularly to soften the feelings of those who are not pleased with the unhappy marriage between mathematics and chemistry. It is not difficult to realise that mathematics bestows precise and logical format to the statements of science.

As far as possible we have used IUPAC recommendations for the symbols of various physical quantities. You have to note carefully the notations used for thermodynamic and physical quantities. Many numerical examples are worked out in the text. Most of these involve substitution of numerical data into the equations. You are particularly advised to work out the numerical problems given as self-assessment and terminal questions since such exercises will give you an idea about the magnitudes of different physico-chemical quantities. Another advantage is that you get drilled to the usage of proper SI units for various quantities. Whenever you study the derivation of an expression, you must be careful to know its significance also. Some books are suggested for further reading at the end of this block.

PHYSICAL CHEMISTRY

Physical chemistry is one of the electives for Bachelor's Degree Programme in science. The course on physical chemistry deals with the fundamental principles governing the chemical transformations. It describes the interaction between matter and energy. In physical chemistry, the influence of physical factors such as temperature, pressure, concentration, light, electricity etc., on chemical reactions is discussed in detail. It uses the theoretical principles and the experimental techniques to investigate the chemical transformations and the physical changes accompanying them.

Physical chemistry deals with a wide variety of topics ranging from the states of matter to the reaction rates. The modern approach to physical chemistry is to deal with the following three aspects of matter :

- Structure
- Equilibrium properties
- Ability to change

Some of the aspects regarding structure have been dealt with in the course on Atoms and Molecules. In that course, we explained some of the theoretical concepts of structure such as quantum theory, wave mechanics, molecular orbital theory and valence bond theory. Structure elucidation methods based on electrical, magnetic, spectroscopic and optical characteristics were also discussed.

In physical chemistry, we deal with the remaining two aspects, namely, equilibrium properties and ability to change. There are five blocks in this course. The first block starts with a discussion on the states of matter. The study of the properties of matter in gas, liquid and solid forms is essential since the substances that take part in a chemical reaction are found in one of these three forms.

The second block explains various aspects of chemical thermodynamics. It provides a basis for rationalising the energy changes that occur in the course of chemical reactions. It is useful in calculating the maximum amount of work that may be generated by a system while undergoing a change. It also enables us to predict whether a particular chemical change is possible or not.

In the third block, thermodynamics of solutions and phase equilibria are discussed. The characteristics of systems such as liquid-liquid, solid-liquid and gas-liquid are explained in detail. In the fourth block, we deal with chemical equilibria and electrochemistry. The study of chemical equilibria is useful to assess the characteristics associated with the equilibrium conditions of a chemical reaction. It is helpful in determining what conditions are required to optimise the yield of a particular product. In electrochemistry, we consider the correlation between chemical energy and electrical energy.

In the last block, we study chemical kinetics, photochemistry, surface chemistry and colloids. Chemical kinetics is the study of rate of chemical reactions. The dependence of chemical reaction rate on factors like concentration and temperature forms the main theme of chemical kinetics. The surface chemistry deals with the properties of interfaces. Surfaces can play an important role to accelerate or impede a chemical reaction. Photochemistry comprises the study of interaction between light energy and chemical energy. In the unit on colloids, we describe the characteristics of colloids, emulsions and gels and again study various aspects of interfaces.

The study of physical chemistry is quite vital for the understanding of chemical reactions. Large scale industrial operations such as liquefaction of gases, refrigeration and manufacture of chemicals are facilitated by physico-chemical investigations. Further, physico-chemical methods are effectively used by inorganic, organic and analytical chemists as the key for unlocking the structural problems. Physico-chemical principles find application in allied fields like agriculture, engineering, metallurgy, pharmaceuticals and petroleum industries.

After studying physical chemistry course you should be able to :

- explain the main features of gas, liquid and solid states,
- discuss the importance of X-ray diffraction in structure determination,
- state and explain the laws of thermodynamics;
- discuss the importance of free energy change of a reaction in determining its feasibility,

- describe the salient features of physical and chemical equilibria,
- explain the dependence of reaction rate on concentration, surface and temperature,
- list the main aspects of a photochemical reaction, and
- discuss the characteristics and the importance of colloids, gels and emulsions.

UNIT 1 UNITS AND DIMENSIONS

Structure

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.

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

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	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Temperature	T	kelvin	K
Luminous intensity	I_v	candela	cd
Amount of substance	n	mole	mol

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 × length	l^2	square metre	m^2
Volume*	Length × length × 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 × acceleration	mlt^{-2}	newton	N or $kg\ m\ s^{-2}$
Pressure	$\frac{\text{Force}}{\text{Area}}$	mlt^{-2}/l^2 $= ml^{-1}t^{-2}$	pascal	Pa or $N\ m^{-2}$ or $kg\ m^{-1}\ s^{-2}$
Energy or Work	Force × distance	$mlt^{-2}l$ $= ml^2t^{-2}$	joule	J or N m or $Pa\ m^3$ or $kg\ m^2 s^{-2}$
Electric charge	Electric current × 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	$\frac{\text{(Electric potential difference)}}{\text{Electric current}}$	$\frac{ml^2 I^{-1} t^{-3}}{I}$ $= ml^2 I^{-2} t^{-3}$	ohm	Ω or V A^{-1} or kg $m^2 A^{-2} s^{-3}$
Electric conductance	$\frac{1}{\text{(Electric resistance)}}$	$\frac{1}{ml^2 I^{-2} t^{-3}}$ $= I^2 t^3 m^{-1} l^{-2}$	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 examble, 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.

Pressure × volume = Amount of the substance × gas constant × temperature ... (1.1)

Rearranging this,

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

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 :

$$\text{Dimensions of } R = \text{Dimensions of} \left[\frac{\text{Pressure} \times \text{volume}}{\text{Amount of the substance} \times \text{temperature}} \right]$$

$$= \frac{ml^{-1}t^{-2}l^3}{n.T} = (ml^2t^{-2})(n^{-1})(T^{-1})$$

Hence, the units of R = joule mole^{-1} 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 mol^{-1} 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) :

i) Write an equation relating the test quantity to other quantities of **known dimensions.**

ii) Rearrange this equation such that only the test quantity is on the left hand side and others are on the right hand side.

iii) Substitute the dimensions of the quantities on the right hand side and simplify.

iv) 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 × mass × $(\text{velocity})^2$, 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 μkg.

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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SAQ 4

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

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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.

Three no's in SI units :
No plurals;
No full stops (except at the end of a sentence);
No dashes.

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.

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

x) Exponents (or powers) operate on prefixes also. Let us derive the relationship between cm^3 and m^3 using the relation, 1 cm = 10^{-2} m.
$1\ cm^3 = (1\ cm)^3 = (10^{-2}\ m) \times (10^{-2}\ m) \times (10^{-2}\ m) = 10^{-6}\ m^3$
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 (kg m^{-1} s^{-2}) as kg/m s^2 is allowed but not as kg/m/s^2.

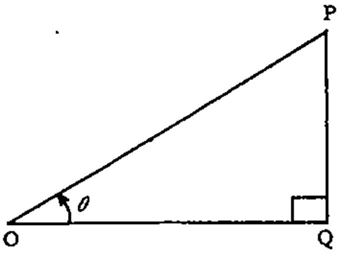
So far, we studied some rules for writing SI units. Let us now discuss the dimensions of some mathematical functions which are useful in studying this course.

While representing the relationship among the physical quantities of substances, we often come across the mathematical functions like sin θ, e^x and ln x. It is to be kept in mind that trigonometric (sin θ, cos θ, 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 θ and e^x.

From the right-angled triangle PQO,

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



Evidently sin θ 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.

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

Since addition or subtraction must be done between quantities of same dimensions, 1, x, x^2, x^3, ... 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,

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

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 now 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 cm), exerts a pressure of 1 atm. (Fig. 1.1).

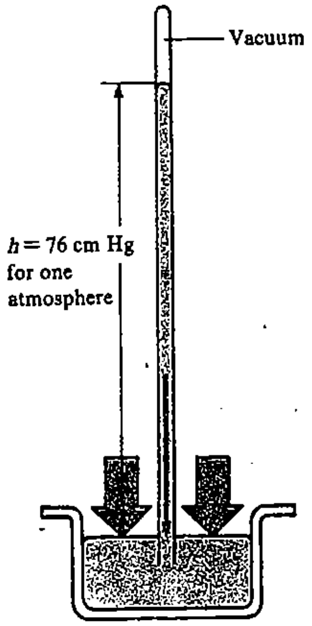

Fig. 1.1 : The pressure of a column of mercury 76 cm high inside the glass tube (black arrow) balances the pressure of air (red arrow) on the rest of the surfaces of mercury

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 :

$$p = hg\rho \qquad \cdots (1.3)$$

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).

$$\frac{100 \text{ cm}}{100 \text{ cm}} = 1 = \frac{1 \text{ m}}{100 \text{ cm}} \qquad \text{... (1.4)}$$

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 (i)	Symbol (ii)	Equivalence statement(s) (iii)	Unit factor (iv)	The actual value of the quantity in non-SI unit(s) (v)	The quantity in SI unit(s) (vi) = (v) × (iv)
Height of mercury column	h	$100 \text{ cm} = 1 \text{ m}$	$\frac{1 \text{ m}}{100 \text{ cm}}$	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 $10^6 \text{ cm}^3 = 1 \text{ m}^3{}^*$	$\frac{(1 \text{ kg})}{(10^3 \text{ g})} \div \frac{(1 \text{ m}^3)^{**}}{(10^6 \text{ cm}^3)}$ $= \frac{10^3 \text{ kg cm}^3}{1 \text{ g m}^3}$	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 cloumn of Table 1.5 are to be substituted in Eq. 1.3 to get the SI equivalent of 1 atm pressure.

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

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

Hence, SI equivalent of 1 atm pressure is 1.0132×10^5 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.

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

Using the above procedure, attempt the follwing SAQ.

SAQ 6

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

1. Examine the following statements and indicate their validity by writing T for true or F for false; if false, indicate the reason.
   i) The SI unit of mass is gram.
   ii) The symbol of SI unit of temperature is k.
   iii) The SI unit of pressure is pascal.
   iv) 1 N = 1 kg ms^{-2}.
   v) 10^{-6} gram = 1 μg.
2. If 25.3 g of a substance occupies a volume of 23 cm^3, calculate its density in SI units.
3. 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.
4. 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?
5. Complete the following conversions :
   a) 1 mg = ... kg = ... g
   b) 1 s = ... ms = ... ns
   c) 1 km = ... m = ... mm

1.9 ANSWERS

Self Assessment Questions

1. Dimensions of u_{rms}

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

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

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

Hence u_{rms} has the dimensions, lt^{-1} and the units, m·s^{-1}.

2. Kinetic energy has the unit, J.

3. (a) nm (b) ps (c) kPa.

4. 10^{-10} m = 10^2 pm; hence pm unit can be used.

5. 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).

6. Value of R in SI unit = The value of R in non-SI unit × 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

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

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

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.

Dimensions of M_m = Dimensions of $\frac{\rho RT}{p}$

$$= \frac{(ml^{-3})(ml^2 t^{-2} n^{-1} T^{-1}) T}{ml^{-1} t^{-2}}$$

$$= mn^{-1}.$$

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

4. The unit of reduced mass is kg.

5. a) 1 mg = 10^{-6} kg = 10^{-3} g
   b) 1 s = 10^3 ms = 10^9 ns
   c) 1 km = 10^3 m = 10^6 mm.

UNIT 2 KINETIC THEORY OF GASES

Structure

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 :

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

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.

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

or $pV = K_1$ ... (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.

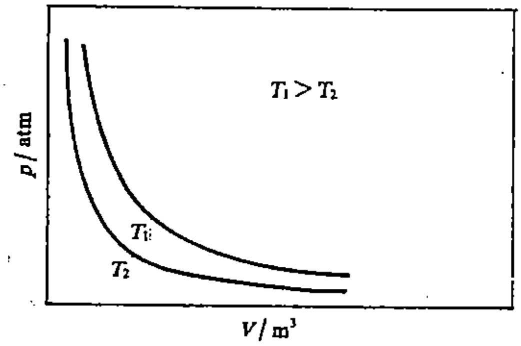

Fig. 2.1 : Isotherms at T_1 and T_2

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).

i.e., $V \propto T$ ... (2.3)

or $V = K_2T$ ... (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.

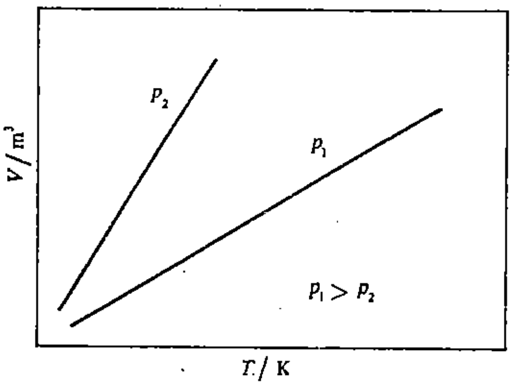

Fig. 2.2 : Isobars at p_1 and p_2

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,

$V \propto N$ ... (2.5)

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

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,

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

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

$V \propto n$ ... (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.,

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

or $pV = nRT$ ... (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.

Let us now discuss the units of R.

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 J mol^{-1} 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 × 10^4 Pa assuming ideal behaviour.

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

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

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

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

$$\frac{\left(\frac{0.0660}{0.044} \text{ mol}\right) \times 8.314 \text{ J mol}^{-1} \text{K}^{-1}) \times (300.2 \text{ K})}{9.41 \times 10^4 \text{ Pa}}$$

$$= 0.0398 \text{ m}^3$$

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

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

Using the ideas developed above, attempt the following SAQ.

SAQ 1

Calculate the density of oxygen gas at 273.2 K and 1.013 × 10^5 Pa, assuming ideal behaviour

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

(ii) Density = Mass/Volume)

....

....

....

SAQ 2

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

....

....

....

....

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 ndividual 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 ot 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,

$$p_t = p_A + p_B + p_C \qquad \text{... (2.10)}$$

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

$$p_A = \frac{n_A RT}{V} \qquad \text{... (2.11)}$$

$$p_B = \frac{n_B RT}{V} \qquad \text{... (2.12)}$$

$$\text{and } p_C = \frac{n_C RT}{V} \qquad \text{... (2.13)}$$

Using Eqs. 2.10 to 2.13, we can write,

$$p_t = (n_A + n_B + n_C)\frac{RT}{V} = \frac{n_t RT}{V} \qquad \text{... (2.14)}$$

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,

$$p_A = \frac{n_A}{n_t} p_t \qquad \text{... (2.15)}$$

$$p_B = \frac{n_B}{n_t} p_t \qquad \text{... (2.16)}$$

$$\text{and } p_C = \frac{n_C}{n_t} p_t \qquad \text{... (2.17)}$$

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,

$$p_A = x_A p_t \qquad \text{... (2.18)}$$

$$p_B = x_B p_t \qquad \text{... (2.19)}$$

$$p_A = x_C p_t \qquad \text{... (2.20)}$$

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.

....

....

....

....

SAQ 4

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

....

....

....

....

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.

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.

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

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

or

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

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,

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

Using Eq. 2.23, answer the following SAQ.

SAQ 5

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

....

....

....

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 (**u**) is a vector quantity. The components of **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 **u** and the latter is represented by **OC** (Fig. 2.3).

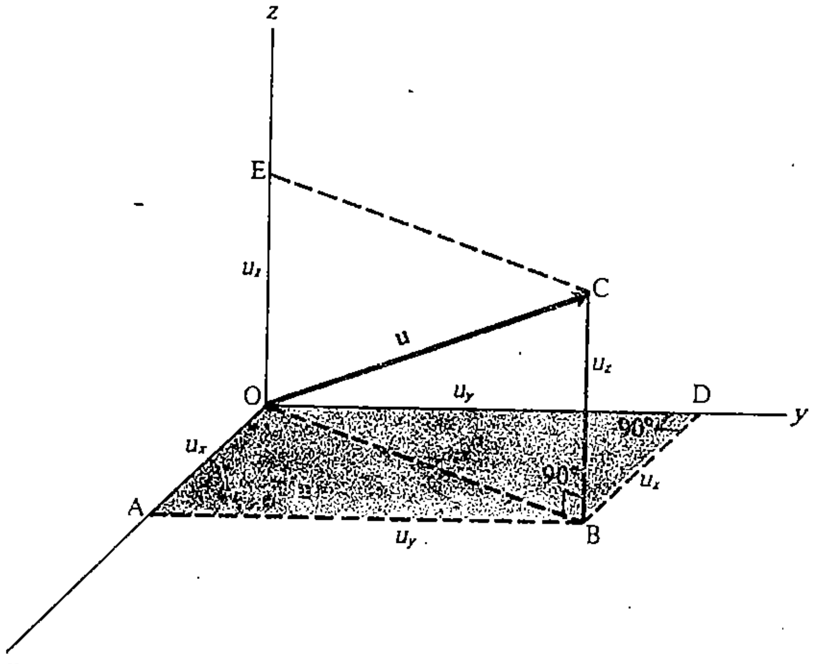

Fig. 2.3 : Components of velocity, u

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, $\angle OBC = 90°$

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

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

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

$$\therefore\ u^2 = OB^2 + u_z^2 = u_x^2 + u_y^2 + u_z^2 \qquad \text{....(2.24)}$$

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 $u_{1x}^2, u_{2x}^2, u_{3x}^2, \ldots\ldots u_{Nx}^2$ are the square of the x components of the velocities for the molecules, 1, 2, 3, ... N, then the average of these values, $\overline{u_x^2}$, is given by,

$$\overline{u_x^2} = \frac{(u_{1x}^2 + u_{2x}^2 + u_{3x}^2 + \ldots\ldots + u_{Nx}^2)}{N} \qquad \text{... (2.25)}$$

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

For $\overline{u_y^2}$ and $\overline{u_z^2}$ 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, $\overline{u^2}$, is related to $\overline{u_x^2}$, $\overline{u_y^2}$ and $\overline{u_z^2}$ as,

$$\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2} \qquad \text{... (2.26)}$$

The quantity $\overline{u^2}$ is called the mean square speed. Since the gas molecules are in random motion, no particular direction is preferred. The quantities, $\overline{u_x^2}$, $\overline{u_y^2}$ and $\overline{u_z^2}$ are equal. Hence,

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \overline{u^2}/3 \qquad \text{... (2.27)}$$

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

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 $- mu_{1x}$.

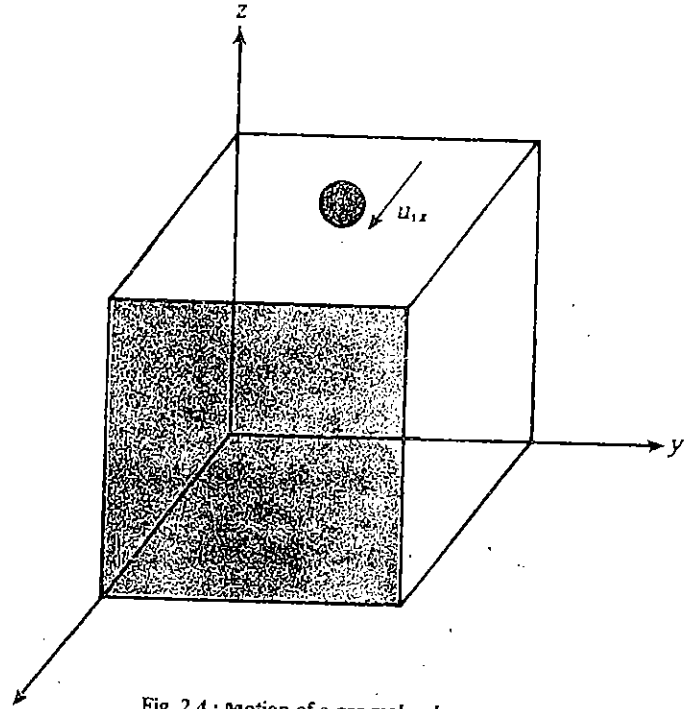

Fig. 2.4 : Motion of a gas molecule.

We consider the momentum change along x axis only.

The change in momentum of the molecule in one collision is, $mu_{1x} - (- mu_{1x}) = 2\, mu_{1x}$. This molecule has to travel a distance of $2l$ before it collides with the shaded face again. The ime required for the next collision can be calculated as follows :

The molecule travels a distance of u_{1x} in one second. Hence, to travel a distance of $2l$, the time equired $= \frac{2l}{u_{1x}}$ second. That is, the time interval required for each successive collision with he shaded face is $2l/u_{1x}$ second. Hence the number of collisions between the molecule and the haded face taking place in unit time will be the inverse of the above expression, i.e., $u_{1x}/2l$.

$$\begin{array}{l} \text{he change of momentum in} \\ \text{ne second (or rate of change} \\ \text{f momentum) per molecule} \end{array} = \begin{array}{l} \text{Change of momentum per} \\ \text{molecule per collision} \end{array} \times \begin{array}{l} \text{number of collisions a} \\ \text{molecule undergoes in one} \\ \text{second} \end{array}$$

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

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

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

ence force due to collisions by one molecule $= \frac{mu_{1x}^2}{l}$ ... (2.28)

imilarly we can derive expressions for the force exerted by second, third ..... N^{th} olecule over the shaded face.

he total force (F) exerted by N molecules over the shaded face can be calculated as llows:

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

$$= \frac{m}{l} N\overline{u_x^2} \qquad \text{(using Eq. 2.25)}$$

Using Eq. 2.27,

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

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

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

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

$$p = \frac{mN\overline{u^2}}{3V} \qquad \text{... (2.30)}$$

$$\therefore pV = \frac{1}{3} mN\overline{u^2} \qquad \text{... (2.31)}$$

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,

$$pV = \frac{2}{3} N\left(\frac{1}{2} m\overline{u^2}\right) \qquad \text{... (2.32)}$$

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.,

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

$$\text{or } \frac{1}{2} m\overline{u^2} = K_1 T \qquad \text{... (2.33)}$$

where K_1 is a constant.

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

Substituting this in Eq. 2.32, we obtain,

$$pV = \frac{2}{3} NK_1 T \qquad \text{... (2.34)}$$

This can be written as

$$pV = NkT \qquad \text{... (2.35)}$$

Where k, known as Boltzmann constant is equal to 2/3 K_1. The value of k is 1.38×10^{-23} 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,

$$N = nN_A \qquad \text{... (2.36)}$$

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

$$pV = nN_A kT = nRT \qquad \text{... (2.37)}$$

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

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

Average kinetic energy per molecule $= \frac{1}{2} m \overline{u^2} = \frac{3}{2} kT$ ... (2.38)

$$\text{Similarly, average kinetic energy per mole } = (N_A)\left(\frac{1}{2} m \overline{u^2}\right)$$

$$= (N_A)\left(\frac{3}{2} kT\right)$$

$$= \frac{3}{2} N_A kT$$

$$= \frac{3}{2} RT \; (\because R = N_A k) \qquad \text{... (2.39)}$$

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.

Using Eq. 2.38, the translational energy of nitrogen per molecule at 300 K $= \frac{3}{2} kT$

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

$$= 6.21 \times 10^{-21}\ \text{J}.$$

Similarly using Eq. 2.39, the translational energy of nitrogen per mole at 300 K $= \frac{3}{2} RT$

$$= \frac{3}{2} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 300\ \text{K}$$

$$= 3.74 \times 10^{3}\ \text{J mol}^{-1}.$$

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.

Number density of a gas $(n_o) = \frac{N}{V} = \frac{p}{kT}$ ... (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.

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

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

Number density (n_o) of nitrogen molecules at 298.2 K $= \frac{p}{kT} = \frac{1.013 \times 10^5\ \text{Pa}}{1.38 \times 10^{-23}\ \text{J K}^{-1} \times 298.2\ \text{K}}$

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

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

$$= 40.86\ \text{mol m}^{-3}$$

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 $(\overline{u_x^2})$ 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

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

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

Root mean square speed $\left(\sqrt{\overline{u^2}}\right) = u_{rms} = \sqrt{\frac{3RT}{M_m}}$ ... (2.43)

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

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

Air has average molar mass of 0.029 kg mol^{-}. 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.

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

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 kg mol^{-1})

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....

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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).

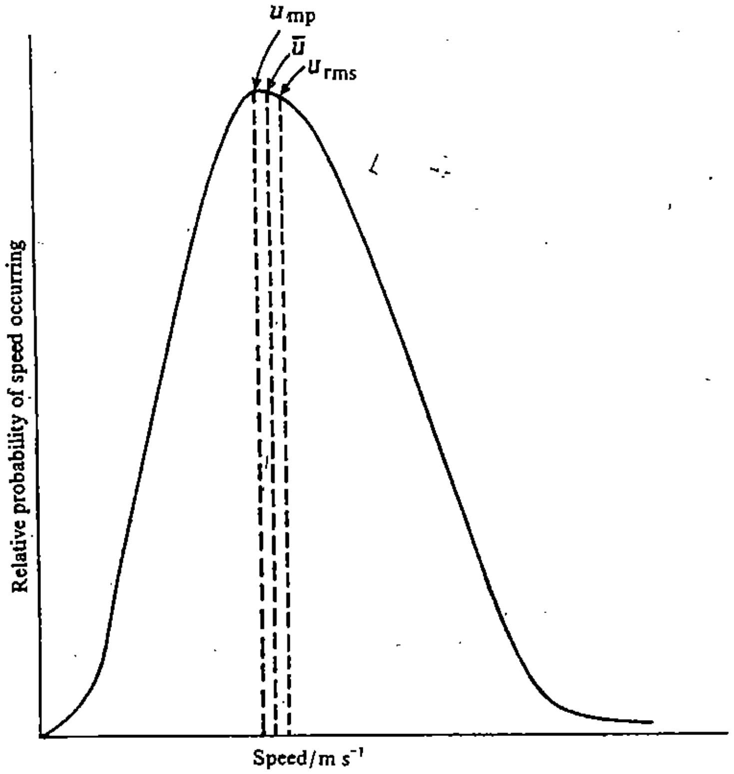

Fig. 2.5 : Distribution of speeds of nitrogen molecules at 273 K.

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

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

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 :

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{1}{N}(u_1^2 + u_2^2 + u_3^2 + \ldots\ldots + u_N^2)} \qquad \ldots (2.45)$$

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 :

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M_{\text{m}}}} \qquad \ldots (2.46)$$

$$\bar{u} = \sqrt{\frac{8RT}{\pi M_{\text{m}}}} \qquad \ldots (2.47)$$

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M_{\text{m}}}} \qquad \ldots (2.48)$$

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

$$\text{Average speed } (\bar{u}) \text{ of nitrogen molecules at 298.2 K} = \sqrt{\frac{8RT}{\pi M_{\text{m}}}}$$

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

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

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.

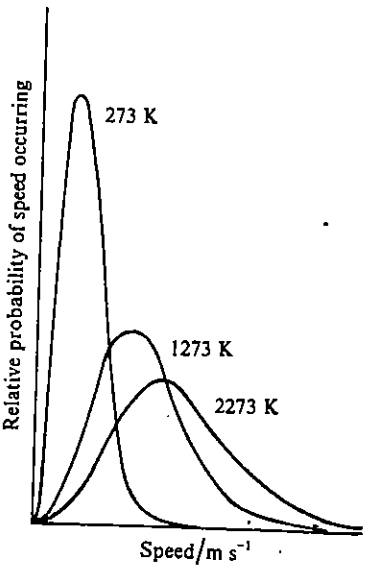

Fig. 2.6 : Distribution of speeds of nitrogen molecules at three different temperatures.

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

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

....

....

....

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:

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

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) :

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

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

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

Molar heat capacity = Molar mass × specific heat

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

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	$\frac{U^*}{\text{J mol}^{-1}}$	$\frac{\bar{C}_v}{\text{J mol}^{-1}\,\text{K}^{-1}}$	$\frac{\bar{C}_p}{\text{J mol}^{-1}\,\text{K}^{-1}}$	$\frac{\bar{C}_p}{\bar{C}_V}$
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) 2 (rotational) 1 (vibrational not active at 298 K)	$\left.\begin{array}{l}\frac{3}{2}RT\\2\times\frac{1}{2}RT\end{array}\right\}\frac{5}{2}RT$	$\frac{5}{2}R$	$\frac{7}{2}R$	1.40
Non-linear triatomic molecule	Water	3 (translational) 3 (rotational) 3 (vibrational not active at 298 K)	$\left.\begin{array}{l}\frac{3}{2}RT\\3\times\frac{1}{2}RT\end{array}\right\}3RT$	$3R$	$4R$	1.33

Using the ideas given above, answer the following SAQ.

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 × molar mass)

....

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.

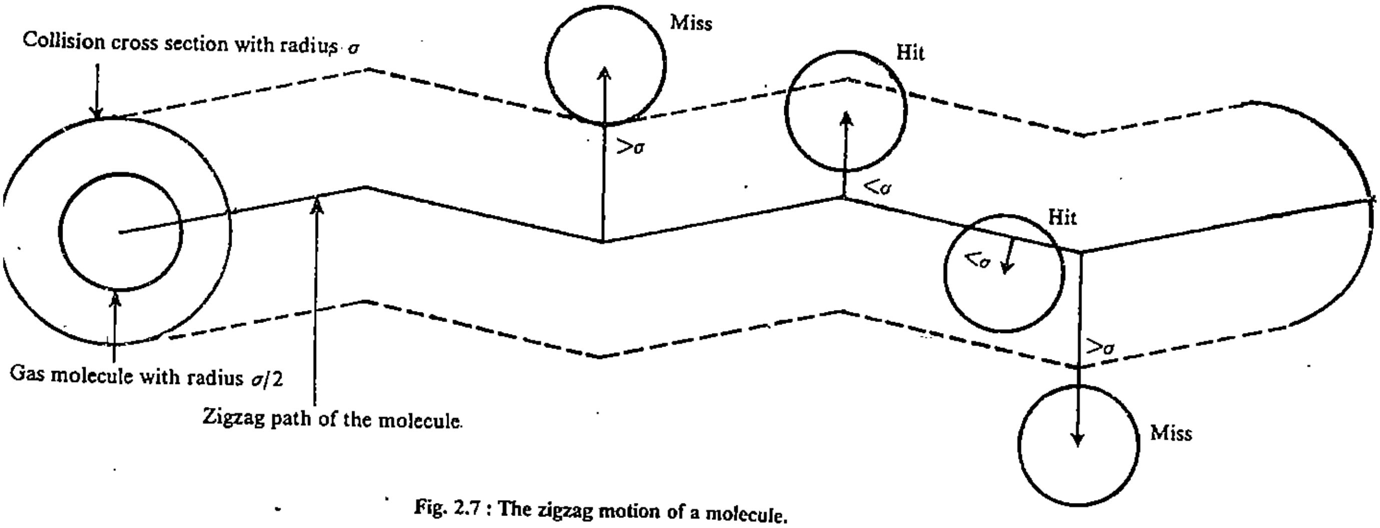

Fig. 2.7 : The zigzag motion of a molecule.

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.

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

The number of molecules present per unit volume (number density) is n_o. 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.

$$z_{11} = \pi\sigma^2\bar{u}n_o \qquad \text{... (2.50)}$$

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,

$$z_{11} = \sqrt{2}\,\pi\sigma^2\bar{u}n_o \qquad \text{... (2.51)}$$

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

$$Z_{11} = \frac{1}{2} z_{11} n_o = \frac{1}{\sqrt{2}}\,\pi\sigma^2\bar{u}n_o^2 \qquad \text{... (2.52)}$$

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,

$$Z_{11} = \frac{1}{\sqrt{2}}\,\pi\sigma^2\bar{u}n_o^2$$

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

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

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

$$= \frac{\bar{u}}{z_{11}} \qquad \text{... (2.53)}$$

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

i.e.,

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

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.

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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 1.250×10^3 kg m^{-3} at 273.2 K and 1.013×10^5 Pa.

2) 1.000×10^{-3} 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 2.00×10^{-3} kg of H_2 and 2.00×10^{-3} kg of He exerts a pressure of 1.50×10^5 Pa. What are the partial pressures of H_2 and He?

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 1.013×10^5 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) $pV = nRT = \frac{w}{M_m} RT$

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

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

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

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

) 6.022×10^{22} molecules.

) Total number of moles (n_t)

$$= n_{N_2} + n_{O_2} + n_{CH_4} = 5.00 \text{ mol.}$$

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

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

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

$$p_{N_2} = \frac{n_{N_2}}{n_t} p_t = \frac{2.00}{5.00} \times 1.73 \times 10^5 \text{ Pa}$$

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

Similarly $p_{O_2} = 3.46 \times 10^4$ Pa
and $p_{CH_4} = 6.92 \times 10^4$ Pa

Nitrogen

4

6) Root mean square speed of hydrogen at 500 K

$$= \sqrt{\frac{3RT}{M_m}} = \sqrt{\frac{3 \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 500\ \text{K}}{0.002\ \text{kg mol}^{-1}}}$$

$$= 2.50 \times 10^3\ \text{m s}^{-1}.$$

7) $u_{mp} : \bar{u} : u_{rms}$

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

$$= 1.000 : 1.128 : 1.225 \text{ (Dividing by } \sqrt{\frac{2RT}{M_m}}\text{)}$$

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

8) $\bar{C}_v = 692\ \text{J kg}^{-1}\ \text{K}^{-1} \times 0.018\ \text{kg mol}^{-1}$
$= 12.5\ \text{J mol}^{-1}\ \text{K}^{-1}$
Since $\bar{C}_p = \bar{C}_v + R$
$\bar{C}_p = 20.8\ \text{J mol}^{-1}\ \text{K}^{-1}$

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

9) $\lambda = \dfrac{1}{\sqrt{2}\,\pi\sigma^2 n_o}$

Using n_o calculated in Subsec. 2.8.2,

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

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

Terminal Questions

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

2) 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).

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

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

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

$$\frac{t_{\text{oxygen}}}{t_{\text{Argon}}} = \sqrt{\frac{\text{Molar mass of oxygen}}{\text{Molar mass of argon}}}$$

$$= \sqrt{\frac{32}{40}}$$

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

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

4) $\dfrac{\overline{u^2}_{\text{Oxygen}}}{\overline{u^2}_{\text{Nitrogen}}} = \dfrac{7}{8}$

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

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

$\bar{C}_V = 7/2\ R$ and $\bar{C}_p = \dfrac{9}{2} R$

Hence, $\bar{C}_p/\bar{C}_V = \dfrac{9}{7}$

UNIT 3 REAL GASES AND THEIR LIQUEFACTION

Structure

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.

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.

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

$$z = \frac{pV}{nRT} \qquad \text{... (3.1)}$$

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.

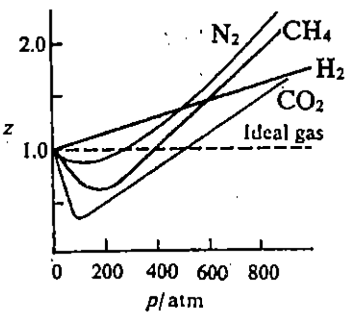

Fig. 3.1 : Plots of z against p for several gases.

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.

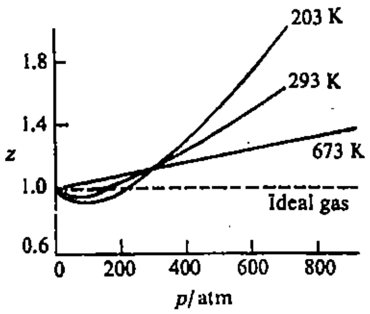

Fig. 3.2 : Plots of z against p for nitrogen gas at three temperatures.

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.

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

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

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.

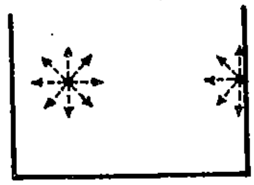

Fig. 3.3 : The attraction experienced by the molecules of a gas.

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

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

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

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

Hence, it can be written that,

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

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

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

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

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

If the corrected pressure and the corrected volume of the gas are substituted in the ideal gas equation (Eq. 2.3), we obtain

$$(p + \frac{n^2a}{V^2})(V - nb) = nRT \qquad \text{... (3.5)}$$

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

$$(p + \frac{a}{V_m^2})(V_m - b) = RT \qquad \text{... (3.6)}$$

/an 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 :alled the van der Waals constants or parameters. The values of 'a' and 'b' are obtained :mpirically by fitting in experimental $p - V - T$ data to Eq. 3.5. It may be pointed that 'b' is . measure of the molecular size and 'a' is related to the intermolecular interaction. Table 3.1 ives the values of the parameters 'a' and 'b' of some selected gases. It can be seen that 'b' ıcreases as the size of the molecule increases whereas 'a' has large value for an easily ompressible gas. The values of the critical constants p_c, V_c and T_c are also given in Table .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

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

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

planation of the Behaviour of Gases using van der Waals Equation :

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

hen 'b' is negligible

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

$$+ \frac{a}{V_m^2}) V_m = RT \qquad \text{... (3.7)}$$

$$pV_m = RT - \frac{a}{V_m}$$

$$= \frac{pV_m}{RT} = 1 - \frac{a}{RTV_m} \qquad \text{... (3.8)}$$

shows that under these conditions, pV_m will be less than RT or z will be less than y. Eq. 3.8 will be valid for substances like water vapour for which 'a' is large and 'b' is nparatively small (See Table 3.1). Also for gases such as N_2, CH_4 and CO_2 (Fig. 3.1) at derately low pressures, V_m is large such that $(V_m - b)$ is nearly equal to V_m. Hence, Eq. is applicable for such gases at moderately low pressures.

en 'a' is negligible

' is negligible, we have

$$_m - b) = RT \qquad \text{... (3.9)}$$

$$pV_m = RT + pb$$

$$= \frac{pV_m}{RT} = 1 + \frac{pb}{RT} \qquad \text{... (3.10)}$$

ce, pV_m will be greater that RT or z will be greater than unity. Particularly this is true ydrogen (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 5.000×10^{-2} m^3

Rearranging Eq. 3.5 we can write,

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

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

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

substituting the values of the parameters we get,

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

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

Applying van der Waals equation to methane at 1.000×10^3 K, the pressure calculated is 3.328×10^5 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 :

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

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.

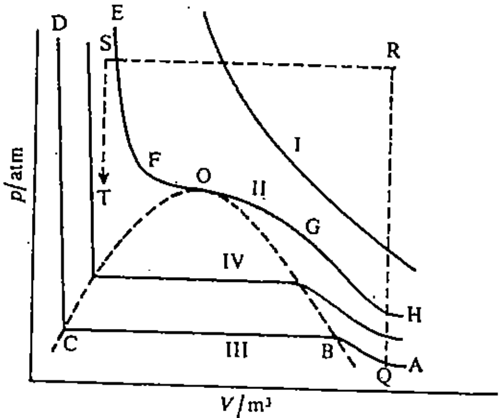

Fig. 3.4 · Isotherms of carbon dioxide.

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

At high temperature, the isotherm is a hyperbola (curve I) in accordance with Boyle's law (Unit 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.

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,

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

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

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

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

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

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 perturbance, then portions BC and EF are realisable; these portions represent the supersaturated vapour and superheated liquid, respectively.

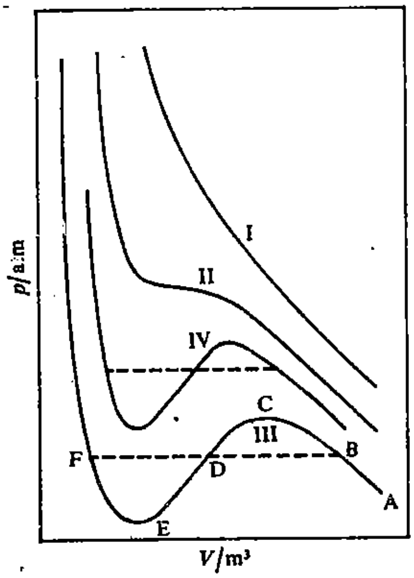

Fig. 3.5 : van der Waals isotherms.

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.

i.e., $V_m = V_c$ or $V_m - V_c = 0$

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

$$(V_m - V_c)^3 = 0 \qquad \text{... (3.14)}$$

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

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

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

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

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

$$3V_c^2 = \frac{a}{p_c} \qquad \text{.. (3.18)}$$

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

From Eqs. 3.18 and 3.19, we obtain

$$\frac{V_c}{3} = b \text{ or } V_c = 3b \qquad \text{... (3.20)}$$

Substituting the value of V_c in Eq. 3.18,

$$p_c = \frac{a}{27b^2} \qquad \text{... (3.21)}$$

From Eqs 3.17 and 3.20, we get

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

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

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

$$= \frac{8a}{27Rb} \qquad \text{... (3.22)}$$

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).

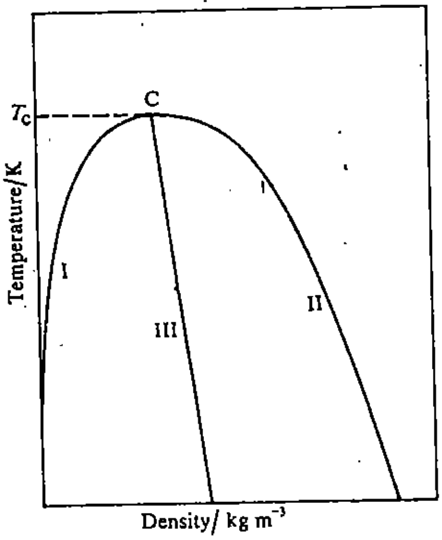

Fig. 3.6 : Plot of densities of vapour (I), liquid (II) and their mean values (III) against temperature.

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 :

$$z_c = \frac{p_c V_c}{RT_c} \qquad \ldots (3.23)$$

$$= \left(\frac{a}{27b^2}\right) \cdot (3b) \cdot \frac{1}{R} \cdot \frac{1}{8a/27Rb}$$

$$= \frac{3}{8} = 0.375$$

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 :

Thus, reduced pressure $= \pi = \dfrac{p}{p_c}$ or $p = \pi p_c$ ... (3.24)

Reduced volume $= \phi = \dfrac{V_m}{V_c}$ or $V_m = \phi V_c$ ... (3.25)

Reduced temperature $= \theta = \dfrac{T}{T_c}$ or $T = \theta T_c$ ... (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,

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

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

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

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

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

$$\text{or } \left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta \qquad \text{... (3 30)}$$

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 5.000×10^{-2} m^3 space at 3.328×10^5 pa.

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(Hint : First find out π and ϕ and then evaluate θ using Eq. 3.30)

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.

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.

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 inversion temperature (T_i) of a gas is related to its van der Walls 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.

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

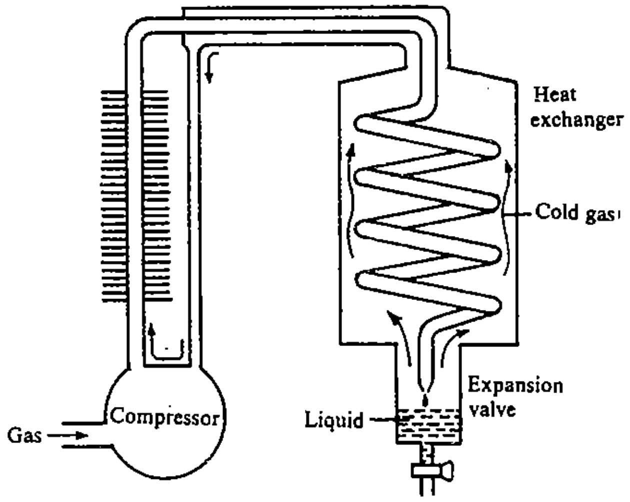

Fig. 3.7 : Liquefaction using Linde's method

Tha 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

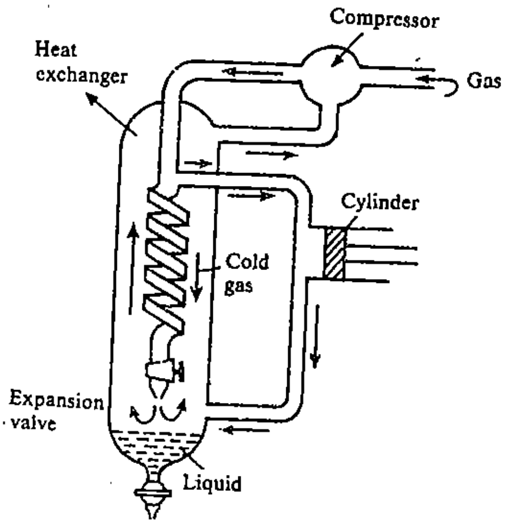

Fig. 3.8 : Liquefaction using Claude's method.

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.

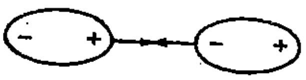

Fig. 3.9 : The electrostatic interaction of two polar molecules; → ← shows attraction.

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

The interaction energy ($V_{\mu\mu}$) between two polar molecules separated by a distance r is ound to be

- directly proportional to the square of the product of the dipole moments of the two molecules

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

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

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

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

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.

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

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.

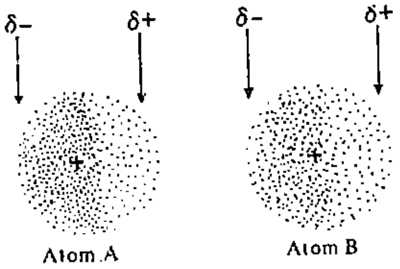

Fig. 3.10 : Instantaneous dipole on atom A induces a dipole on atom B. δ^+ and δ^- refer to dipolar charges and + stands for the nucles.

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,

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.

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.

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

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

$$V_t = V_{\mu\mu} + V_{\mu d} + V_{dis} + V_{rep} \qquad \text{... (3.31)}$$

This equation can also be written as

$$V_t = \frac{p}{r^{12}} - \frac{q}{r^6} \qquad \text{... (3.32)}$$

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_t 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_t due to attractive forces (along ABC) is gradual but the increase in V_t due to repulsive forces (along CD) is very steep (Guess the reason!).

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

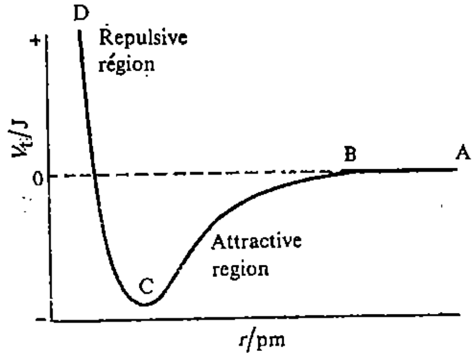

Fig. 3.11 : Total interaction energy as a function of intermolecular distance.

3.8.3 Hydrogen Bonding

The strength of hydrogen bonding is of the order of 10-40 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).

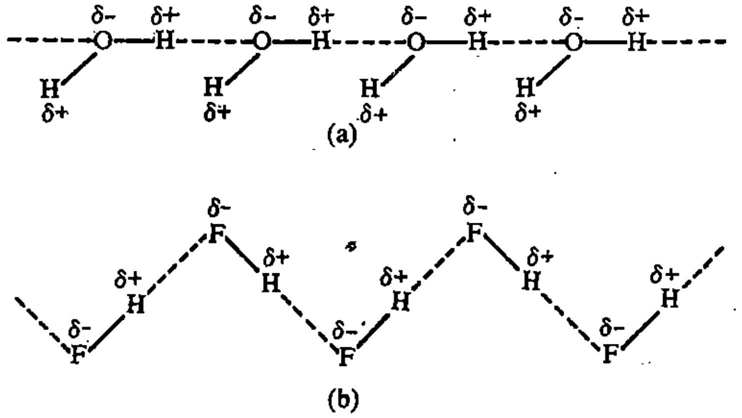

Fig. 3.12 : Hydrogen bonding : (a) in water (b) in hydrogen fluoride.

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.

i) Polar molecules have higher melting and boiling points than the nonpolar molecules of similar molecular size. It is so since in the polar molecules, in addition to London forces, 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.

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

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

ii) 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)

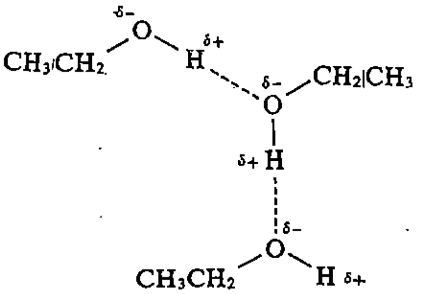

Fig. 3.13 : Hydrogen bonding in ethanol.

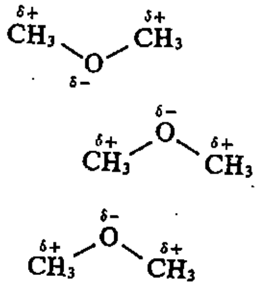

Fig. 3.14 : Dipole-dipole interaction in dimethyl ether.

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).

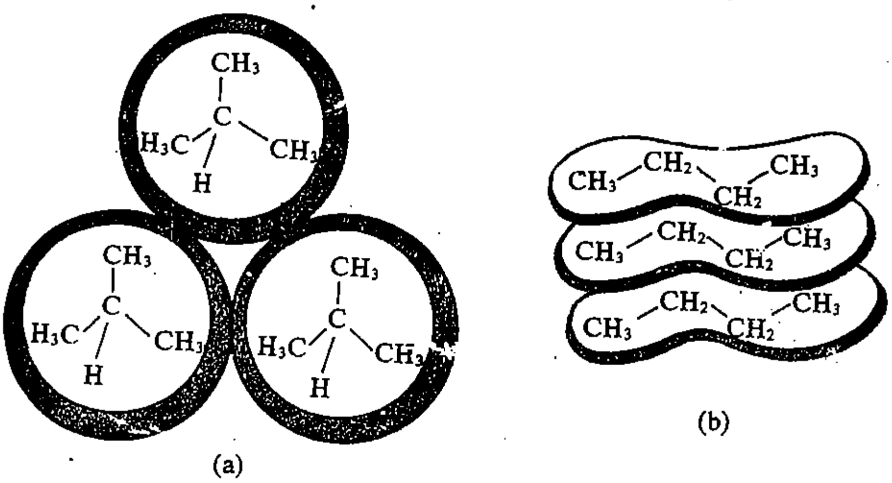

Fig. 3.15 : (a) Interactions among nearly spherical molecules of 2-methylpropane
(b) Interactions among distorted rod-like molecules of butane.

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 variatjon.

....

....

....

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

1. 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.
2. What is the pressure change if two moles of steam at 5.000×10^2 K occupying 0.0300 m^3 of volume is heated upto 1.000×10^3 K at constant volume. Assume that steam behaves as a van der Waals gas.
   $a = 0.5536$ Pa m^6 mol^{-2} and
   $b = 3.049 \times 10^{-5}$ m^3 mol^{-1}
3. Which of the substances listed in Table 3.1 can be liquefied at 298 K?
4. State the principle of corresponding states in as many ways as you can.
5. Why is the liquefaction of gases easier at low temperatures and high pressures?
6. Ethanol has higher boiling point than butane although the latter has higher relative molecular mass. Explain.
7. A vessel of 1.000×10^{-3} m^3 volume contains 0.0180 kg of argon at 300.0 K. Calculate its pressure using ideal gas and van der Waals equations. Use Table 3.1.
8. Calculate the reduced pressure and reduced temperature for oxygen gas at 273.2 K and 1.013×10^5 Pa. Use Table 3.1.

3.11 ANSWERS

Self Assessment Questions

1. 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 :

$p = 9.917 \times 10^4$ 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:
   $V_c = 1.174 \times 10^{-4}\ m^3\ mol^{-1}$
   $p_c = 3.400 \times 10^6$ Pa
   $T_c = 128.2$ K

2. Using van der Waals equation, the pressure values at 5.000×10^2 K and 1.000×10^3 K are 2.752×10^5 Pa and 5.530×10^5 Pa. The pressure change is
   $(5.530 - 2.752) \times 10^5$ Pa $= 2.778 \times 10^5$ 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 2.440×10^6 Pa, whereas as per ideal gas equation, it is 2.494×10^6 Pa.

8. $\theta = 1.765$; $\pi = 1.996 \times 10^{-2}$.

UNIT 4 LIQUIDS

Structure

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.

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.

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^0_{fus}). 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^0_{vap}). The values of ΔH^0_{fus}, ΔH^0_{vap} and boiling points (BP) are given in Table 4.1 for some substances. It is seen that ΔH^0_{vap} is larger than ΔH^0_{fus} 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.

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} are given in Secs. 4.5 and 4.6.

Table 4.1 : Molar Enthalpies of Fusion (ΔH°_{fus}) and Vaporization (ΔH°_{vap}) and Boiling Points (BP) of the Substances

Substance	ΔH^0_{fus}/kJ mol^{-1}	ΔH^0_{vap}/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
ilver	12.2	259	2430
luminium	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 he lines are diffuse (i.e., not quite sharp). The diffuse diffraction pattern makes it clear that he order in the arrangement of particles is only partial but not total. Experimental data ndicate 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 ame. A model for the structure of liquids is shown in Fig. 4.1.

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

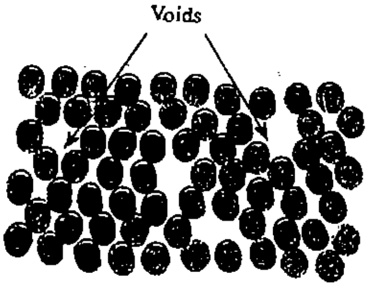

Fig. 4.1 : A model for the structure of liquids

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.

- These voids [illegible] the liquid to [illegible]
- 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.

....

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....

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

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.

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.

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).

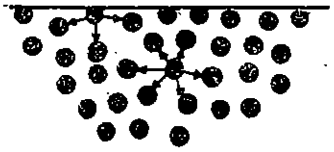


Fig. 4.2 : Molecules in the bulk and on the surface of liquid being attracted by neighbours.

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.

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.

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

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.

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.

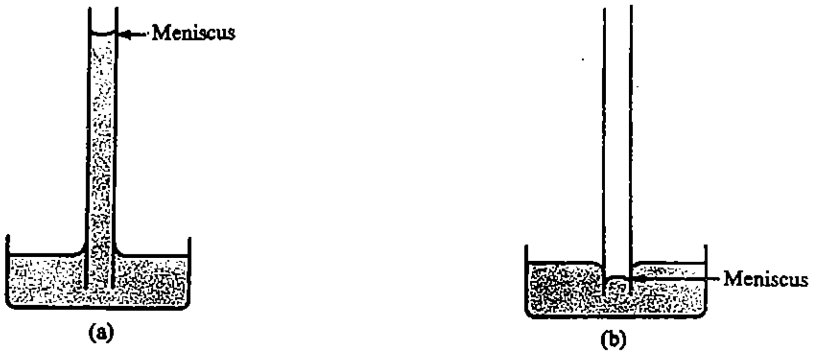
The adhesive forces enable water to "wet" the glass. The adhesive forces acting upward pull up a water column inside a capillary tube when the latter is in contact with water. The height of the water column inside the capillary tube is such that the adhesive forces acting upwards balance the cohesive 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.

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.

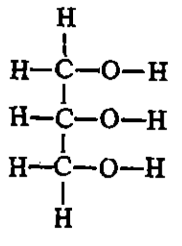


(a) (b)

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.



Glycerol

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}

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.

Viscosity measurements help in evaluating relative molecular masses of polymers.

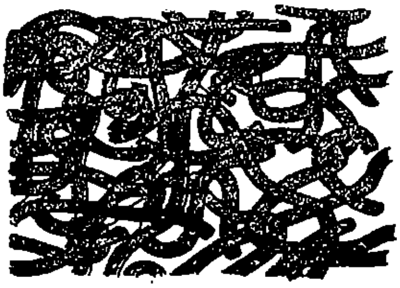


Fig. 4.4 : The molecules in the heavy hydrocarbon oil entangled together.

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

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

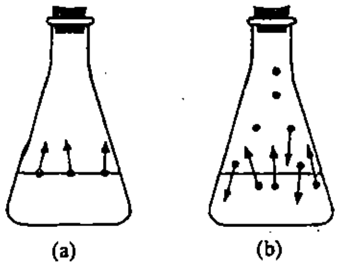

Fig. 4.5 : (a) Initially molecules are transferred from the liquid to the vapour phase; (b) at equilibrium the rate of vaporization is equal to the rate of condensation.

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).

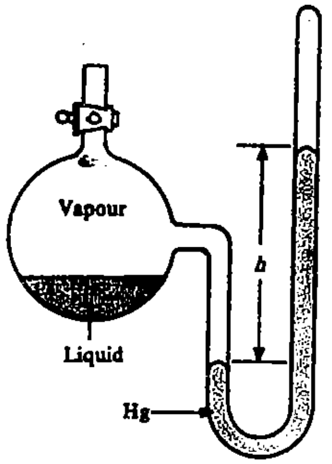

Fig. 4.6 : Vapour pressure measurement.

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 mm of Hg = 1.013×10^5 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.

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.

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.

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 untill 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.

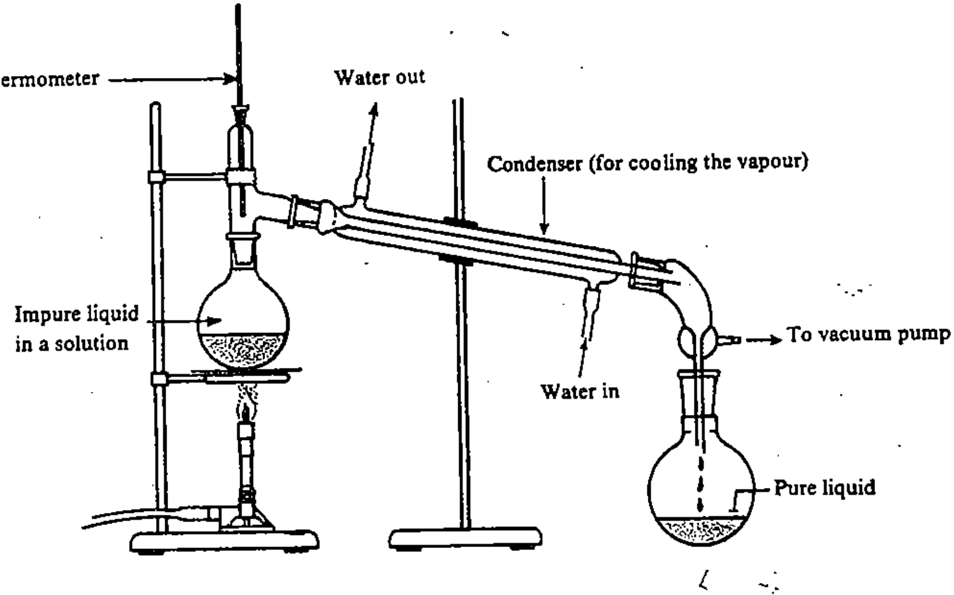

Fig. 4.7 : Reduced pressure distillation.

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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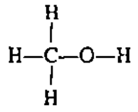

Methanol

SAQ 5

Arrange the following compounds in the increasing order of boiling points:
Ethanol, glycerol and ethylene glycol.

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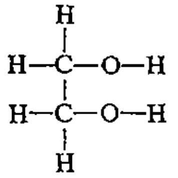

Ethylene glycol

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 J mol^{-1} K^{-}.

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

Trouton's rule holds good for liquids in which hydrogen bonding is **absent**. The ratio, $\Delta H^0_{vap}/BP$ 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 $\Delta H^0_{vap}/BP$ is more than 85 J mol^{-1} K^{-1} for hydrogen bonded liquids. For example, the values of $\Delta H^0_{vap}/BP$ for water and ethyl alcohol are 109 and 112 J mol^{-1} 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.

$$\Delta H^0_{vap} = 353\ \text{K} \times 85\ \text{J mol}^{-1}\ \text{K}^{-1}$$
$$= 30\ \text{kJ mol}^{-1}$$

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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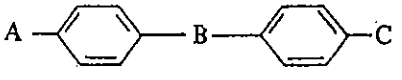
4.7 LIQUID CRYSTALS

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.

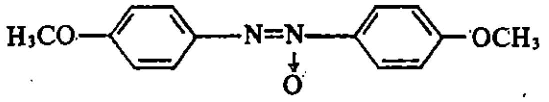
Some organic compounds often have two melting points. On heating such a crystal, it melts into a turbid liquid at a definite temperature; and on heating further, the turbid liquid becomes clear at another temperature. The turbid liquid is called **'liquid crystal'**.

A number of compounds of the following type exist as liquid crystals :



; A, B and C are substituents or carbon chains.

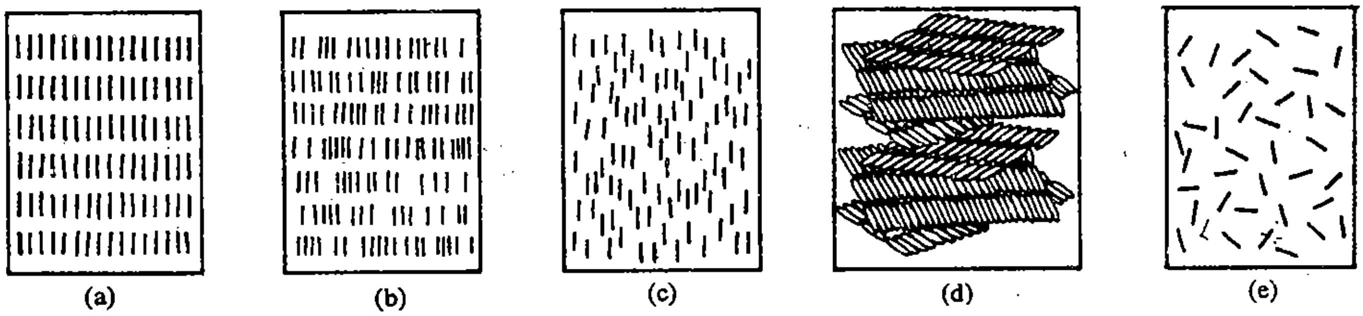
An example is p-azoxyanisole.



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.



(a) Arrangement in equidistant planes; regularity within planes—a single crystal.

(b) Same orientation, arrangement in equidistant planes; no regularity within planes-smectic liquid crystal

(c) Same orientation; absence of planar arrangement-nematic liquid crystal

(d) Multiple layers with successive twist; same orientation within a layer-cholesteric liquid crystal

(e) Neither orientation nor planar arrangement—liquid (giving rise to isotropy)

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

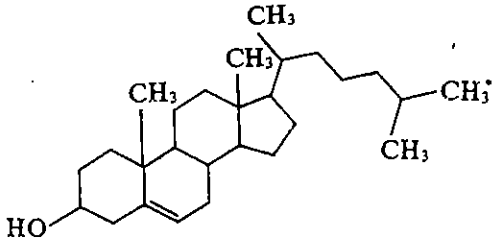
The optical (opaque or transparent) nature of a nematic liquid crystal depends on the way the molecules are oriented.

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.



Cholesterol

We see that a difference in the orientation of molecules in a nematic or a cholesteric liquid crystal causes a difference in its optical properties, thereby pointing to its anisotropic nature. 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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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 1.251×10^{-3} kg dm^{-3}, respectively.

(2) In a polythene tube, water meniscus is convex. Explain.

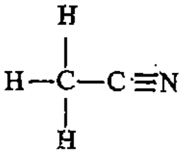
(3) Explain the reason for the anisotropy in the optical properties of nematic and cholesteric liquid crystals.

(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) $\Delta H^0_{vap} = 29.75$ 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^0_{vap} 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 ΔH^0_{vap}/BP = 97.1 J mol^{-1} K^{-1} for ammonia; it doesn't obey Trouton's rule due to hydrogen bonding.

UNIT 5 SOLID STATE

Structure

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 nonprimitve 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.

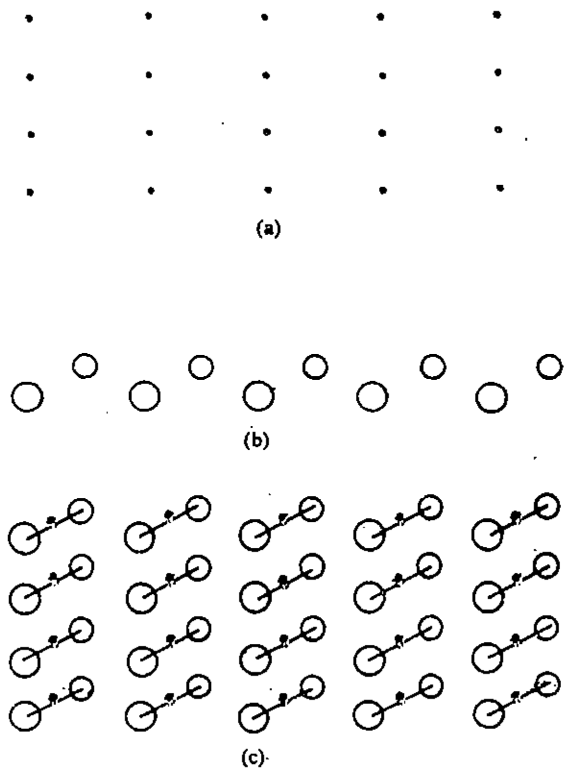

(a)
(b)
(c)

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.

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

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.

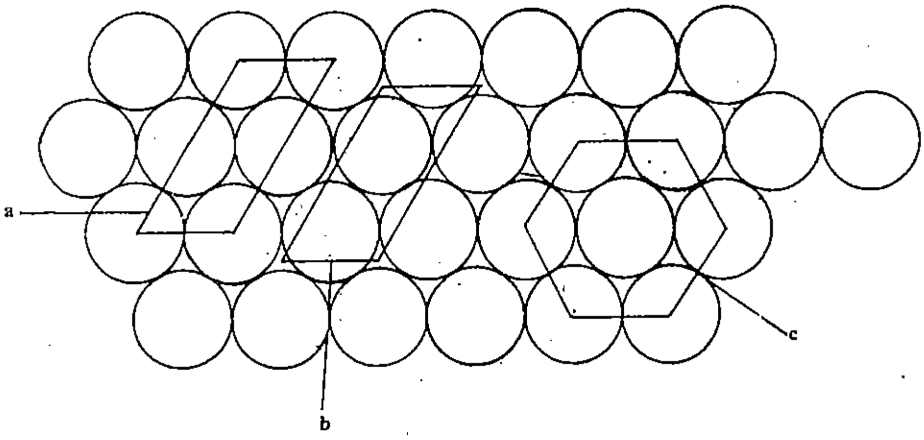


Fig. 5.2 : Choice of unit cell.

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—

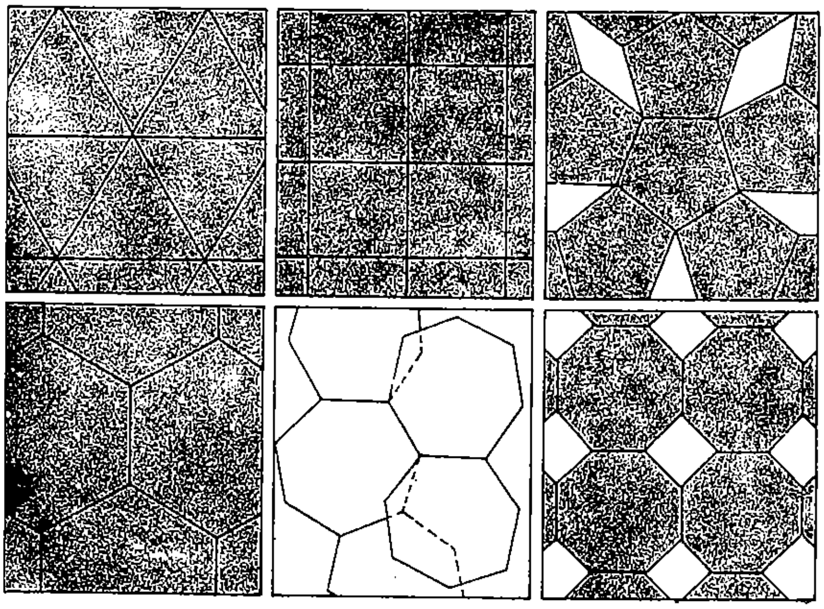


Fig. 5.3: Of all the regular polygons, only triangles, squares and hexagons can fill a floor space without gap. Filled-in space is denoted by grey area.

triangular, square, pentagonal, hexagonal, heptagonal or octagonal? Again 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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....

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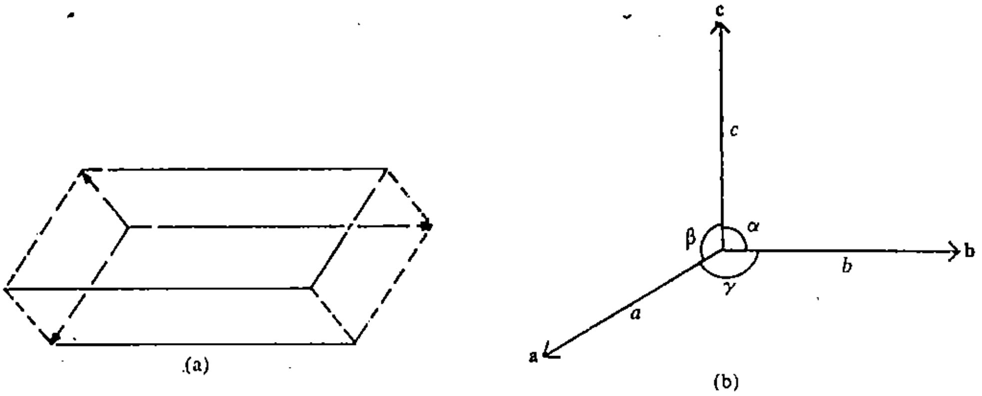
5.3 BRAVAIS LATTICES AND CRYSTAL SYSTEMS

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, **a**, **b** and **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 **a** and **b** axes, **b** and **c** axes and **c** and **a** axes are γ, α and β, respectively. The quantities *a*, *b* and *c* are called lattice parameters or unit cell parameters.



(a) (b)

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	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, CsCl
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	TiO_2 (rutile)
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	$CdSO_4$, $HgBr_2$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$CaCO_3$ (calcite)
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$; $\gamma = 120°$	SiO_2
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$; $\beta \neq 90°$	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!

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

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.

In ΔABC, $\angle ABC = 90°$

Length of face diagonal, AC

$= \sqrt{AB^2 + BC^2}$

$= a\sqrt{2}$

In ΔACG, $\angle ACG = 90°$.

(See Fig. 5.5c)

Length of the body diagonal, AG

$= \sqrt{AC^2 + CG^2}$

$= \sqrt{2a^2 + a^2}$

$= a\sqrt{3}$

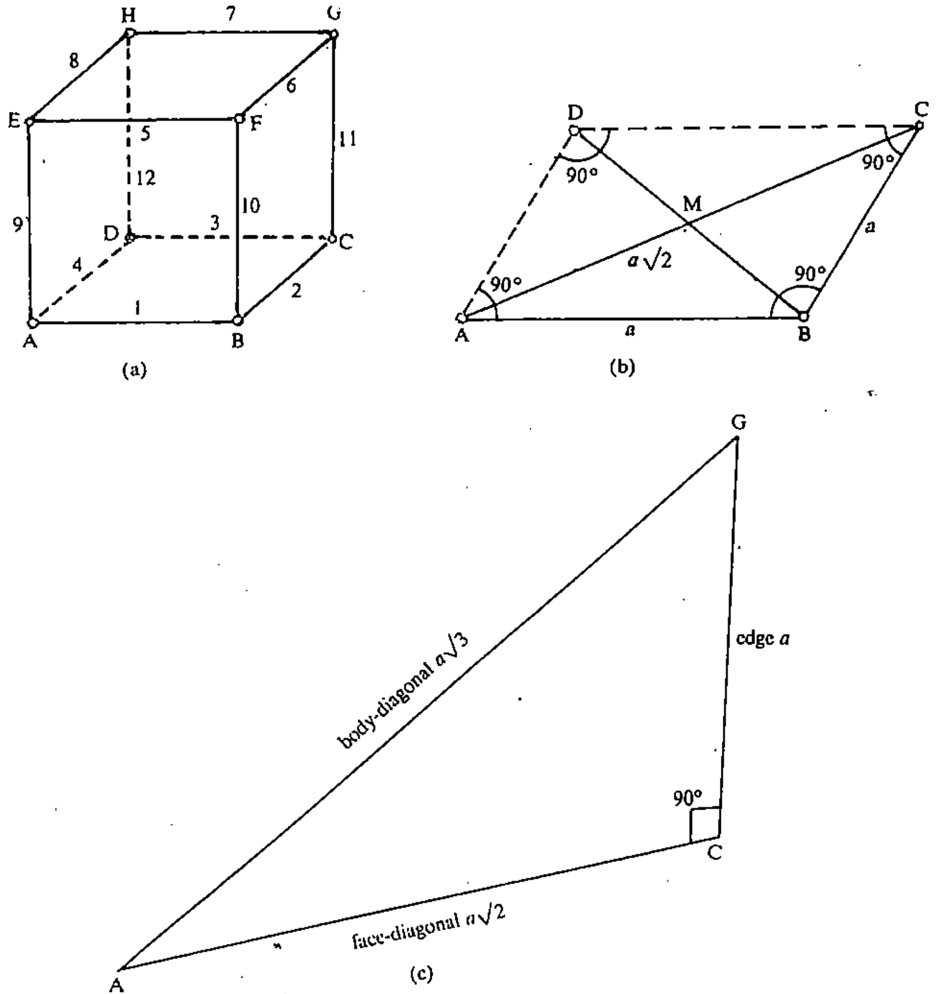


Fig. 5.5 : a) Eight corners in a cube indicated by letters A to H—each corner is marked by red dot; twelve edges indicated by number 1 to 12; b) bottom face ABCD of the cube shown; AC and BD are the face diagonals and M is face-centre; c) The right-angled ΔACG.

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.

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

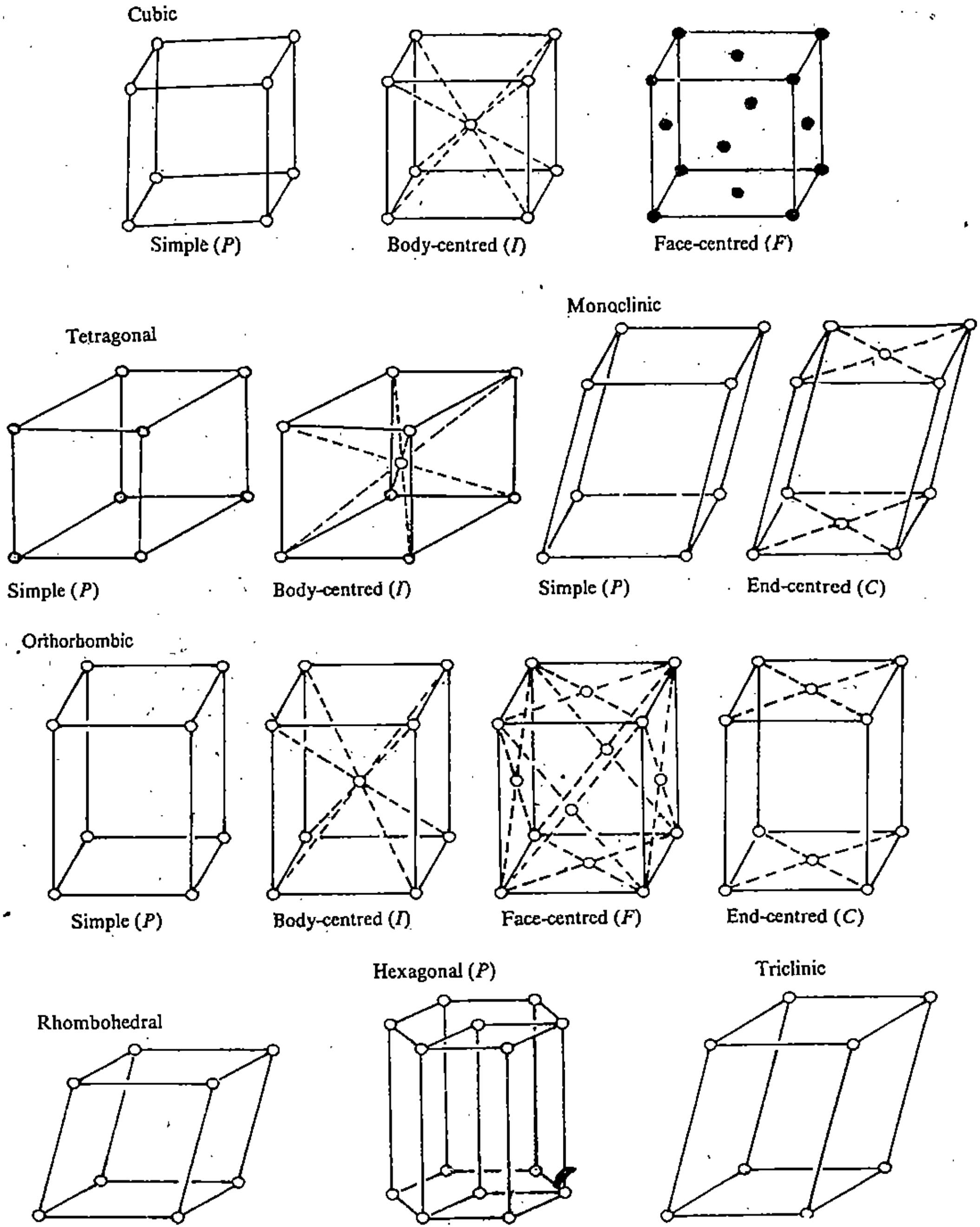


Fig. 5.6 : Fourteen Bravais Lattices.

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.

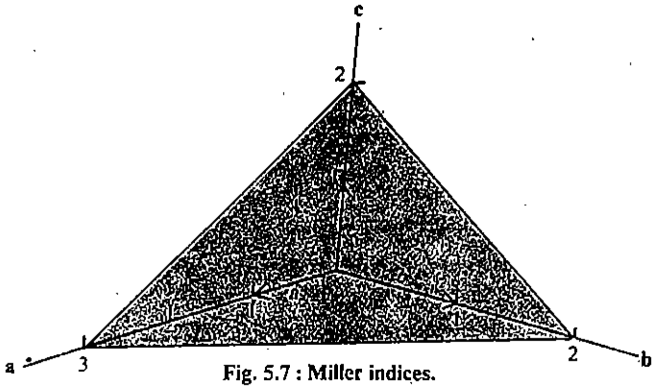


Fig. 5.7 : Miller indices.

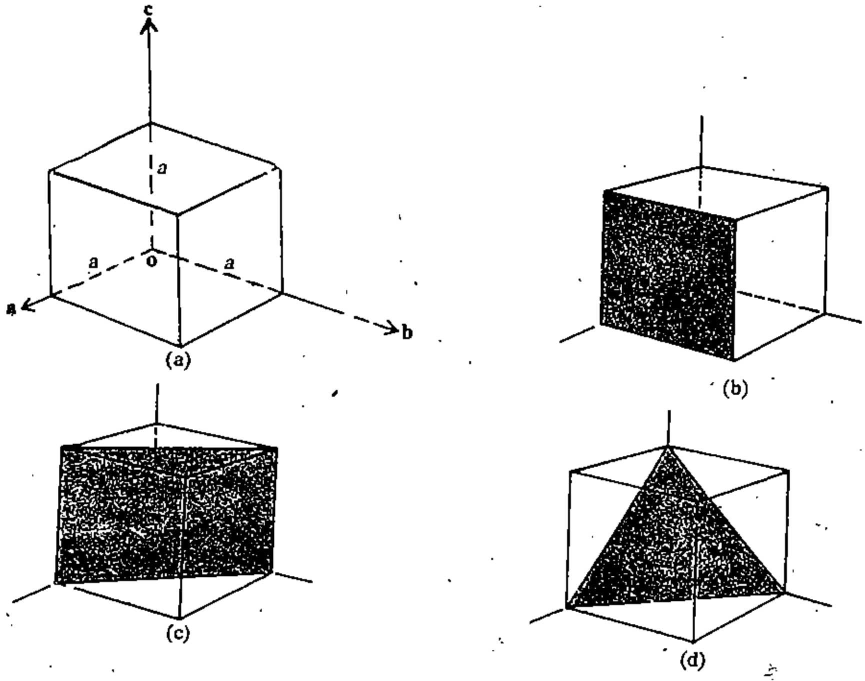
ii) Divide the intercepts by the respective cell-edge lengths (a, b and c). For the crystal plane in Fig. 5.7, this step gives $\frac{3a}{a}, \frac{2b}{b}, \frac{2c}{c}$, i.e., 3, 2, 2 as the answer.

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 parantheses 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 he 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.



(a)

(b)

(c)

(d)

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

We can calculate the distance between the adjacent planes 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,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad \text{... (5.1)}$$

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,

$$\frac{1}{d^2_{hkl}} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2 \qquad \text{... (5.2)}$$

Using Eq. 5.2, work out the following SAQ.

SAQ 3

An orthorhombic crystal has the following parameters:

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

What is the distance between (123) planes?

....

....

....

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

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

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.

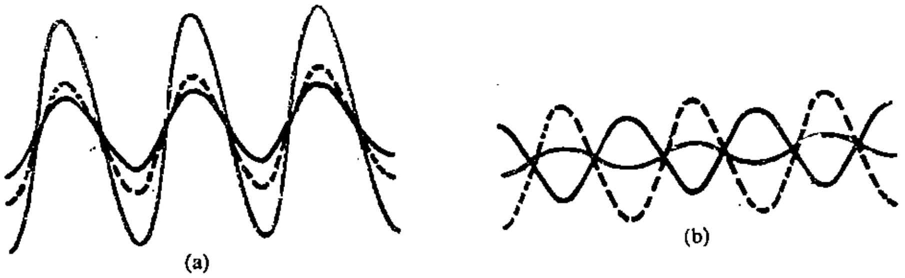


Fig. 5.9 : Two waves (shown by dotted and solid lines) giving rise to a resultant (shown by red colour) : a) constructive interference (in-phase wave—greater amplitude); b) destructive interference (out-of-phase wave—smaller amplitude).

The 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.

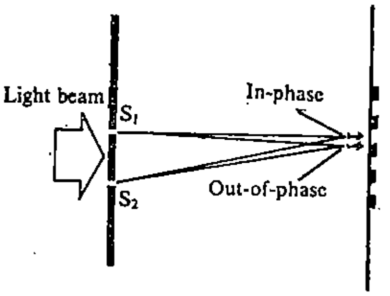


Fig. 5.10 : In-phase and out-of-phase waves.

5.5.2 Bragg Law and Bragg Equation

If the path difference between the two rays is an integral multiple ($n = 1, 2, 3, \ldots$) 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,

$$\text{path difference} = n\,\lambda \qquad \ldots (5.3)$$

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.

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.

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.

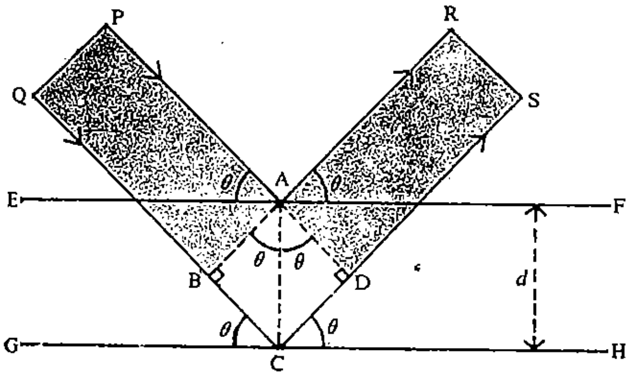


Fig. 5.11 : The incident and the reflected beams and the two parallel lattice planes.

$$\begin{aligned}\text{Path difference} &= (QC + CS) - (PA + AR)\\ &= (QB + BC) + (CD + DS) - (PA + AR)\\ &= BC + CD \qquad \text{... (5.4)}\end{aligned}$$

[$\because$ QB = PA and DS = AR, being opposite sides of the rectangles shown by the shaded portions in Fig. 5.11].

Since $AC \perp GH$, $\angle ACG = 90° = \angle ACB + \angle BCG = \angle ACB + \theta$

[$\because$ $\angle QCG$ and $\angle BCG$ are same as θ]

$\angle ACB = 90° - \theta$ ... (5.5)

In the right-angled ΔABC, $\angle BAC + \angle ACB + \angle CBA = 180°$

Using Eq. 5.5, $\angle BAC + (90° - \theta) + 90° = 180°$

$\angle BAC = 180° - (180° - \theta) = \theta$

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

Since, $AC = d$, $BC = d \sin\theta$ ... (5.6)

Similarly, we can prove that $CD = d \sin\theta$ ... (5.7)

Using Eqs. 5.4, 5.6 and 5.7,

path difference $= 2d \sin\theta$ ... (5.8)

Again substituting in Eq. 5.3, we get,

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

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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

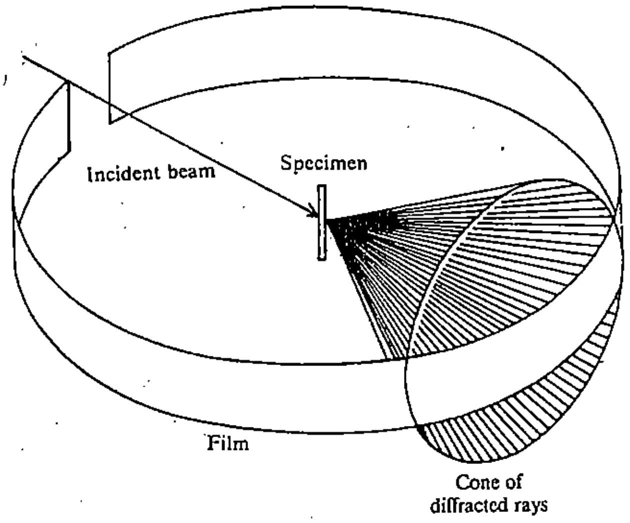

Fig. 5.12 : Powder method.

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.

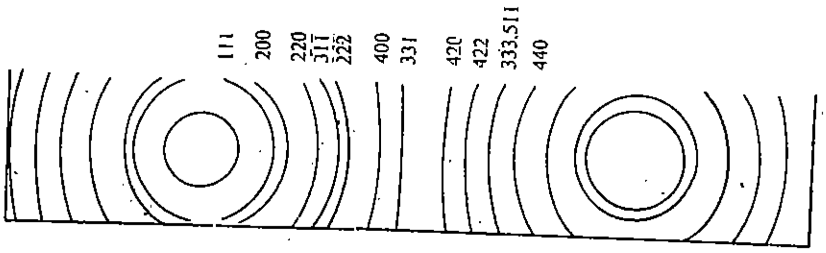

Fig. 5.13 : X-ray powder pattern for sodium chloride.

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.

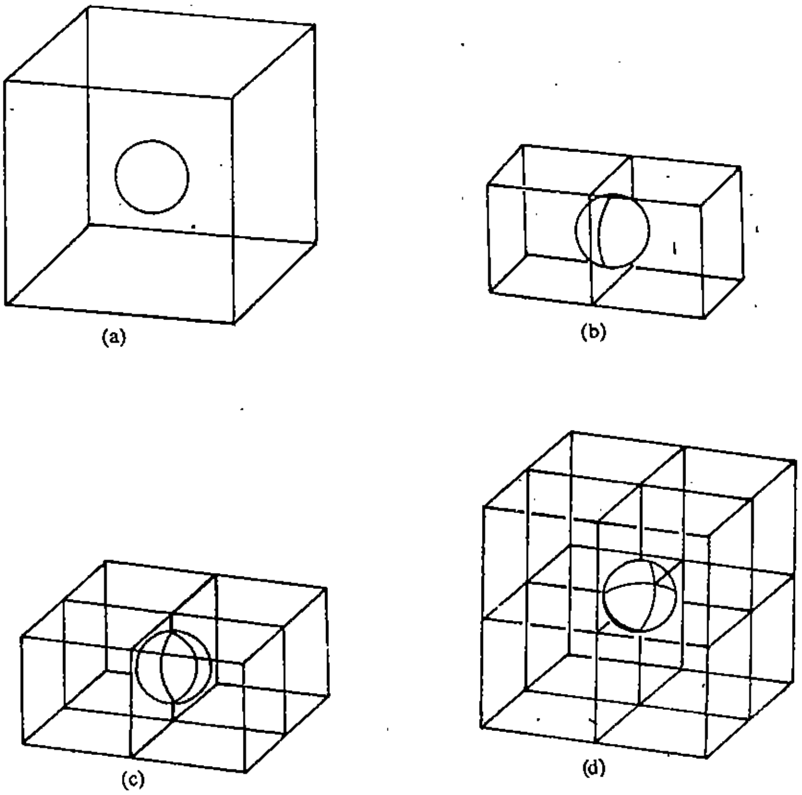

Fig. 5.14 : a) An atom at the body-centre of a unit cell; b) An atom at the face-centre shared by two unit cells; c) An atom at the edge-centre shared by four unit cells; d) An atom in the corner shared by eight unit cells.

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

It is known that density $= \frac{\text{Mass}}{\text{Volume}}$. ... (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 Å = 10^{-10} 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 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 Avogardo constant (N_A, which is a equal to 6.022×10^{23} mol^{-1}).

Mass of on atom $= \frac{w \text{ kg mol}^{-1}}{N_A \text{ mol}^{-1}} = \frac{w}{N_A}$ kg ... (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,

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

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 :

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

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

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

where n is the number of net atoms per unit cell.
Rearranging Eq. 5.16, we get,

$$n = \frac{\rho N_A a^3}{w} \qquad \text{... (5.17)}$$

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

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

$$= \frac{8.90 \times 10^3\ \text{kg m}^{-3} \times 6.022 \times 10^{23}\ \text{mol}^{-1} \times (3.524 \times 10^{-10}\ \text{m})^3}{0.0587\ \text{kg mol}^{-1}}$$

$= 4$ (rounded to the nearest whole number).

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 arrangment 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.

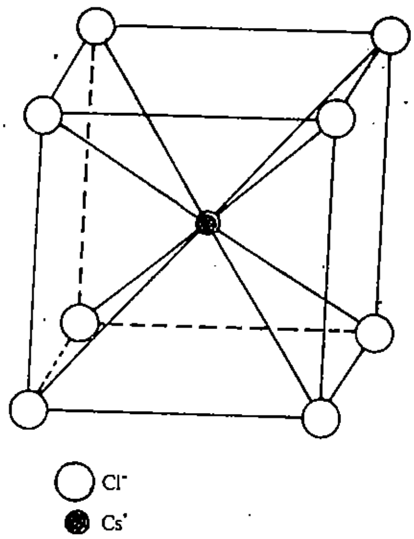

Fig. 5.15 : CsCl structure

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).

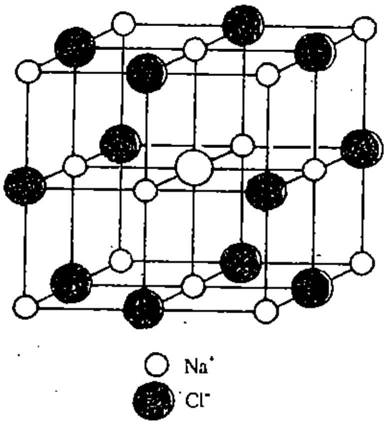

Fig. 5.16 : Structure of sodium chloride.

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.

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 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.

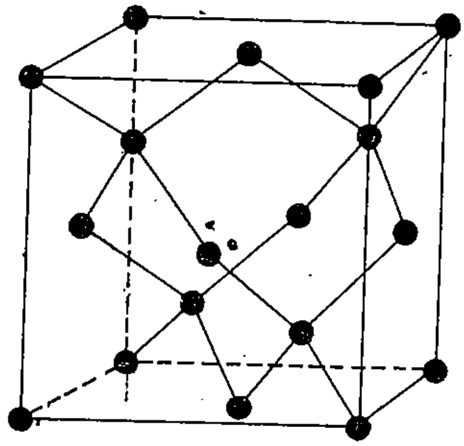

Fig. 5.17 : Structure of diamond.

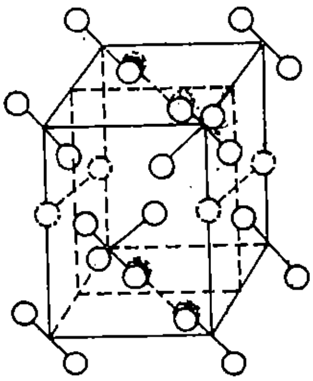

Fig. 5. 18 : Structure of iodine crystal—the basis is I_2 molecule.

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 2.826×10^3 kg m^{-3}. Its cell edge-length is 6.54×10^{-10} 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.

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.

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

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.

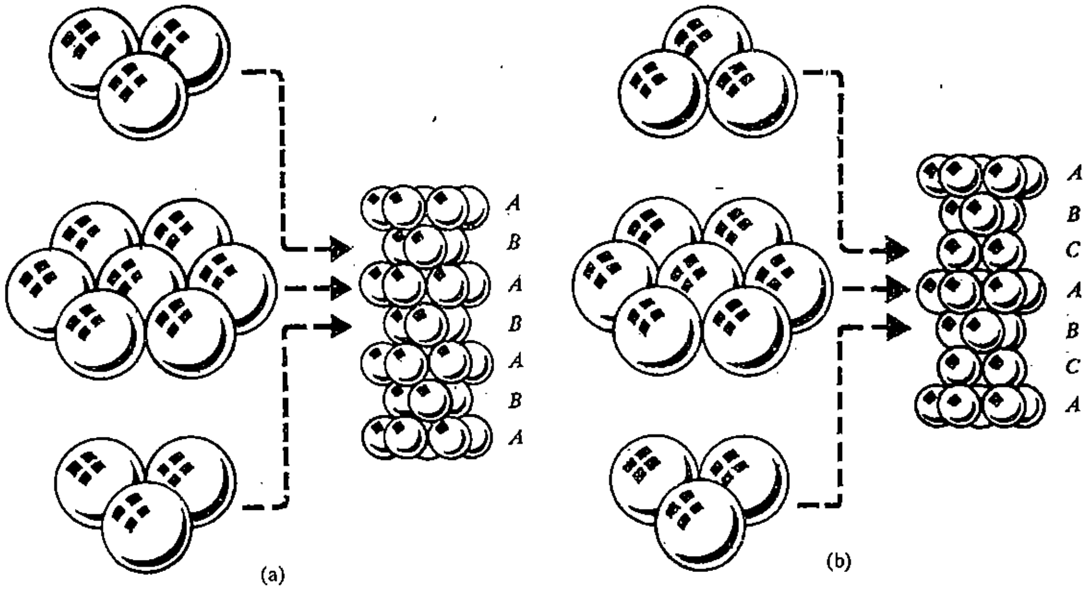

Fig. 5.19 : a) *hcp* arrangement—the atoms in the third layer are straignt above those in the first layer-called ABAB ..... arrangement; b) *ccp* arrangement—the atoms in the third layer arranged differently from those in the first-called ABCABC ..... arrangement.

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.

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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., radius $= \frac{a}{2}$).

2) In the following cases, mark '√' for correct statement and 'X' 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 2.163×10^{3} 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 $= 1.936 \times 10^{4}$ 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 = Molar mass of KBr = 0.119 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 $= a^3$
$$\therefore \text{ Fraction of the volume filled} = \frac{\text{Volume occupied}}{\text{unit cell volume}}$$
$$= \frac{\pi a^3}{6 \times a^3} = 0.52$$

2) (i) × (ii) √ (iii) √ (iv) ×.

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

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Uttar Pradesh Rajarshi Tandon
Open University

UGCHE-04
Physical Chemistry

Block

2

CHEMICAL THERMODYNAMICS

UG CHE-04(11A)

CHEMICAL THERMODYNAMICS

In Block 1, we discussed the states of matter. In this block, we shall study the laws of thermodynamics. This material gives us the necessary foundation to understand the different aspects of equilibrium which we shall discuss in detail in Blocks 3 and 4.

Thermodynamics deals with the familiar concepts of heat and temperature; it is concerned with the interconversion of various forms of energy (such as heat, mechanical energy, electrical energy and chemical energy) into one another. All the laws of thermodynamics are based on experience. Applications of thermodynamics are numerous, and the subject embraces such diverse areas as chemistry, physics, biology, engineering and earth sciences. It is concerned with the description of a system under equilibrium and how the properties of a system change when it moves from one equilibrium state to another. Thermodynamics can predict the feasibility of a process and the extent to which a process will proceed.

With all its power, thermodynamics has a number of limitations. Thus, it cannot fully describe the behaviour of a system, not in equilibrium. It does not answer the question how a system undergoes a change and what path does it follow. It cannot say how long will it take to complete a process. Thermodynamics is not concerned with time. It deals with matter in bulk and does not bother about its constituents or structure.

The independence of thermodynamics from structure of matter is both its strength and weakness. The thermodynamic description has remained unchanged although our ideas regarding structure of matter have been revolutionised. This at the same time leads to incomplete description of the system. A new discipline called statistical thermodynamics has evolved which calculates thermodynamic properties from the known structure of molecules and interaction between them. Those who want to study thermodynamics in depth are advised to take the elective course, Thermodynamics and Statistical Mechanics.

This block consists of four units. In Unit 6, we shall discuss the first law of hermodynamics; also we shall introduce two thermodynamic functions, internal nergy and enthalpy. In Unit 7, the relationship between thermal and chemical energy vill be discussed. The applications of thermochemical calculations will be illustrated. n Unit 8, the second law of thermodynamics will be explained. Using Carnot cycle, nother thermodynamic function, entropy, will be introduced. The change in entropy vill be used as a pointer to differentiate between a reversible and an irreversible process r cycle. In Unit 9, we shall discuss the importance of two more thermodynamic unctions, Helmholtz free energy function and Gibbs free energy function, in deciding he spontaneity of a process. The third law of thermodynamics will be explained with articular reference to entropy calculation.

bjectives

fter studying this block, you should be able to :

- state and explain the first law of thermodynamics,
- define internal energy and enthalpy,
- relate heat capacities to internal energy and enthalpy,
- state Hess's law and use it in thermochemical calculations,
- explain the temperature dependence of internal energy change and enthalpy change,
- define Joule–Thomson coefficient and inversion temperature,
- state the second law of thermodynamics,
- define entropy, Helmholtz free energy and Gibbs free energy and calculate the changes in these functions for typical processes,
- explain the criteria for the feasibility of a given process in terms of changes in thermodynamic quantities,
- define chemical potential, and
- state and explain the third law of thermodynamics.

UNIT 6 THE FIRST LAW OF THERMODYNAMICS

Structure

6.1 INTRODUCTION

In this unit, we shall introduce you to some of the terms used in thermodynamics. The definitions of work, heat and heat capacity will be stated. The first law of thermodynamics will be explained with particular reference to isothermal and adiabatic processes. The calculation of work, internal energy change and heat absorbed or evolved in reversible and irreversible processes will be outlined. The significance of enthalpy and enthalpy change of a system will be stated. Towards the end of this unit, you will study the importance of Joule–Thomson effect. In the next unit, we shall study the applications of the first law of thermodynamics in making thermochemical calculations.

Objectives

After studying this unit, you should be able to

- explain the terms—system, surroundings and thermodynamic variables,
- state the zeroth law of thermodynamics,
- differentiate between extensive and intensive variables,
- define isothermal, adiabatic and cyclic processes,
- explain the terms—work, heat and heat capacity,
- state the first law of thermodynamics,
- explain the term, internal energy of a system,
- calculate the work done on an ideal gas in isothermal and adiabatic processes,
- state the significance of enthalpy and enthalpy change of a system,
- derive the relationship between $\bar{C}_p$ and $\bar{C}_V$ of an ideal gas, and
- explain Joule–Thomson effect.

6.2 THERMODYNAMIC TERMINOLOGY

In this section, a number of commonly used terms in thermodynamics are defined and explained. These terms should be understood clearly before you proceed further.

System

Any part of the universe which is under study is called a system. It can be as simple as a gas contained in a closed vessel or as complicated as a rocket shooting towards moon. A system may be homogeneous or heterogeneous depending on its contents and conditions. A system is homogeneous if physical properties and chemical composition are identical throughout the system. Such a system is also called a single phase system.

A heterogeneous system consists of two or more than two phases separated by mechanical boundaries.

Surroundings

The rest of the universe around the system is considered its surroundings. A system and its surroundings are always separated by boundaries across which matter and energy may be exchanged. The boundaries can be real (fixed or moveable) or imaginary.

Based on the exchange of matter and energy between the system and the surroundings, a system can be classified into the following three types:

- Isolated system
- Closed system
- Open system

Let us explain these terms.

A thin soft layer of polymer or natural material through which a specific substance can flow is called a membrane permeable to that specific substance.

Isolated system is one which exchanges neither energy nor matter with its surroundings. There is no perfectly isolated system; but, a system which is thermally well insulated (i.e., does not allow heat flow) and is sealed to inflow or outflow of matter can be considered as an isolated system. A sealed thermos flask having some matter thus approximates to an isolated system.

Closed system allows exchange of energy (heat or work) with the surroundings but, matter is not allowed to enter or leave it. A properly sealed system (to prevent the passage of matter across its boundary) can be considered as a closed system.

Open system allows exchange of both matter and energy with its surroundings. This is the most common type of system encountered in our daily life. All living things are examples of open system since these are capable of freely exchanging energy and matter with their surroundings. Reaction vessels with permeable membranes are examples of open system.

Let us now explain the terms, state variables and state of the system.

State Variables

A thermodynamic system has to be macroscopic (i.e. of sufficiently large size); this facilitates measurement of its properties such as pressure, volume, temperature, composition and density. Such properties are therefore called macroscopic or bulk properties. These are also called state or thermodynamic variables. These do not depend on the past history of the system. A state variable which depends on other variables is called a dependent variable; others, on which it is dependent, are called independent variables.

For example, if you write ideal gas equation as

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

then, V is the dependent variable, whereas n, T and p are independent variables. We know that R is the gas constant. On the other hand, if you write this equation as,

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

then p is the dependent variable, whereas n, T and V are independent variables. The choice of dependent and independent variables is a matter of convenience.

State of a System

The state of a system is defined when the state variables have definite values. It is not necessary to specify all the state variables since these are interdependent. For example, if the system is an ideal gas, then its pressure, volume, temperature, and the amount of the gas (number of moles) are related by the gas equation. Thus, if we specify three of these, the fourth variable is automatically fixed. Similarly many of its other properties like density, heat capacity etc. are also fixed although through more complicated relations.

SAQ 1

Identify the type of system in each of the following cases:

i) A beaker covered with a lid
ii) A closed thermos flask
iii) A beaker without lid.

6.3 THE ZEROTH LAW OF THERMODYNAMICS

The zeroth law of thermodynamics is based on the concept of thermal equilibrium. It helps us in defining temperature. If two closed systems are brought together so that these are in thermal contact, changes take place in the properties of both the systems, but, eventually a state is reached when there is no further change in any of the systems. This is the state of thermal equilibrium. Both the systems are at the same temperature. In order to find whether two systems are at the same temperature, the two can be brought into thermal contact; then the changes in the properties of either of these are to be observed. If no change occurs, they are at the same temperature.

The zeroth law of thermodynamics states that if a system A is in thermal equilibrium with system C and, system B is also in thermal equilibrium with C, then A and B are also in thermal equilibrium with each other. This is an experimental fact. This may be illustrated by assuming that systems A and B are two vessels containing different liquids, and C is an ordinary mercury thermometer. If A is in thermal equilibrium with C, then mercury level in the thermometer will show a constant reading. This indicates the temperature of system A as well as that of C. Now if A is also in thermal equilibrium with B, then the height of mercury level in the thermometer (in contact with B) is the same as before; B also has the same temperature as A. There is thermal equilibrium in both A and B or these are at the same temperature. Here we have only explained the concept of temperature; the temperature scale will be discussed in Unit 8.

The zeroth law of thermodynamics can be stated as follows:

Two objects, that are in thermal equilibrium with a third object, are in thermal equilibrium with each other.

6.4 EXTENSIVE AND INTENSIVE VARIABLES

We have defined homogeneous and heterogeneous systems in Sec.6.2. Let us now discuss the difference between the two with respect to the value of some variables. In this connection, we must first define extensive and intensive variables.

An extensive property of a homogeneous system is one which is dependent on the amount of a phase in the system. For a heterogeneous system made up of several phases, the total value of an extensive property is equal to the sum of the contributions from various phases. Mass, volume and energy are examples of extensive properties. Thus, if a system, at equilibrium consists of 0.100 kg of ice and 0.100 kg of liquid water at 273.15 K, the total volume of the system is the sum of the two volumes, each of which is directly proportional to its mass.

$$\text{Volume of } 0.100\text{ kg of ice} = \frac{\text{Mass of ice}}{\text{Density of ice}} = \frac{0.100\text{ kg}}{917\text{ kg m}^{-3}}$$

$$= 1.09 \times 10^{-4}\text{m}^3$$

$$\text{Similarly, the volume } 0.100\text{ kg of water} = \frac{\text{Mass of water}}{\text{Density of water}}$$

$$= \frac{0.100\text{ kg}}{1.00 \times 10^3\text{ kg m}^{-3}} = 1.00 \times 10^{-4}\text{ m}^3$$

$$\text{Total volume} = (1.09 + 1.00) \times 10^{-4}\text{ m}^3$$

$$= 2.09 \times 10^{-4}\text{ m}^3$$

An intensive property of a phase is independent of the amount of the phase. Thus refractive index, density and pressure are intensive properties. However, if a system consists of several phases, then some of the intensive properties may be different. For example, density is an intensive property but its value is different for ice and liquid water in equilibrium at 273.15 K. For thermal equilibrium, the intensive property, temperature, has to be same throughout the system. Otherwise heat will flow from one point of the system to another. Similarly, for mechanical equilibrium, the intensive property, pressure, has to be the same throughout the system. An extensive property when divided by mass or molar mass of the system becomes an intensive property.

SAQ 2

Identify the extensive or intensive variables from among those indicated below:

i) Energy required to cook your meals.

ii) Volume per unit mass of milk.

iii) Your body temperature.

6.5 TYPES OF PROCESSES

When the state of a system changes, it is said to have undergone a process. Thus a process means change in at least one of the state variables of the system. The process may be accompanied by an exchange of matter and energy between the system and the surroundings. There are certain processes in which a particular state variable (thermodynamic property of the system) remains unchanged. Such processes are of the following types:

In an **isothermal process,** the temperature of the system remains constant. When a system undergoes an isothermal process, it is in thermal contact with a large constant temperature bath, known as thermostat. The system maintains its temperature by exchange of heat with the thermostat.

In an **adiabatic process,** no heat is allowed to enter or leave the system. Systems in which such processes occur are thermally insulated from the surroundings. An adiabatic process may involve increase or decrease in the temperature of the system. We shall discuss these two processes in detail in Secs. 6.8 and 6.12.

An **isobaric process** is one in which the pressure of the system remains unchanged. A reaction taking place in an open beaker is always at atmospheric pressure and hence, the process is isobaric.

In an **isochoric process,** the volume of the system remains constant. Thus, a chemical reaction in a sealed flask of constant volume is an isochoric process.

A process is **cyclic** if the system (after any number of intermediate changes) returns to its original state. The initial and final values of each thermodynamic variable is identical after the completion of a cyclic process. Based on the value of the driving force applied, we can classify the processes into two types, namely, reversible and irreversible.

A reversible process is one in which at any time, the driving force exceeds the opposing force only very slightly. Hence, the direction of the process can be reversed by merely a small change in a variable like temperature and pressure. The idea of a reversible process will become clear by considering the following example.

A tiny change in a property is called an infinitesimal change.

Consider a gas at pressure p in a cylinder fitted with an air–tight piston. If the external pressure on the gas is equal to the pressure of the gas, then there is neither expansion nor compression and the piston remains at its position. However, on increasing the external pressure (p_{ext}) infinitesimally, the gas can be compressed. On the other hand by slightly decreasing the external pressure, the gas may be expanded. Thus

Note that "if" is common to all the three statements.

$$\text{If} \begin{cases} p_{\text{ext}} = p & \text{the system is static and piston does not move} \\ p_{\text{ext}} = p + \mathrm{d}p & \text{the gas is compressed and the piston moves downwards infinitesimally slowly} \\ p_{\text{ext}} = p - \mathrm{d}p & \text{the gas expands and the piston moves outwards infinitesimally slowly} \end{cases}$$

Hence, you can see that in a reversible process, the direction of a process is changed by changing the magnitude of the driving force by a small amount. In Block IV, you will study how reversible condition is used in constructing electrochemical cells.

Any process which is not reversible is termed as irreversible. All natural processes are irreversible. The flow of heat from a high temperature body to a low temperature body is a natural process and hence, irreversible. So is the expansion of a gas against vacuum, known as free expansion. Irreversible processes are also called spontaneous processes. We will be studying reversible and irreversible processes in detail in Secs. 6.8 and 6.12.

6.6 WORK, HEAT AND HEAT CAPACITY

Work, heat and energy have the same units, namely joule (J). Energy is a thermodynamic property of a system, whereas work and heat are not. The latter two are meaningful only when a process takes place. Let us first define heat.

Heat is a form of energy. Heat is not the property of a system but is exchanged between a system and the surroundings during a process, when there is a temperature difference between the two. Let us now explain the term, work, and its different kinds.

Work *(W)* is defined as the product of the force applied *(F)* and the distance *(X)* moved along the direction of the force.

$$W = F.X \qquad \dots (6.1)$$

Forces have different physical origin, and work can be done in a variety of ways.

- Gravitational Work: When a body of mass m is moved through a height h against gravity, then force is equal to mg and the gravitational work done is mgh.
- Electrical work: If an electric potential E is applied across a resistance R so that current i flows through it, then work done per second is Ei and in t seconds it is equal to Eit.
- Pressure–volume work: This is a type of mechanical work performed when a system changes its volume against an opposing pressure. This also is known as work of expansion or compression. We will study this in detail in later sections.

The energy gained or lost during heat exchange between the system and the surroundings can be stated in terms of heat capacity values. Let us now define the term, heat capacity.

Molar heat capacity = Specific heat × molar mass

Heat capacity is the heat required to raise the temperature of a body by 1K. If, during the process, the volume of the system remains constant, then it is called heat capacity at constant volume (C_V); if the pressure remains unchanged, it is called heat capacity at constant pressure (C_p). For one mole of a pure substance, these are called molar heat capacity at constant pressure, $\bar{C}_p$ and at constant volume, $\bar{C}_V$. Heat capacities per unit mass are called specific heats. The heat capacities change with temperature. This means that, the heat required to change the temperature by 1 K is different at different temperatures. However, over small ranges of temperature, these are usually taken as constant. The molar heat capacity and specific heat are intensive properties whereas heat capacity is an extensive property (guess the reason).

Note that C_p and C_v are heat capacities under constant pressure, and under constant volume, respectively for a given amount of a substance. $\bar{C}_p$ and $\bar{C}_v$ are molar heat capacities under constant pressure and, under constant volume, respectively; note the "bar above" in $\bar{C}_p$ and $\bar{C}_V$.

For changing the temperature of a particular system by dT, if the heat required is dq_V (at constant volume) or dq_p (at constant pressure), then we have

$$C_v = n\bar{C}_V = \frac{dq_v}{dT} \qquad \dots (6.2)$$

$$C_p = n\bar{C}_p = \frac{dq_p}{dT} \qquad \dots (6.3)$$

where n is the amount (i.e., number of moles) of the substance constituting the system.

From these equations, it is possible to determine the heat required for a process, by integration over the temperature range T_1 and T_2. Hence,

$$q_v = \int_{T_1}^{T_2} C_v dT = \int_{T_1}^{T_2} n\bar{C}_v dT \qquad \dots (6.4)$$

$$q_p = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} n\bar{C}_p dT \qquad \dots (6.5)$$

You will find many of the differentiation and integration formulae in this course. Integration is a process of continuous summation. The integration symbol is represented as ∫; the numbers or letters at its bottom and top refer to initial and final limits of a variable. In Example 1 discussed here, temperature is the variable and its initial and final limits are 298 K and 573 K, respectively. Note that the constants (such as n in Eq. 6.5) are taken outside the integration sign.

In later sections, we will be studying the use of C_p and C_v in the calculation of energy changes. Let us give an example here for the calculation of q_p, if n, C_p, T_1, and T_2 are given.

Example 1

The equation for the molar heat capacity of butane is $\bar{C}_p = (19.41 + 0.233T)\ \mathrm{J\ mol^{-1}\ K^{-1}}$.

Calculate the heat necessary to raise the temperature of 3.00 mol of butane from 298 K to 573 K at constant pressure. We have to calculate q_p as per Eq. 6.5.

$$q_p = \int_{T_1}^{T_2} n\bar{C}_p \mathrm{d}T \qquad \begin{aligned} T_1 &= 298\,\mathrm{K} \\ T_2 &= 573\,\mathrm{K} \\ n &= 3.00\,\mathrm{mol} \\ \bar{C}_p &= (19.41+0.233\,T)\,\mathrm{J\,mol^{-1}\,K^{-1}} \end{aligned}$$

$$= \int_{298}^{573} 3.00\,(19.41 + 0.233\,T)\,\mathrm{d}T$$

$$= \underset{\mathrm{I}}{\boxed{3.00 \times 19.41 \int_{298}^{573} \mathrm{d}T}} + \underset{\mathrm{II}}{\boxed{3.00 \times 0.233 \int_{298}^{573} T\mathrm{d}T}}$$

$$= \left[3.00 \times 19.41\,(573-298) + \frac{3.00 \times 0.233}{2}\,(573^2-298^2)\right]\mathrm{J}$$

$$= 9.97 \times 10^4\,\mathrm{J}$$

$$= 99.7\,\mathrm{kJ}$$

See the box below for understanding the simplification of the terms I and II.

Hence, heat required to raise the temperature of 3.00 mol of butane from 298 K to 573 K is 99.7 kJ.

We give below two general formulae for integration; these two formulae will be useful throughout this course in working out numericals. Formula 1 is used in this unit in Example 1 and Formula 2 in Example 3.

Formula 1

If m is not equal to −1

$$\int_{x_1}^{x_2} ax^m \mathrm{d}x = a\int_{x_1}^{x_2} x^m \mathrm{d}x = \frac{a}{m+1}\Big[x^{m+1}\Big]_{x_1}^{x_2} = \frac{a}{(m+1)}\,(x_2^{m+1} - x_1^{m+1})$$

where, a is a constant. This formula is used in the term marked II in Example 1, where a=3.00 × 0.233, $x=T$, $m=1$, x_1=298 and x_2=573.

Note that I term in Example 1 is also a special case of formula 1. If $m=0$, then x^m =1 and formula 1 becomes

$$\int_{x_1}^{x_2} a\mathrm{d}x = \frac{a}{(0+1)}\,(x_2-x_1) = a(x_2-x_1)$$

In I term of Example 1, a=3.00×19.41, $x=T$, x_1=298 and x_2=573

Formula 2

If m is equal to −1

Formula 2 finds use throughout our course (although not in this example).

$$\int_{x_1}^{x_2} a\,\frac{\mathrm{d}x}{x} = a\,\ln\frac{x_2}{x_1}$$

Again, a is a constant. Note that 'ln' stands for logarithm to the base e. Since we use natural logarithm (i.e., logarithm to the base 10) in our calculations, it is better to modify formula 2 as follows:

$$\int_{x_1}^{x_2} a\,\frac{\mathrm{d}x}{x} = 2.303\,a\log\frac{x_2}{x_1}$$

Note that ln x=2.303 log x

Logarithmic representation helps in denoting a very large or a small number as a number which is of convenient magnitude.

Eg: (i) Avogadro number = N_A=6.022 × 10^{23}
log N_A=23.78 (to four digits)

(ii) Dissociation constant of acetic acid (K_a) = 1.8×10^{-5}
−log K_a=4.74 (to three digits)

'log' representation depicts a number in powers of 10. Similarly 'ln' representation depicts a number in powers of 'e'.

$$e = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \ldots$$

= 2.718 (to four digits)

For representing population of energy levels, radioactive decay etc., 'ln' is quite useful.

We are now familiar with various terms used in the study of thermodynamics. In the next section, we shall discuss the first law of thermodynamics. Before proceeding to the next section, answer the following SAQ.

SAQ 3

The molar heat capacity of ethane at constant pressure is 52.6 J K^{-1} mol^{-1}. Calculate the energy required to heat 3.00 mol of ethane from 305 K to 405 K at constant pressure.

Hints: i) Use Eq. 6.5
ii) Integration is to be done as per formula 1 and I term in Example 1.

6.7 THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics was first stated by Mayer and Helmholtz in 1840 in Germany, Joule in England, and Colding in Denmark. This law is also known as the law of conservation of energy.

The first law of thermodynamics can be stated in any one of the following ways:

- The energy of an isolated system remains constant.
- Energy can neither be created nor destroyed although it can be changed from one form to another.
- It is not possible to construct a perpetual motion machine which can work endlessly without the expenditure of energy. (Such a machine is known as perpetual motion machine of the first kind.)

All the above statements are equivalent to the principle of conservation of energy. These statements point out that energy of a system will remain constant if it is left undisturbed. If, on the other hand, the system interacts with the surroundings, then its energy may change; but then, there will also be equal and opposite change in the energy of the surroundings. Since work is a form of energy, it is not possible for a machine to keep on doing work indefinitely. As soon as its own energy is exhausted, it will require a source of energy to continue doing work. The first law of thermodynamics has no theoretical proof. It is a law based on observation. Since the law has never been contradicted, its truth is taken for granted.

Einstein in 1905 showed that matter and energy are interconvertible according to the equation.

$$E = mc^2 \qquad \dots (6.6)$$

This means that if mass m is destroyed, then energy E is produced; c is the velocity of light. This is not a contradiction since mass can also be considered as a form of energy.

We shall shortly arrive at the mathematical forms of the first law of thermodynamics. Before that let us first introduce the term, internal energy.

Internal Energy

The internal energy U of a system is the entire energy of its constituent atoms or molecules including all forms of kinetic energy (due to translation, vibration and rotation) as well as energy due to all types of interactions between the molecules and subparticles. It is a state variable and an extensive property and its absolute value cannot be determined. However, in thermodynamics we are interested in the changes in internal energy which accompany any process, but not in the absolute value of U. These changes in internal energy can be brought about only by interaction of the system with its surroundings. The change in internal energy (ΔU) depends only on the initial and final states and is independent of the path adopted.

The total energy of a system is the sum of the internal energy and some energy due to the motion or position of the system as a whole. For example, the total energy of water on the ground floor is different from its energy on the top of the building. The difference in total energy is mgh (m is the mass of water, h the height of the building and g the acceleration due to gravity) whereas the internal energy is the same in both cases. Similarly for a moving bullet, the total energy is the sum of the internal energy and its kinetic energy, $\frac{1}{2}mv^2$ (where m is the mass of the bullet and v its velocity).

The heat change, dq, and the work done, dw, contribute towards the change in the internal energy of the system. We adopt the convention that the change in the internal energy is equal to the sum of the heat absorbed by the system and the work done on it.

If dq is positive (heat absorbed by the system is positive), this leads to an increase in the internal energy of the system. A negative dq implies loss of heat from the system and denotes a decrease in internal energy.

If the work done on the system (dw) is positive, this increases the internal energy of the system.

A negative value of dw implies that work has been done by the system at the expense of its internal energy.

Let us now derive the mathematical forms of the first law of thermodynamics.

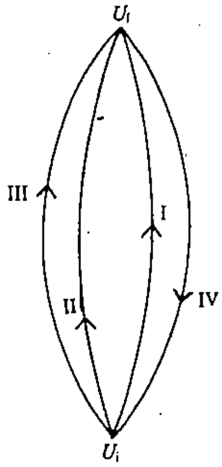

Fig. 6.1: Energy change through different onward paths, I, II and III and return path, IV.

Mathematical Forms of the First Law of Thermodynamics

As mentioned earlier, work and heat bring about changes in the internal energy of the system. If the system absorbs a certain amount of heat, dq, then its internal energy increases by this amount; further if dw is work done on the system, then the internal energy again increases. Hence, the net change in the internal energy is given by

$$dU = dq + dw \qquad \dots (6.7)$$

This equation is for infinitesimal changes. If, however, a system is taken from its initial state to another state by a process in which the heat absorbed is q and work done on the system is w, then the net change in internal energy will be given by

$$\Delta U = U_f - U_i = q + w \qquad \dots (6.8)$$

where U_i and U_f are the initial and final internal energies of the system, and ΔU, the net change. It is obvious that ΔU can have either negative or positive value depending on q and w. But once the initial and final states of a system are fixed, ΔU is automatically fixed, no matter what path is adopted in carrying out the process. In other words, internal energy is a state function while heat and work are not. As an example, consider a system being taken from the initial state where it has energy U_i to the final state having energy U_f along different paths I, II and III (Fig.6.1). Then in all these cases, ΔU is same. If this were not so, then it would have been possible to construct a perpetual motion machine by reaching the final state via a high energy change path (say, III) and coming back via a low energy change path (IV) thereby releasing the energy difference for work. Eqs. 6.7 and 6.8 are mathematical expressions of the first law of thermodynamics.

SAQ 4

Suggest a statement for the first law of thermodynamics such that the law of conservation of mass is not violated.

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6.8 ISOTHERMAL EXPANSION

In this section, we are going to calculate the work done on the gas in an isothermal process. For this we must first arrive at a general expression for pressure – volume work done in an infinitesimal process. Suppose that a gas is enclosed in a cylinder fitted with an air tight piston of area A. Assume that pressure of the gas is p and the external pressure is p_{ext} which is slightly less than the gas pressure. The gas will, hence, expand against an opposing force which is given by

$$F = p_{ext}A \qquad \dots (6.9)$$

If during expansion, the piston moves through a distance dx, then this small amount of work dw' done by the system is given by,

$$dw' = Fdx = p_{ext}Adx \qquad \dots (6.10)$$

But Adx is the change in volume of the gas, dV. Hence,

$$dw' = p_{ext}dV \qquad \dots (6.11)$$

Thus the work done by the system (i.e., by the gas) is dw'. Therefore, the work done on the gas is $-$dw' which we shall denote by dw. Hence, work dw done on the system is

$$dw = -p_{ext}dV \qquad \dots (6.12)$$

Eq. 6.12 is a general expression useful in calculating pressure – volume work whether it is isothermal or adiabatic process. It can be seen that dw is negative when the gas expands and it is positive when the gas contracts. [dv = +ve in expansion and dv = −ve in compression].

Note that the value of the work (dw) done on the gas is obtained by reversing the sign of work (dw') done by the gas; or dw = −dw'

We shall now calculate the work of expansion (as also of compression) under isothermal conditions. First let us take up the work done under isothermal irreversible conditions.

Isothermal Irreversible Process

Let us assume that the gas kept in a cylinder expands isothermally and irreversibly against a constant pressure.

This means that (i) the gas expands against a constant external pressure (p_{ext} = constant) (ii) there is considerable difference between the gas pressure (inside the cylinder) and the external pressure (iii) that the temperature does not change during the process.

Note that the pressure of the gas inside the cylinder and the external pressure are very much different in an irreversible process.

Let the initial and final volumes be V_I and V_2, respectively. The total work, W, done on the system is obtained by integrating Eq. 6.12.

$$\left.\begin{aligned} W &= -\int_{V_1}^{V_2} p_{ext}\mathrm{d}V = -p_{ext}\int_{V_1}^{V_2}\mathrm{d}V \\ &= -p_{ext}(V_2-V_1) = -p_{ext}\,\Delta V \end{aligned}\right\} \quad \ldots (6.13)$$

The integration procedure used in Eq. 6.13 is similar to that of part I discussed in Example 1. Again, this is an application of formula 1 discussed in Sec. 6.6.

The symbol, ΔV, denotes the total change in volume during the process.

Let us work out an example to illustrate the use of Eq. 6.13.

Example 2

A gas expands from 10 m^3 to 12 m^3 against a constant pressure of 1 bar at 298 K. What is the work done on the gas?

We have to calculate work done under constant pressure using Eq. 6.13.

Note that dx and Δx refer to infinitesimal and finite (considerable or even large) changes in x, respectively. If dx or Δx is

i) +ve, then x increases;
ii) −ve, then x decreases and
iii) zero, then x does not change or x remains a constant.

$$\begin{aligned} \text{Hence, } W &= -p_{ext}(V_2-V_1) = -1\times10^5\ \text{Pa}\times(12\ \text{m}^3-10\ \text{m}^3) \\ &= -2\times10^5\ \text{Pa m}^3 \\ &= -2\times10^5\ \text{J} \end{aligned} \quad \left\{\begin{aligned} &\text{because } 1\ \text{bar} = 1\times10^5\ \text{Pa} \\ &\text{and } 1\ \text{Pa m}^3 = 1\ \text{J} \end{aligned}\right\}$$

It can be seen that the work done on the system is negative, this means, actually system has done work equal to 2 × 10^5 J during expansion.

It is also possible to calculate the work done under irreversible isothermal conditions, when the external pressure changes continuously. But then, the concerned equation is more complex than Eq. 6.13. Let us now calculate the work done under isothermal reversible process.

Isothermal Reversible Process

We have already mentioned that a reversible process can be carried out when external pressure (p_{ext}) is only infinitesimally different from the gas pressure inside a cylinder (p).

In such a case, $p_{ext} \simeq p$ and hence, Eq. 6.12 can be written as,

$$\mathrm{d}w = -p\mathrm{d}V \quad \ldots (6.14)$$

The total work done, W, as the gas expands isothermally and reversibly from a volume V_I to a volume V_2 is then given by integrating Eq. 6.14 within limits V_I and V_2.

$$W = -\int_{V}^{V_2} p\mathrm{d}V \quad \ldots (6.15)$$

Note that the difference between Eqs. 6.13 and 6.15 is that p depends on volume in the latter; whereas, p_{ext} in Eq. 6.13 is constant throughout. As a result of this, p_{ext} is taken out of integration sign in Eq. 6.13 whereas p in Eq. 6.15 is to be expressed as a function of volume.

Let us assume that the gas behaves ideally. Hence,

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

Using this in Eq. 6.15,

$$\begin{aligned} W &= -\int_{V_1}^{V_2} \frac{nRT}{V}\mathrm{d}V \\ &= -nRT\int_{V_1}^{V_2}\frac{\mathrm{d}V}{V} && \ldots (6.16) \\ &= -nRT\ \ln\frac{V_2}{V_1} = nRT\ \ln\frac{V_1}{V_2} && \ldots (6.17) \end{aligned}$$

$$\text{Hence, } W = -2.303nRT\log\frac{V_2}{V_1} = 2.303\,nRT\log\frac{V_1}{V_2} \quad \ldots (6.18)$$

Note that n, R and T are constants and are taken out of the integration sign in Eq. 6.16. Note that formula 2 of Sec. 6.6 is used here.

As compared to formula 2,

$a = nRT$
$x_1 = V_1$
$x_2 = V_2$
$x = V$

It can be seen that if V_2 is less than V_I, then the gas has been compressed and, W is positive. Also, the value of W then happens to be the minimum work required for compressing the gas from (volume) V_1 to V_2.

Similarly, if V_2 is greater than V_1 then the gas undergoes expansion and W is negative.

This means, work is done by the gas; $-W$ represents the maximum work available through expansion.

Eq. 6.18 can also be given in terms of initial and final pressures (p_1 and p_2) of the ideal gas.

Note that Eqs 6.18 and 6.21 are applicable only for an ideal gas undergoing isothermal reversible expansion or compression. If the gas does not have ideal behaviour, suitable equation of state must be used.

For an ideal gas at constant temperature,

$$p_1V_1 = p_2V_2 \quad \ldots (6.19)$$

$$\frac{V_2}{V_1} = \frac{p_1}{p_2} \quad \ldots (6.20)$$

Using Eqs. 6.18 and 6.20

$$\begin{aligned} W &= -2.303\,nRT \log \frac{p_1}{p_2} \\ &= 2.303\,nRT \log \frac{p_2}{p_1} \quad \ldots (6.21) \end{aligned}$$

Note that $-\log \frac{p_1}{p_2} = \log \frac{p_2}{p_1}$; this follows from the mathematical principle that the numerator and denominator inside the "log" term can be interchanged by reversing the sign outside.

Step (i) :

Note that this step contains logarithmic term.

$$\log \frac{6.00 \times 10^6\,\text{Pa}}{3.00 \times 10^5\,\text{Pa}}$$

When you come across a logarithmic term, first see whether the number inside the logterm is greater than or less than one.

In the present case, $\frac{6.00 \times 10^6}{3.00 \times 10^5}$ is greater than one. Hence, do the following steps:

Step (ii) :

From the logarithm of the numerator, subtract the logarithm of the denominator. In Example 3, this step gives (6.7782−5.4771).

Step (iii) :

The answer to step (ii) is written (in Example 3, it is 1.3011); the multiplication is carried out in the usual way.

Let us illustrate the use of Eq. 6.21.

Example 3

An ideal gas initially at 3.00×10^2 K and 3.00×10^5 Pa pressure occupies 0.831 m^3 space. What is the minimum amount of work required to compress the gas isothermally and reversibly so that the final pressure is 6.00×10^6 Pa?

$$p_1 = 3.00 \times 10^5\,\text{Pa};\ p_2 = 6.00 \times 10^6\,\text{Pa}$$

$$R = 8.314\,\text{J mol}^{-1}\,\text{K}^{-1};\ T = 3.00 \times 10^2\,\text{K}$$

We have to calculate the value of n (the amount of the gas) in order to use Eq. 6.21; the value of n can be found out from the initial conditions using ideal gas equation.

$$n = \frac{pV}{RT} = \frac{3.00 \times 10^5\,\text{Pa} \times 0.831\,\text{m}^3}{8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 3.00 \times 10^2\,\text{K}}$$

$$n = 1.00 \times 10^2\,\text{mol}$$

Substituting the values in Eq. 6.21.

$$\begin{aligned} W &= 2.303 \times 1.00 \times 10^2\,\text{mol} \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 3.00 \times 10^2\,\text{K}\ \boxed{\log \frac{6:00 \times 10^6\,\text{Pa}}{3.00 \times 10^5\,\text{Pa}}} \\ &= 2.303 \times 1.00 \times 10^2 \times 8.314 \times 3.00 \times 10^2 \times \boxed{(6.7782-5.4771)}\ \text{J} \qquad \text{Step (i)} \\ & \qquad\qquad \text{Step (ii)} \\ &= 2.303 \times 1.00 \times 10^2 \times 8.314 \times 3.00 \times 10^2 \times \boxed{1.3011}\ \text{J} \\ W &= 7.47 \times 10^5\,\text{J} \qquad \text{Step (iii)} \end{aligned}$$

Using the principles studied above, answer the following SAQ.

SAQ 5

A gas expands against vacuum. What is the work done on it?

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6.9 HEAT CHANGE UNDER CONSTANT VOLUME

If the logarithmic term is less than 1 (or if the numerator is less than the denominator inside the logarithmic term), do as shown in the answer to the Terminal Question 5.

The reactions are carried out under constant volume or under constant pressure conditions. Let us now arrive at an expression useful in calculating the heat change in a system under constant volume conditions. In the next section, we shall discuss heat change under constant pressure conditions.

Let us examine Eq. 6.7. Let us assume that the work done on the system is only pressure-volume work, whereas electrical, magnetic or other types of work are not involved. Then from Eqs. 6.7 and 6.14,

$$\text{d}U = \text{d}q - p\text{d}V \quad \ldots (6.22)$$

$$\text{or } \text{d}q = \text{d}U + p\text{d}V \quad \ldots (6.23)$$

If the process is carried out at constant volume, then,

$$dV = pdV = 0$$

Hence, $dq_V = dU$ ... (6.24)

For finite changes in internal energy Eq. 6.24 becomes,

$$q_V = \Delta U \qquad \text{... (6.25)}$$

That is, heat absorbed by a system at constant volume is exactly equal to its internal energy change.

Let us try to correlate internal energy change with heat capacity at constant volume assuming that there is no phase change or chemical reaction. From Eqs. 6.2 and 6.24,

$$dU = C_V dT = n\bar{C}_V dT \qquad \text{... (6.26)}$$

This holds good for n mol of an ideal gas.

Eq. 6.26 can be rewritten as,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \qquad \text{... (6.27)}$$

i.e., heat capacity at constant volume is equal to change in internal energy per 1 K rise in temperature at constant volume.

$\left(\frac{\partial U}{\partial T} \right)_V$ is called the partial differential of internal energy with respect to temperature at constant volume. It means the value U of a gas depends on V and T; but only the variation in U with respect to T is measured at constant volume. Interestingly for an ideal gas, U depends only on T but not on V, i.e.,

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

In order to obtain ΔU when an ideal gas is heated from temperature T_1 to T_2 at constant volume, the integrated form of Eq. 6.26 is to be used.

$$\text{i.e.,} \qquad \Delta U = \int_{T_1}^{T_2} C_V dT = \int_{T_1}^{T_2} n\bar{C}_V dT \qquad \text{...(6.28)}$$

Hence, by knowing $\bar{C}_V$ over the temperatures T_1, to T_2, it is possible to obtain the value of ΔU.

We have defined C_V through Eq. 6.27. What about C_p? Is there some thermodynamic property to which C_p can be related in a similar way? For this purpose, we define the term, enthalpy, in the next section.

Using the ideas developed in this section, answer the following SAQ.

SAQ 6

Calculate the

i) change in internal energy of an ideal gas undergoing isothermal reversible compression as discussed in Example 3.

....

ii) What is the value of q for the same case?

....

6.10 ENTHALPY AND ENTHALPY CHANGES

Enthalpy of a system is defined by the relation,

$$H = U + pV \qquad \text{... (6.29)}$$

where U, p, and V, are the internal energy, pressure and volume of the system. Since U, p and V are state variables, H also is a state function. That is, the enthalpy of a system in a particular state is completely independent of the manner in which that state has been achieved. If H_1, and H_2 are the enthalpies of the initial and final states of a system, then the enthalpy change accompanying the process is given by,

$$\Delta H = H_2 - H_1 \qquad \text{... (6.30)}$$

$$= (U_2 + p_2V_2) - (U_1 + p_1V_1)$$

$$= \Delta U + (p_2V_2 - p_1V_1) \qquad \text{... (6.31)}$$

In case of a constant pressure process ($p_1 = p_2 = p$). Eq. 6.31 can be written as,

$$\Delta H = \Delta U + p(V_2 - V_1)$$

$$\Delta H = \Delta U + p\Delta V \qquad \text{...(6.32)}$$

Rewriting Eq. 6.23 for a finite change, we get

$$q_p = \Delta U + p\Delta V \qquad \text{... (6.33)}$$

Using this equation in Eq. 6.32, $q_p = \Delta H$ ...(6.34)

The subscript p in q_p stands for the constant pressure condition.

In other words, the enthalpy change is equal to the heat absorbed by the system at constant pressure.

For a small change in enthalpy, we can write

$$dq_p = dH \qquad ...(6.35)$$

Using Eq. 6.3 and assuming that there is no phase change or chemical reaction we have,

$$dH = C_p dT = n\bar{C}_p dT \qquad ...(6.36)$$

In order to obtain ΔH value when an ideal gas is heated from temperature T_1 to T_2, at constant pressure, the integrated form of Eq. 6.36 is to be used.

$$\Delta H = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} n\bar{C}_p dT \qquad ...(6.37)$$

Using Eq. 6.36 C_p can be defined as. $C_p = \left(\frac{\partial H}{\partial T}\right)_p$; this means, the heat capacity at constant pressure is equal to the partial differential of H with respect to temperature at constant pressure. Interestingly for an ideal gas, H depends on T only and not on p; i.e. $\left(\frac{\partial H}{\partial p}\right)_T = 0$ for an ideal gas.

Since many laboratory processes are carried out at constant pressure (atmospheric pressure), the enthalpy change of a system is of great significance. It may be noted that since the absolute value of the internal energy of a system is not known, it is also impossible to know the absolute enthalpy of the system. Fortunately, for most processes we are only concerned with the changes in enthalpy which may be measured by taking any suitable reference states of elements.

Those processes in which heat is supplied to the system are called endothermic and, ΔH is given a positive sign; in exothermic processes (in which heat is evolved), ΔH is negative.

Enthalphy changes connected with certain typical processes are given special names. For example, enthalpy of vaporization or evaporation is the enthalpy change accompanying the conversion of one mole of a liquid to its vapour. Similarly, enthalpy of fusion and sublimation are the enthalpy changes accompanying fusion or sublimation of one mole of a substance. For a chemical reaction, the enthalpy of reaction is the difference in the enthalpies of the products and the reactants as per the stoichiometry given in the chemical equation. We shall study enthalpy changes in detail in the next unit. In the next section, we shall study the relationship between $\bar{C}_p$ and $\bar{C}_v$ values of an ideal gas.

6.11 RELATION BETWEEN $\bar{C}_p$ and $\bar{C}_V$ OF AN IDEAL GAS

The internal energy of an ideal gas depends only on its temperature and is independent of pressure or volume. This is quite understandable because in an ideal gas, there are no intermolecular interactions; no attractive or repulsive forces have to be overcome during expansion. However, the enthalpy of the gas changes considerably when a gas expands or contracts.

For one mole of an ideal gas,

$$H = U + pV = U + RT \qquad ...(6.38)$$

On differentiating we get,

$$dH = dU + RdT \qquad \text{[because } R \text{ is a constant]}$$

Using Eqs. 6.26 and 6.36 **(for one mole of an ideal gas)**

$$\bar{C}_p dT = \bar{C}_V dT + RdT \qquad ...(6.39)$$

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

and hence, $\bar{C}_p - \bar{C}_V = R$ ... (6.40)

Also, for n mol, $C_p - C_V = nR$ ... (6.41)

This means that $\bar{C}_p$ is always greater than $\bar{C}_V$ for an ideal gas. This is because when the temperature of a gas is raised at a constant pressure, there will be expansion of the gas. This will require some extra amount of heat (as compared to heating an ideal gas under constant volume conditions). Hence, more heat will be required in raising the temperature of the gas through 1 K under constant pressure conditions than under constant volume.

6.12 ADIABATIC EXPANSION

In Sec. 6.8, we discussed the work done in an isothermal process. Let us now study how the work is calculated in an adiabatic process.

In an adiabatic process, heat absorbed is zero, i.e., $dq=0$

Hence, from Eq. 6.7 $dU=0+dw=dw$ ...(6.42)

But for one mole of an ideal gas, dU is given by Eq. 6.26 as,

$$dU=\bar{C}_V dT$$

During expansion, dw and hence, dU are negative. That is, as the system does expansion work, its internal energy decreases. This, again, according to Eq. 6.26 means that dT is negative; i.e., temperature decreases. In other words, during adiabatic expansion, temperature of the system decreases. This principle is used in Claude's method of liquefaction of gases.

Let us now study the temperature-volume relation in a reversible adiabatic process. This could help us in determining the final temperature of a system undergoing adiabatic expansion or compression.

Temperature-Volume Relationship in a Reversible Adiabatic Process

According to Eq. 6.42, $dU=dw$

Substituting for dw and dU from Eqs. 6.14 and 6.26, we get for one mole of an ideal gas,

$$\bar{C}_V dT = -p dV \qquad \text{...(6.43)}$$

For one mole of an ideal gas,

$$p=\frac{RT}{V}$$

Using this relationship in Eq. 6.43, we get

$$\bar{C}_V dT=\frac{-RT dV}{V} \qquad \text{...(6.44)}$$

Rearranging we get,

$$\bar{C}_V \frac{dT}{T} = -R\frac{dV}{V} \qquad \text{...(6.45)}$$

Integrating Eq. 6.45 between temperature limits T_1 and T_2 and volume limits V_1 and V_2, we get

$$\bar{C}_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V} \qquad \text{...(6.46)}$$

The integrals on the left and right sides of Eq. 6.46 are solved using formula 2 given in Sec. 6.6. Note that $\bar{C}_V$ is considered a constant in the temperature range T_1 to T_2. Of course, R is a constant.

The change of numerator and denominator inside the 'ln' term with a reversal of the sign outside it has already been explained in Sec. 6.8.

$$\bar{C}_V \ln \frac{T_2}{T_1} = -R \ln\frac{V_2}{V_1} = R \ln \frac{V_1}{V_2}$$

$$= (\bar{C}_p-\bar{C}_V) \ln \frac{V_1}{V_2} \qquad \text{(using Eq. 6.40)}$$

$$\ln \frac{T_2}{T_1} = \left(\frac{\bar{C}_p}{\bar{C}_V} - 1 \right) \ln \frac{V_1}{V_2}$$

$$= (\gamma-1) \ln \frac{V_1}{V_2} \qquad \text{...(6.47)}$$

Rearrangement of Eq. 6.47 is done using the general formula, $m \ln x = \ln x^m$ or $m \log x = \log x^m$. You can verify this formula using logarithmic tables in the following cases. You look for the logarithm of 10, 100, 2 and 8; see whether the following are true.

$2 \log 10 = \log 10^2 = \log 100$

$3 \log 2 = \log 2^3 = \log 8$

Where γ is the ratio of the molar heat capacities, $\bar{C}_p/\bar{C}_V$.

Rearranging Eq. 6.47, we get,

$$\ln\frac{T_2}{T_1} = \ln \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

Taking antilogarithms both the sides

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad \ldots(6.48)$$

$$\text{or } T_2V_2^{\gamma-1}=T_1V_1^{\gamma-1} \text{ or } TV^{\gamma-1}=\text{Constant}$$

This equation gives the volume — temperature relationship in a reversible adiabatic process.

Also, we can get pressure-temperature relationship knowing that, for an ideal gas,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

$$\frac{V_1}{V_2} = \frac{p_2T_1}{p_1T_2} \qquad \ldots(6.49)$$

substituting this in Eq. 6.48

$$\frac{T_2}{T_1} = \left(\frac{p_2T_1}{p_1T_2}\right)^{\gamma-1}$$

$$T_2(p_1T_2)^{\gamma-1} = T_1(p_2T_1)^{\gamma-1}$$

i.e.,

$$T_2^{\gamma}\,p_1^{\gamma-1} = T_1^{\gamma}\,p_2^{\gamma-1}$$

or

$$\left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{p_2}{p_1}\right)^{\gamma-1} \qquad \ldots(6.50)$$

For any reversible adiabatic expansion, T_2 can be determined using Eq. 6.48 or 6.50.

Also it is possible to get pressure-volume relationship in a reversible adiabatic process using the rearranged form of Eq. 6.49,

$$\frac{T_2}{T_1} = \frac{p_2V_2}{p_1V_1}$$

in Eq. 6.48 as follows:

$$\frac{p_2V_2}{p_1V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Cross multiplying the terms,

$$p_2V_2V_2^{\gamma-1} = p_1V_1V_1^{\gamma-1}$$

$$\text{or } p_1V_1^{\gamma} = p_2V_2^{\gamma} \qquad \ldots(6.51)$$

$$\text{or } pV^{\gamma} = \text{Constant}$$

For an ideal gas undergoing isothermal reversible expansion (or contraction), the pressure-volume relationship is, $p_1V_1 = p_2V_2$ whereas in an adiabatic reversible process, it is $p_1V_1^{\gamma}=p_2V_2^{\gamma}$. Here subscripts 1 and 2 stand for initial and final conditions.

Eq. 6.51 describes pressure-volume relationship for an ideal gas undergoing reversible adiabatic expansion (or compression).

ΔU and W in a Reversible Adiabatic Process

The quantities dU and dw for an adiabatic process are related through Eq. 6.42. Using this equation and Eq. 6.26, we get for 1 mol of an ideal gas,

$$\mathrm{d}U=\mathrm{d}w=\bar{C}_V\mathrm{d}T$$

In case of n mol of an ideal gas,

$$\mathrm{d}U=\mathrm{d}w=n\bar{C}_V\mathrm{d}T \qquad \ldots(6.52)$$

Note that $\bar{C}_V$ is assumed to be a constant in Eq. 6.53 in the temperature range T_1 and T_2.

The work done on the gas during an adiabatic expansion (W) as also the change in internal energy (ΔU) can be calculated by integrating Eq. 6.52 within temperature limits T_1 and T_2

$$\Delta U = W = n\bar{C}_V\int_{T_1}^{T_2}\mathrm{d}T$$

$$= n\bar{C}_V\,(T_2-T_1) = n\bar{C}_V\Delta T \qquad \ldots(6.53)$$

Hence, ΔU and W can be calculated when n, $\bar{C}_V$, T_1 and T_2 are known.

Irreversible Adiabatic Expansion

If the work is done irreversibly and adiabatically, then the work done on the system is given by Eq. 6.13,

$$W = -p_{ext}\Delta V \qquad \ldots(6.54)$$

as in the case of irreversible isothermal process.

We can arrive at the temperature-volume relationship for an adiabatic irreversible process as follows:

using Eq. 6.54 in Eq. 6.53 $\quad -p_{ext}\,\Delta V = n\,\bar{C}_V\Delta T$

Hence,

$$\Delta T = (T_2 - T_1) = \frac{-p_{ext}\,\Delta V}{n\bar{C}_V} \qquad \ldots(6.55)$$

Eq. 6.55 is useful in calculating the final temperature of an ideal gas undergoing adiabatic irreversible expansion while Eq. 6.48 or 6.50 is of help in an adiabatic reversible process.

Answer the following SAQ using Eq. 6.55.

SAQ 7

Show that against zero external pressure, the expansion is simultaneously adiabatic and isothermal.

....

....

6.13 JOULE-THOMSON EFFECT

Our discussion so far centered around ideal gases. It was mentioned earlier that internal energy of an ideal gas is independent of presssure or volume. This, however, is not true for real gases since intermolecular forces exist among their molecules. So when a real gas is expanded, work has to be done in overcoming these forces. If no energy is supplied from an external source, then the internal energy of the gas is used up in doing this work. This results in a fall in the temperature of the gas. However, some gases show rise in temperature. This phenomenon of change in temperature when a gas is made to expand adiabatically from a high pressure region to a low pressure region, is known as the Joule-Thomson effect. The phenomenon can be understood if we consider the apparatus shown in Fig. 6.2. It consists of an insulated tube fitted with a porous plug and two airtight pistons one on either side of the plug. The gas is kept under pressures p_1 and p_2 in the two compartments. Note that p_1 is greater than p_2. The left hand side piston is then slowly pushed inwards so that, without changing the value of p_1, a volume V_1 of gas is introduced through the plug into the other compartment. This results in the outward movement of the other piston and also in the volume increase. Let the final volume be V_2. Accurate temperature measurements are made in both compartments.

A detailed discussion of intermolecular forces and their effects on liquefaction, vaporization and fusion is available in Unit 3 of this course.

A porous plug has small holes which permit the flow of the gas from one side to another.

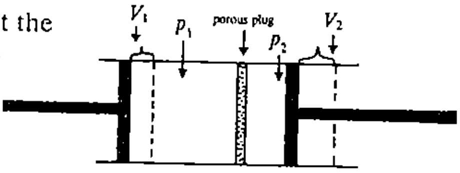

Fig. 6.2: Joule-Thomson Experiment.

The net work done on the system is given by

$$W = -(p_2V_2 - p_1V_1) = p_1V_1 - p_2V_2 \qquad \ldots(6.56)$$

It should be remembered that p_2V_2 is the work done by the system and p_1V_1, the work on it. The conditions are adiabatic and so q=0. For a finite process, Eqs. 6.42 and 6.56 can be combined and written as,

$$\Delta U = W = (p_1V_1 - p_2V_2) \qquad \ldots(6.57)$$

Or $\quad \Delta U + (p_2V_2 - p_1V_1) = 0 \qquad \ldots(6.58)$

Using Eq. 6.31, $\Delta U + (p_2V_2 - p_1V_1) = \Delta H$

From Eqs. 6.31 and 6.58 we note that

$$\Delta H = 0 \qquad \ldots(6.59)$$

Hence in the Joule-Thompson experiment, $\Delta H=0$ or enthalpy is constant.

Since, in the Joule-Thomson experiment, we measure the temperature change with change in pressure at constant enthalpy, we define Joule-Thomson coefficient, μ_{JT}, as

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H \qquad \text{...(6.60)}$$

If μ_{JT} is positive, expansion causes cooling and if μ_{JT} is negative, expansion causes heating. But if μ_{JT} is equal to zero, there is neither cooling nor heating due to Joule-Thomson expansion. The temperature at which $\mu_{JT}=0$ is called the inversion temperature (T_i) of the gas. If a gas is expanded above its inversion temperature, it is heated; if it is expanded below its inversion temperature, it is cooled. In order to decrease the temperature of a gas and then to liquefy by Joule-Thomson process, it is essential to bring its temperature below its inversion temperature. The application of Joule-Thomson effect in the liquefaction of gases was discussed in Unit 3 of this course. A detailed study of Joule-Thomson effect is made in Block 2 of the course on Thermodynamics and Statistical Mechanics.

The inversion temperature of hydrogen gas is much below room temperature. Therefore, it is dangerous to open a compressed hydrogen gas cylinder under atmospheric conditions. As hydrogen gas is released from the cylinder, it expands, gets heated and also combines with oxygen present in the air; the latter reaction causes an explosion.

6.14 SUMMARY

In this unit, you have been introduced to the first law of thermodynamics. The main aspects of this unit are given below:

- The zeroth law of thermodynamics and the first law of thermodynamics have been stated.
- The extensive and intensive variables are explained with examples.
- The terms heat capacity, internal energy and enthalpy have been defined and discussed.
- The formulae for the calculation of work, heat exchange and internal energy change in isothermal and adiabatic processes are derived. Examples are also worked out to explain the use of these formulae.
- Joule-Thomson effect is explained and its importance in the liquefaction of gases is indicated.

6.15 TERMINAL QUESTIONS

1. A gas is expanded from $4.00 \times 10^{-3} m^3$ to $8.00 \times 10^{-3} m^3$ against a constant pressure of 1.00×10^5 Pa and it has been used to heat 0.010 kg of water. Calculate the final temperature of water. Given: Initial temperature of water = 296.2 K and $\bar{C}_p$ for water = 75.2 J mol^{-1} K^{-1}.
2. A sample of 0.200 mol of argon expands adiabatically and reversibly such that temperature drops from 298 K to 188 K. If molar heat capacity for argon at constant volume is 12.48 J·mol^{-1} K^{-1}, calculate the change in internal energy and the work done on the gas.
3. According to equipartition principle, the internal energy of n mol of helium gas is $\frac{3}{2} nRT$. Find out its $\bar{C}_p$ and $\bar{C}_V$ values. Assume that helium behaves ideally.
4. Calculate the heat required to increase the temperature of 1.00 mol of methane from 298 K to 398 K at constant pressure. $\bar{C}_p$ for methane = 35.3 J mol^{-1}K^{-1}.
5. 1.00 mol of an ideal gas at 3.00×10^2 K and 2.00×10^6 Pa pressure is expanded reversibly and isothermally till its pressure is 2.00×10^5 Pa. Calculate ΔU, q and W.

6.16 ANSWERS

Self-assessment Questions

1. i) closed system
   ii) isolated system
   iii) open system

2. i) extensive
   ii) intensive (note that volume is an extensive property but volume per unit mass is an intensive property)
   iii) intensive

3. $\bar{C}_p = 52.6 \text{ J mol}^{-1} \text{ K}^{-1}$; $n = 3.00$ mol
   $T_1 = 305$ K; $T_2 = 405$ K

   Using Eq. 6.5, $q_p = \int_{T_1}^{T_2} n\bar{C}_p dT = \int_{305}^{405} 3.00 \times 52.6 dT$

   $= 3.00 \times 52.6\,(405-305)$ J

   ≈ 15.8 kJ

4. In a system of constant mass, energy can neither be created nor be destroyed.

5. Work done on the gas against vacuum is zero as per Eq.6.13.

6. i) In an isothermal process, $\Delta U = 0$ as per Eq. 6.26 for an ideal gas.
   ii) Using Eq. 6.8, $q = -W$
   Since $W = 7.47 \times 10^5$ J as per Example 3,
   $q = -7.47 \times 10^5$ J

7. Since p_{ext} is zero, $\Delta T = 0$ as per Eq.6.55; hence, expansion against zero external pressure is simultaneously adiabatic and isothermal.

Terminal Questions

1. $$W = -p_{ext}(V_2 - V_1)$$
   $$= -4.00 \times 10^2 \text{ J}$$
   $$W = -4.00 \times 10^2 \text{ J} = -q_p = -\int_{T_1}^{T_2} n\bar{C}_p dT$$
   $$= -n\,\bar{C}_p\,(T_2 - T_1) \text{ (since } n \text{ and } \bar{C}_p \text{ are constants)}$$
   $$n = \text{number of moles of water} = \frac{0.010 \text{ kg}}{0.018 \text{ kg mol}^{-1}}$$
   $$(T_2 - T_1) = \frac{4.00 \times 10^2 \text{ J}}{75.2 \text{ J mol}^{-1} \text{ K}^{-1}} \times \frac{0.018 \text{ mol}^{-1}}{0.010}$$
   Hence, $T_2 = 306$ K

2. $$\Delta U = \int_{298}^{188} n\bar{C}_V dT = n\bar{C}_V \int_{298}^{188} dT$$
   $$= (0.200 \text{ mol} \times 12.48 \text{ J mol}^{-1} \text{ K}^{-1} \times (188-298) \text{ K}$$
   $$= -(0.200 \times 12.48 \times 110) \text{ J}$$
   $$= -275 \text{ J}$$
   In an adiabatic process, $W = \Delta U$
   Hence, $W = \Delta U = -275$ J

3. $$U = \frac{3}{2}nRT; \quad \bar{C}_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}nR$$
   $$\bar{C}_p = \bar{C}_V + nR = \frac{5}{2}nR$$

4. $$q_p = \int_{298}^{398} n\,\bar{C}_p \mathrm{d}T = 1.00\times35.3\times(398-298)\ \mathrm{J}$$
$$= 3.53\times10^{3}\ \mathrm{J}$$

5. ΔU for an isothermal expansion of an ideal gas=0

$$W = 2.303\,\mathrm{n}RT\ \log\frac{p_2}{p_1} \qquad \text{Step (i)}$$
$$= 2.303\times1.00\ \mathrm{mol}\times8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}\times3.00\times10^{2}\mathrm{K}\boxed{\log\frac{2.00\times10^{5}\ \mathrm{Pa}}{2.00\times10^{6}\ \mathrm{Pa}}}$$
$$= -\left(2.303\times8.314\times3.00\times10^{2}\boxed{\log\frac{2.00\times10^{6}}{2.00\times10^{5}}}\right)\mathrm{J} \qquad \text{Step (ii)}$$
$$= -2.303\times8.314\times3.00\times10^{2}\times\boxed{(6.3010-5.3010)}\ \mathrm{J} \qquad \text{Step (iii)}$$
$$= -2.303\times8.314\times3.00\times10^{2}\times\boxed{1.0000}\ \mathrm{J} \qquad \text{Step (iv)}$$
$$= -5.74\times10^{3}\ \mathrm{J}$$
$$q = -W = 5.74\times10^{3}\ \mathrm{J}$$

In step (i) of answer to Terminal Question 5, you have a term $\log\frac{2.00\times10^{5}\,\mathrm{Pa}}{2.00\times10^{6}\,\mathrm{Pa}}$. Note that the term $\frac{2.00\times10^{5}}{2.00\times10^{6}}$ for which logarithm is to be taken is less than one. In such cases, use the following steps :

Step (ii) : Interchange the numerator and the denominator within the 'log' term; also change the sign of the right hand side of the equation. In the answer to Terminal Question 5, this step results in the term, $\log\frac{2.00\times10^{6}}{2.00\times10^{5}}$ and a negative sign at the beginning of the right hand side.

Step (iii) : Now we have to subtract the log value of the denominator from the log value of the numerator. In the above example, the simplification of the log term gives (6.3010−5.3010).

Step (iv) : The answer to step (iii) is written and the multiplication is carried out in the usual way.

The above procedure is preferable to the alternate method of subtracting the mantissa from the characteristic and then changing the sign.

UNIT 7 THERMOCHEMISTRY

Structure

7.1 INTRODUCTION

The branch of science dealing with hearchanges during a chemical reaction is known as Thermochemistry. In this unit, we shall deal with heat change accompanying a chemical reaction when it is carried out under constant volume or constant pressure. We shall define standard enthalpy of formation and enthalpy changes in different chemical reactions. We shall discuss the experimental method of determination of enthalpy changes. We will list some of the applications of Hess's Law of constant heat summation. Finally, we shall derive Kirchhoff's equation and discuss its importance.

Objectives

After studying this unit, you should be able to:

- derive the relationship between $\Delta_r U$ and $\Delta_r H$ and make calculations based on this relationship,
- define standard enthalpy of formation,
- state Hess's law of constant heat summation and explain its significance,
- calculate the enthalpy of a reaction using enthalpies of formation of compounds,
- describe an experimental method for the determination of enthalpy of combustion,
- derive Kirchhoff's equation and state its significance,
- define bond enthalpy, and
- calculate enthalpies of reactions from bond enthalpies.

7.2 RELATIONSHIP BETWEEN $\Delta_r U$ AND $\Delta_r H$

A chemical reaction can be carried out in two ways:

i) In a closed vessel, so that there is no volume change.

ii) In a pressure regulated vessel, so that there is no pressure change.

Accordingly, the heat change accompanying a chemical reaction can also be measured in two ways, viz., heat change at constant volume (q_V) and at constant pressure (q_p). From Eqs.6.25 and 6.34, $q_V = \Delta U$ and $q_p = \Delta H$. In thermochemistry, the enthalpy change accompanying a chemical reaction is called the reaction enthalpy and is denoted by the symbol $\Delta_r H$. Similarly, the internal energy change accompanying a chemical reaction is given the symbol $\Delta_r U$. The subscript r after Δ sign indicates a reaction. To denote formation, combustion and vaporization processes, subscripts used are f, c and vap, respectively. As in the case of Eqs. 6.25 and 6.34 we can write,

$$q_V = \Delta_r U \qquad \text{...(7.1)}$$

and

$$q_p = \Delta_r H \qquad \text{...(7.2)}$$

The significance of $\Delta_r U$ and $\Delta_r H$ can be explained by the following equations:

$$\Delta_r U = U_{\text{Products}} - U_{\text{Reactants}} \qquad \text{...(7.3)}$$

$$\Delta_r H = H_{\text{Products}} - H_{\text{Reactants}} \qquad \text{...(7.4)}$$

Since most reactions are carried out at constant pressure $\Delta_r H$ is more commonly used than $\Delta_r U$.

Thermochemical Equations

In a thermochemical equation, in addition to the chemical reaction, the physical states of the various chemical species and the energy change are also specified. For example,

$$H_2(g)+\tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta_r H = -285.8 \text{ kJ mol}^{-1} \quad ...(7.5)$$

$$C(\text{graphite})+O_2(g) \rightarrow CO_2(g) \qquad \Delta_r H = -393.5 \text{ kJ mol}^{-1} \quad ...(7.6)$$

are thermochemical equations. In such equations, *s*, *l* and *g*, refer to solid, liquid and gaseous states, respectively. If a substance can exist in various allotropic forms, the particular form must be mentioned.

Relation between $\Delta_r U$ and $\Delta_r H$

If in a chemical reaction, the enthalpy of the system changes from H_1 to H_2 and if U_1, p_1, V_1 and U_2, p_2, V_2 are the corresponding internal energies, pressures and volumes, then

$$H_1 = U_1 + p_1V_1 \quad ...(7.7)$$

and

$$H_2 = U_2 + p_2V_2 \quad ...(7.8)$$

$$\Delta_r H = H_2 - H_1 = U_2 + p_2V_2 - U_1 - p_1V_1 = U_2 - U_1 + (p_2V_2 - p_1V_1)$$

Hence, $\Delta_r H = \Delta_r U + (p_2V_2 - p_1V_1)$ ...(7.9)

At constant pressure $(p_1 = p_2 = p)$,

$$\Delta_r H = \Delta_r U + (pV_2 - pV_1) = \Delta_r U + p(V_2 - V_1)$$

$$\Delta_r H = \Delta_r U + p\Delta V \quad ...(7.10)$$

Using Eqs. 7.1 and 7.2,

$$q_p = q_V + p\Delta V \quad ...(7.11)$$

For solids and liquids, $p\Delta V$ is negligible. Thus for reactions in condensed phases, $\Delta_r H = \Delta_r U$.

If we assume that (i) all gaseous reactants and products are ideal and (ii) there are n_1 and n_2 moles of gaseous reactants and products, respectively, then,

$$p_1V_1 = n_1RT \quad \text{and} \quad p_2V_2 = n_2RT$$

$$\text{Hence, } p_2V_2 - p_1V_1 = (n_2 - n_1)RT$$

Since pressure is constant,

$$p(V_2 - V_1) = p\Delta V = (n_2 - n_1)RT \quad ...(7.12)$$

Replacing $(n_2 - n_1)$ by Δn_g to represent the change in the number of moles of gaseous species in Eq.7.12,

$$p\Delta V = \Delta n_g RT \quad ...(7.13)$$

Using this in Eq. 7.11,

$$q_p = q_V + \Delta n_g RT \quad ...(7.14)$$

or

$$\Delta_r H = \Delta_r U + \Delta n_g RT \quad ...(7.15)$$

The subscript *g* in Δn_g signifies that only the gaseous reactants and products are considered in the calculation of Δn. It may be noted that Δn_g can be

- positive, if the number of moles of gaseous products is more than those of gaseous reactants
- negative, if the number of moles of gaseous reactants is more than those of gaseous products
- zero, if $n_1 = n_2$.

For example, consider the following reactions:

$$H_2(g)+\tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \quad ...(7.16)$$

$$C(\text{graphite})+O_2(g) \rightarrow CO_2(g) \quad ...(7.17)$$

In Eq. 7.16, $\Delta n_g = (0 - (1 + \frac{1}{2})) = -\frac{3}{2}$; there are no gaseous products, but one mole of hydrogen and half a mole of oxygen are present as gaseous reactants.

In Eq.7.17, $\Delta n_g = (1 - 1) = 0$, since there is one mole each of gaseous reactant and product.

Using the above ideas, answer the following SAQ.

SAQ 1

Calculate Δn_g for the following reactions:

i) $NH_3(g) \rightarrow \frac{1}{2} N_2(g)+\frac{3}{2} H_2(g)$

ii) $\frac{1}{2} H_2(g)+\frac{1}{2}Cl_2(g) \rightarrow HCl(g)$

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7.3 STANDARD ENTHALPY OF FORMATION

The standard enthalpy of formation of a compound is the enthalpy change accompanying the formation of one mole of the compound from its elements in their most stable state, all substances being in their standard state (1 bar pressure and any specified temperature). The standard enthalpy of formation is denoted by $\Delta_f H^\circ$. The superscript ° indicates the standard state and the subscript 'f' denotes formation reaction. Although we do not know the absolute enthalpy of the compound, we know its relative enthalpy with respect to the elements from which it is formed. Therefore, we adopt an arbitrary convention that the standard enthalpies of formation of all elements is zero at any specific temperature at 1 bar. If an element shows allotropy or exists in different phases, then the enthalpy is taken as zero for the most stable allotrope or phase. Phosphorus is an exception (yellow phosphorus is taken as standard). As a result of this, the enthalpy of any substance in its standard state is equal to $\Delta_f H^\circ$, the enthalpy change of the reaction in which one mole of the substance is formed from the elements in their standard state. For example, the enthalpy of the reaction:

$C(graphite)+O_2(g) \rightarrow CO_2(g)$ is $\Delta_r H^\circ = -393.5$ kJ mol^{-1}

Thus, we have

$$\Delta_r H^\circ = \Delta_f H^\circ(CO_2) - \Delta_f H^\circ\,(graphite) - \Delta_f H^\circ(O_2)$$
$$= \Delta_f H^\circ(CO_2) - 0 - 0 = \Delta_f H^\circ(CO_2)$$

Therefore, the standard enthalpy of formation for CO_2 is equal to $\Delta_r H^\circ$ which in turn is equal to -393.5 kJ mol^{-1}. If temperature has also to be indicated, then it is shown in the parenthesis. Thus, $\Delta_f H^\circ$ (298.15 K) means standard enthalpy of formation at 1 bar and 298.15 K. Most of the data are available at 298.15 K in thermodynamic tables. Standard enthalpy of formation of some substances are given in Table 7.1.

Earlier the standard state was defined as 1 atmosphere and any specified temperature but IUPAC has now adopted the standard state as 1 bar at any specified temperature. Since 1 atm. is equal to 1.01325 bar, it does not cause much change in $\Delta_f H^\circ$, specially for substances in liquid and solid states.

Table 7.1: Standard Enthalpy of Formation of Some Selected Substances at 298.15 K

Substance	$\Delta_f H^\circ$ (298.15 K) kJ mol^{-1}	Substance	$\Delta_f H^\circ$ (298.15 K) kJ mol^{-1}
$H_2O\,(l)$	−285.8	$H_2O_2\,(l)$	−187.8
$H_2O\,(g)$	−241.6	$N_2H_4\,(l)$	+ 50.6
$CO_2\,(g)$	−393.5	$NO_2\,(g)$	+ 33.2
$NH_3\,(g)$	− 46.1	$N_2O_4\,(g)$	+ 9.2
$CH_4\,(g)$	− 74.81	$NaCl\,(s)$	−411.2
$C_2H_6\,(g)$	− 84.68	$KCl\,(s)$	−436.8
$CH_3OH\,(l)$	−238.7	Glucose (s)	−1268.0
$C_6H_6\,(l)$	+ 49.0		

Calculation of Reaction Enthalpies

It is possible to calculate standard reaction enthalpies using thermodynamic tables such as Table 7.1. The principle is that,

$$\Delta_r H^\circ = (\text{Sum of } \Delta_f H^\circ \text{ values of products}) - (\text{sum of } \Delta_f H^\circ \text{ values of reactants}) \quad ...(7.18)$$

This relationship can be explained using general reaction of the following type:

$$pA + qB \rightarrow rC + sD \quad ...(7.19)$$

where p, q, r and s are the stoichiometric coefficients and A, B, C and D are reactants and products. Let the standard enthalpies of formation of A, B, C and D be represented by $\Delta_f H^\circ(\mathrm{A})$, $\Delta_f H^\circ(\mathrm{B})$, $\Delta_f H^\circ(\mathrm{C})$, and $\Delta_f H^\circ(\mathrm{D})$, respectively. The standard reaction enthalpy for the reaction mentioned in Eq.7.19 is given by,

$$\Delta_r H^\circ = \Big(r\,\Delta_f H^\circ(\mathrm{C}) + s\,\Delta_f H^\circ(\mathrm{D}) \Big) - \Big(p\,\Delta_f H^\circ(\mathrm{A}) + q\,\Delta_f H^\circ(\mathrm{B}) \Big) \qquad \ldots(7.20)$$

Let us illustrate the calculation of $\Delta_r H^\circ$ using an example.

Example 1

For the reaction given in Eq. 7.21 let us calculate $\Delta_r H^\circ$ at 298.15 K.

$$C_3H_6(g) + \tfrac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l) \qquad \ldots(7.21)$$

Given that : $\Delta_f H^\circ$ values of propene, carbon dioxide and water at 298.15 K are 20.42, −393.5 and −285.8 kJ mol^{-1}, respectively.

From Eqs. 7.18 and 7.21,

$$\Delta_r H^\circ = \Big(3\Delta_f H^\circ(CO_2) + 3\Delta_f H^\circ(H_2O) \Big) - \Big(\Delta_f H^\circ(C_3H_6) + \tfrac{9}{2}\,\Delta_f H^\circ(O_2) \Big)$$

$$= 3\times(-393.5) + 3\times(-285.8) - (1\times 20.42)$$

(since the standard enthalpy of formation of oxygen is zero.)

$\Delta_r H^\circ = -2058$ kJ

Hence, we are in a position to calculate $\Delta_r H^\circ$ for a reaction using $\Delta_f H^\circ$ values.

Enthalpy is a state property; its value changes by the same amount irrespective of the path from the reactants to the products. Hence, it is possible to calculate $\Delta_r H^\circ$ of a reaction from a sequence of reactions.

This is generalised as Hess's law of constant heat summation; we shall study this law in the next section.

SAQ 2

Express the standard reaction enthalpy of the reaction,

$$C_2H_6(g) + \tfrac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

in terms of the standard enthalpies of formation of the components

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7.4 HESS'S LAW OF CONSTANT HEAT SUMMATION

Hess's law can be stated as follows:

The standard enthalpy change for a reaction is the sum of standard enthalpies of a sequence of reactions (at the same temperature and pressure); the overall reaction should be capable of being represented by the given sequence of reactions.

Hess's law is a direct consequence of the law of conservation of energy. It is not necessary that every reaction in the given sequence should be conducted in a laboratory. A particular reaction can also be imaginary. The only requirement is that the individual chemical reactions in the sequence must balance and add up to the equation for a particular reaction. Also Hess's law enables arithmetic operations of chemical equations. This law is helpful in calculating enthalpies of reactions which cannot be experimentally determined; what is required is to select a correct sequence of reactions. We give below the use of Hess's law in calculating the enthalpy of conversion of graphite to diamond which is very difficult to determine.

Example 2

$$\mathrm{C(graphite)} + O_2(g) \rightarrow CO_2(g) \qquad \Delta_r H_1 = -393.5\,\mathrm{kJ}$$

$$\mathrm{C(diamond)} + O_2(g) \rightarrow CO_2(g) \qquad \Delta_r H_2 = -395.4\,\mathrm{kJ}$$

Then subtracting, we get

C(graphite) − C(diamond) = 0 and $\Delta_r H = \Delta_r H_1 - \Delta_r H_2 = -393.5\,\mathrm{kJ} - (-395.4\,\mathrm{kJ}) = 1.9\,\mathrm{kJ}$

Hence, we can write

$$\mathrm{C(graphite)} \rightarrow \mathrm{C(Diamond)} \qquad \Delta_r H = 1.9\,\mathrm{kJ}$$

We shall consider many examples of the use of Hess's Law in the next section. Before proceeding to the next section, answer the following SAQ.

SAQ 3

Calculate $\Delta_r H°$ for the reaction.

$C\,(graphite) + \frac{1}{2}\,O_2(g) \rightarrow CO(g)$

at 298 K, using the following thermochemical equations:

$$C(graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta_r H° = -393.5\text{ kJ}$$

$$CO(g) + \tfrac{1}{2}\,O_2(g) \rightarrow CO_2(g) \qquad \Delta_r H° = -283.5\text{ kJ}$$

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7.5 ENTHALPY CHANGES IN DIFFERENT PROCESSES AND REACTIONS

Enthalpy changes take place in almost all physical and chemical processes. Due to their importance in science and engineering, special names have been assigned to enthalpy changes of some such processes. We define below the enthalpy changes for some of these processes.

Enthalpy of Combustion

The change in enthalpy during the complete combustion of one mole of a substance in oxygen is called its enthalpy of combustion ($\Delta_c H°$). The final oxidation products for a compound containing only C, H, O and N are $CO_2(g)$, $H_2O(l)$ and $N_2(g)$; if a compound also contains Cl, Br, I, F, S, P, the final products include the aqueous solutions of HCl, HBr, HI, HF, H_2SO_4 and H_3PO_4 at infinite dilution. Thus, the enthalpies of combustion for methanol and urea are represented by the reactions:

Combustion is the process of burning a substance in excess of oxygen.

$$CH_3OH(l) + 1.5O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta_c H° = -726.1\text{ kJ mol}^{-1}$$

$$CO(NH_2)_2(s) + 1.5O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + N_2(g) \qquad \Delta_c H° = -633.4\text{ kJ mol}^{-1}$$

The enthalpy of combustion is quite useful to determine the enthalpies of formation of those substances which are difficult to measure experimentally. Here again we make use of Hess's law.

Example 3

The enthalpy of combustion for methanol at 298.15 K is -726.1 kJ mol^{-1}. What is its enthalpy of formation? Given: $\Delta_f H°(CO_2) = -393.5$ kJ mol^{-1} and $\Delta_f H°(H_2O) = -285.8$ kJ mol^{-1}.

The combustion reaction of methanol can be written as,

$$CH_3OH(l) + 1.5O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta_c H° = -726.1\text{ kJ mol}^{-1}$$

Using Eq.7.18,

$$\Delta_r H° = \Delta_c H°(CH_3OH) = \Delta_f H°(CO_2) + 2\Delta_f H°(H_2O) - \Delta_f H°(CH_3OH)$$

$$\left(\text{since } \Delta_f H°(O_2) = 0\right)$$

$$\text{Hence, } \Delta_f H°(CH_3OH) = \Delta_f H°(CO_2) + 2\Delta_f H°(H_2O) - \Delta_c H°\left(CH_3OH\right)$$

$$= \left((-393.5) + \left(2\times(-285.8)\right) + 726.1\right)\ \text{kJ mol}^{-1}$$

$$= -239.0\text{ kJ mol}^{-1}$$

It can be seen that it agrees with the value given in Table 7.1.

Enthalpy of Solution

The formation of solution (by dissolution of a solute in a solvent) is also accompanied by heat changes, but these heat changes are dependent not only on the nature of the solute and solvent but also on the composition of the solution. Therefore, the enthalpy change accompanying the complete dissolution of one mole of solute in a definite amount of the solvent so as to give a solution of a specified concentration is defined as the integral enthalpy of solution (or integral heat of solution). As an example, consider the dissolution of 1 mol of NaCl in 200 mol of water as represented by the equation,

$$NaCl\ (s) + 200H_2O\ (l) \rightarrow NaCl\ (200\ H_2O) \qquad \Delta_{soln}H = 5.36\ kJ\ mol^{-1}$$

where $\Delta_{soln}H = 5.36\ kJ\ mol^{-1}$ represents the integral enthalpy of solution. In general, it can be positive or negative depending on the nature of the solute and solvent. A special case of enthalpy of solution arises when a sufficiently large amount of solvent is used so that further dilution does not bring any heat changes. This is defined as the enthalpy of solution at infinite dilution. For aqueous solution, this reaction is represented by,

$$Urea(s) + H_2O(l) \rightarrow Urea\ (aq)$$

The symbol (*aq*) is used to represent an aqueous solution which is so dilute that additional dilution is not accompanied by any heat changes.

In contrast to integral enthalpy of solution, we define a quantity called **differential enthalpy of solution.** This is the enthalpy change when 1 mol of solute is dissolved in a sufficiently large volume of solution of concentration, *c*, so that the final concentration remains almost unchanged. The differential enthalpy of solution depends on the concentration of the solution. It can be calculated from the integral enthalpy of solution.

Another type of enthalpy term often used in solutions is the **enthalpy of dilution,** $\Delta_{dil}U$. This is defined as the enthalpy change when a solution containing one mole of solute at concentration c_1 is diluted by the addition of solvent so that the final concentration is c_2. It is obvious that the enthalpy of dilution depends on both c_1 and c_2.

Enthalpy of Neutralization

The enthalpy of neutralization of an acid is the enthalpy change which accompanies the complete neutralization of a dilute aqueous solution of an acid containing one mole of H^+ ions by a dilute aqueous solution of a base containing one mole of OH^- ions. An example is given below:

$$HCl(aq) + NaOH\ (aq) \rightarrow NaCl\ (aq) + H_2O \qquad \Delta_{neut}H^\circ = -57.3\ kJ\ mol^{-1}$$

It is observed experimentally that the enthalpy of neutralization of strong acids or bases (with strong bases or acids, respectively) is essentially the same (i.e., -57 kJ mol^{-1}). This is because of the fact that strong acids and bases are completely dissociated in their aqueous solutions, and the process of neutralization of strong acids and bases is represented by

$$H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O \qquad \Delta_rH^\circ = -57.3\ kJ\ mol^{-1}$$

Hence, the enthalpy of neutralization of strong acids and bases is the enthalpy of formation of one mole of water from one mole each of H^+ and OH^- ions.

When a weak acid or base is neutralised, the enthalpy of neutralisation deviates from the value of -57.3 kJ mol^{-1}. This is due to the low dissociation of weak acids and bases; a portion of the energy is utilised in the process of dissociation of the weak acids and bases. So far, we defined enthalpies of some processes; let us now study the experimental determination of enthalpy changes.

On the basis of the above material, answer the following SAQ.

SAQ 4

At 298 K, the standard enthalpies of formation of $NO_2(g)$ and $N_2O_4(g)$ are 33.2 and 9.2 kJ mol^{-1}. Calculate the standard enthalpy of the following reaction:

$$N_2O_4\ (g) \rightarrow 2NO_2(g)$$

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7.6 EXPERIMENTAL DETERMINATION OF ENTHALPY OF COMBUSTION

Calorimeters are used for determining the enthalpy changes in various processes. As a matter of fact, calorimetry is the most important experimental technique in thermodynamics and a lot of attention has been devoted to make it very sensitive. At present calorimeters are available which can measure heat and temperature changes accurately. Let us explain here the experimental determination of the enthalpy of combustion.

The enthalpy of combustion is determined using a Bomb Calorimeter (Fig. 7.1).

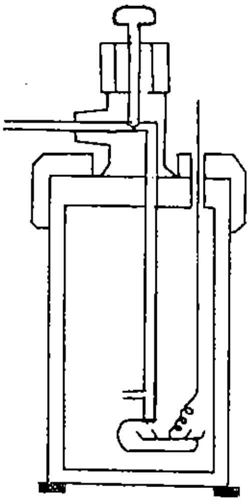

Fig. 7.1: Bomb Calorimeter.

The method consists of the combustion of a definite amount of the substance in an inner vessel called the 'bomb'. The bomb is placed inside a definite quantity of water taken in an outer vessel. The outer vessel is thoroughly insulated. The temperature readings of the water kept in it are measured before and after the combustion using a sensitive thermometer. From the heat capacity of the calorimeter, the amount of the substance taken and the temperature readings, the enthalpy of combustion can be calculated. In general, using adiabatic calorimeters, the enthalpies of reactions can be determined.

7.7 KIRCHHOFF'S EQUATION

For a given reaction, $\Delta_r H$ and $\Delta_r U$ generally vary with temperature. It is of great importance to study these variations quantitatively so that these may be calculated for any temperature from the known values of $\Delta_r H$ and $\Delta_r U$ at any other temperature. The variation of $\Delta_r H$ and $\Delta_r U$ with temperature is described by Kirchhoff's equation. Let us derive this equation.

If C_p is the heat capacity of a substance, then for a temperature rise dT, the increase n enthalpy is given by Eq.6.36 (of Unit 6) as

$$dH = C_p dT \qquad ...(7.22)$$

In the case of enthalpy of a reaction ($\Delta_r H$), we can rewrite Eq.7.22 as,

$$d(\Delta_r H) = \Delta C_p dT \qquad ... (7.23)$$

Where ΔC_p = (sum of C_p values of products) – (sum of C_p values of reactants)

Also, $d(\Delta_r H)$ is the change in enthalpy of reaction due to change in temperature, dT.

Eq. 7.23 on integration gives,

$$\Delta_r H_2 - \Delta_r H_1 = \int_{T_1}^{T_2} \Delta C_p dT \qquad ...(7.24)$$

Where $\Delta_r H_2$ and $\Delta_r H_1$ are the enthalpies of reaction at temperatures T_2 and T_1, espectively. Eq. 7.24 is called Kirchhoff's equation. Similarly we can also obtain he expression,

$$\Delta_r U_2 = \Delta_r U_1 + \int_{T_1}^{T_2} \Delta C_V dT \qquad ...(7.25)$$

Where $\Delta_r U_1$ and $\Delta_r U_2$ are the changes in internal energy of the reaction at temperatures T_1 and T_2, and ΔC_V is the difference in heat capacities between products and reactants at constant volume. Let us now consider three of the special cases of Eq. 7.24:

i) If $\Delta C_p = 0$, then $\Delta_r H_2 = \Delta_r H_1$ implying thereby that the enthalpy of reaction does not change.

ii) If ΔC_p is constant i.e. it does not vary with temperature, then

$$\Delta_r H_2 = \Delta_r H_1 + \Delta C_p\,(T_2 - T_1) \qquad \ldots (7.26)$$

i.e. $\Delta_r H$ either decreases or increases regularly with temperature. For most reactions Eq. 7.26 is valid for a small range of temperatures.

iii) If ΔC_p changes with temperature, then Eq. 7.24 has to be integrated by expressing $\bar{C}_p$ as a function of temperature. The variation in $\bar{C}_p$ is usually expressed in the following way:

$\bar{C}_p^{\bullet} = a + bT + cT^2 + \ldots$; the coefficients a, b, c, ...etc., are characteristic of a particular substance.

Let us work out an example to show the use of Eq. 7.26.

Example 4 : $\Delta_r H$ for the reaction,

$$\mathrm{C\ (graphite) + H_2O\ (}g) \rightarrow \mathrm{CO}(g) + \mathrm{H_2}(g)$$

at 298 K is 131.2 kJ. The $\bar{C}_p$ values are given below in the temperature range, 298 to 348 K.

Substance	$\bar{C}_p$/J mol^{-1} K^{-1}
Graphite	15.93
H_2O (g)	30.04
CO (g)	26.51
H_2 (g)	29.04

Calculate $\Delta_r H$ at 348 K.

The $\bar{C}_p$ values given above are independent of temperature; hence, we can find $\Delta_r H$ at 348 K using Eq. 7.26.

Let us first calculate ΔC_p,

$$\Delta C_p = \left\{ \left[1\times\bar{C}_p(\mathrm{CO}) + 1\times\bar{C}_p(\mathrm{H_2}) \right] - \left[1\times\bar{C}_p\,(\mathrm{graphite}) + 1\times\bar{C}_p(\mathrm{H_2O}) \right] \right\} \mathrm{J\ K^{-1}}$$

(Since one mole of each component appears in the thermochemical equation)

$$= \left\{ (26.51+29.04) - (15.93+30.04) \right\} \mathrm{J\ K^{-1}}$$

$$= 9.58\ \mathrm{J\ K^{-1}}$$

$$\approx 9.58\times10^{-3}\ \mathrm{kJ\ K^{-1}}\ (\text{Remember } 1\mathrm{J} = 10^{-3}\ \mathrm{kJ})$$

$\bar{C}_p$ is usually given in J mol^{-1} K^{-1} units. You should remember to convert it into kJ mol^{-1} K^{-1} (by division by 1000), if ΔH is in kJ mol^{-1} units.

ΔC_p is expressed in kJ K^{-1}, since $\Delta_r H$ at 298 K is given in kJ.

Using Eq. 7.26,

$$\Delta_r H \text{ at } 348\ \mathrm{K} = \Delta_r H \text{ at } 298\ \mathrm{K} + \Delta C_p\,(348-298)$$

$$= (131.2 + 9.58 \times 10^{-3} \times 50)\ \mathrm{kJ}$$

$$= 131.7\ \mathrm{kJ}$$

Using the ideas developed above, work out the following SAQ.

SAQ 5

For the reaction,

$$\mathrm{C(graphite) + H_2O}(g) \rightarrow \mathrm{CO}(g) + \mathrm{H_2}(g)$$

Calculate ΔC_p, if the molar heat capacities at constant pressure for various species vary as per the equation, $\bar{C}_p = a + bT + cT^2$ where $\bar{C}_p$ is in J mol^{-1}K^{-1}. The a, b, and c values of each of the substances are given below:

	a	$b\times10^3$	$c\times10^7$
Graphite	15.93	6.52	0.0
H_2O (g)	30.04	9.920	8.71
CO (g)	26.51	7.68	11.71
H_2 (g)	29.04	−0.836	20.09

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7.8 BOND ENTHALPIES AND ESTIMATION OF ENTHALPIES OF FORMATION

Bond enthalpy is a useful concept in thermochemistry. It finds application in the calculation of standard enthalpy of formation and standard enthalpy of reaction of many compounds.

In a molecule, atoms are linked through chemical bonds. When a molecule decomposes into atoms, the bonds are broken and the enthalpy increases. This is also defined as the enthalpy of atomization, $\Delta_{atom}H$, and is always positive. For example, the enthalpy of the following reaction is the enthalpy of atomization of ethane gas:

$$C_2H_6\,(g) \rightarrow 2C(g)+6H(g) \qquad \Delta_{atom}H=-2828.38 \text{ kJ mol}^{-1}$$

Enthalpy of atomization is the enthalpy change accompanying a reaction in which a molecule is shattered into its component atoms.

On analysis of $\Delta_{atom}H$ for a large number of such reactions, it has been found that specific values of bond enthalpies may be assigned to different types of bonds (Table 7.2). These bond enthalpies correspond to the decomposition of a molecule in the gaseous state to atoms in the gaseous state. Certain substances in the solid state when sublimed are converted into gaseous atoms. Thus, graphite when heated is converted into gaseous atoms, and the heat required for one mole can be called the molar enthalpy of atomization of graphite which is equal to 717 kJ mol^{-1}. If graphite is considered the reference state for carbon, then the atomization can be written as follows:

$$C(\text{graphite}) \rightarrow C(g) \qquad \Delta_{atom}H=717 \text{ kJ mol}^{-1}$$

Enthalpy of atomization of graphite is useful in the calculation of standard enthalpy of formation of organic compounds.

Table 7.2: Bond Enthalpies (B)

Bond	$\frac{B}{\text{kJ mol}^{-1}}$	Bond	$\frac{B}{\text{kJ mol}^{-1}}$	Bond	$\frac{B}{\text{kJ mol}^{-1}}$
H–H	436	C–F	484	C≡C	813
O–H	463	C–Cl	338	N–N	163
C–H	412	C–Br	276	N=N	409
F–F	155	C–I	238	N≡N	945
Cl–Cl	242	C–C	348	O–O	146
Br–Br	193	C=C^a	612	O=O	497
I–I	151	C=C^b	518	F–H	565
		C–O	358	Cl–H	431
		C=O	745	Br–H	366
				I–H	299

a—in alkenes

b—in aromatic compounds

The significance of bond enthalpy in deciding the bond strength has been discussed in Unit 3 of Atoms and Molecules course.

4

The enthalpies of atomization of some more elements which become atomized on sublimation are given in Table 7.3.

Table 7.3 : Standard enthalpies of Atomization at 298.15 K

Substance	$\frac{\Delta_{atom}H^\circ}{\text{kJ mol}^{-1}}$
C (graphite)	717
Na (s)	108
K (s)	90
Cu (s)	339

It should be made clear that bond enthalpy is not bond dissociation energy (as discussed in Unit 3 of Atoms and Molecules course). This could be understood if we consider bond dissociation energy of water:

$$H_2O\,(g) \rightarrow OH\,(g)+H\,(g) \quad D_1=501.9 \text{ kJ mol}^{-1}$$

$$OH\,(g) \rightarrow O(g) + H(g) \quad D_2 = 423.4 \text{ kJ mol}^{-1}$$

The quantities D_1 and D_2 are the first and second bond dissociation energies and are different from the bond enthalpy given for O—H in Table 7.2. Again, bond enthalpy is some kind of average of a large amounts of experimental data. These are of immense value in estimating the standard enthalpy of formation of a large number of compounds being synthesized and also for estimating the standard enthalpy of reactions involving these new molecules.

Bond enthalpy is the average amount of energy required to break one mole of similar bonds present in different gaseous compounds into gaseous atoms.

The following steps will help you in the calculation of standard enthalpy of formation from the bond enthalpies and enthalpies of atomization of elements:

Note that in the place of bond enthalpy, the enthalpy of atomization is used for carbon (graphite) and other elements in the solid state.

i) First write the stoichiometric equation; then write (the most acceptable) Lewis structure of each of the reactants and the product.

ii) Use bond enthalpies from Table 7.2 and enthalpies of atomization from Table 7.3 to calculate the heat required to break all the bonds in the reactants and the heat released when the atoms form the product. The bond enthalpy of X-X bond can be denoted as B(X-X) in arithmetic expressions.

iii) The standard enthalpy of formation
= (Heat required to break all the bonds in the reactants) — (heat released when the atoms form the product) ...(7.27)

iv) Bond enthalpy values can be applied to compounds only if these are in gaseous state; if the compounds are in solid or liquid state, molar enthalpies of sublimation or vaporization also must be considered.

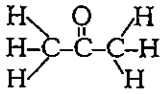
Example 5 : Estimate the standard enthalpy of formation of acetone vapour and acetone liquid. (Enthalpy of vaporization of liquid acetone = 29 kJ mol^{-1})

Step (i) : The stoichiometric equation for the formation of acetone vapour is

$$3H_2(g) + 3C(\text{graphite}) + \tfrac{1}{2}O_2\,(g) \rightarrow C_2H_6CO\,(g) \qquad \text{...(7.28)}$$

In terms of Lewis structures, the equation is given below:

3H−H + 3C + ½O=O →



Step (ii) : The heat required to atomize the reactants

$$= 3B(\text{H−H}) + 3\,\Delta_{\text{atom}}H(\text{graphite}) + \tfrac{1}{2}B\,(\text{O=O})$$
$$= [(3\times436) + (3\times717) + \tfrac{1}{2}(497)]\text{kJ}$$
$$= 3708\,\text{kJ}$$

The heat released when the atoms form the product

$$= 6B(\text{C−H}) + 2B(\text{C−C}) + B(\text{C=O})$$
$$= [(6\times412) + (2\times348) + 745]\,\text{kJ}$$
$$= 3913\,\text{kJ}$$

Step (iii) : $\Delta_f H^\circ(\text{acetone}(g)) = (3708-3913)\ \text{kJ mol}^{-1}$
$= -205\ \text{kJ mol}^{-1}$

Hence the standard enthalpy of formation of acetone vapour is −205 kJ mol^{-1} and, the actual value is −216 kJ mol^{-1}.

Step (iv) : Let us now calculate the standard enthalpy of formation of liquid acetone. The condensation of acetone (l), from acetone (g) can be represented by Eq. 7.29.

Note that for condensation of acetone (g), the enthalpy change

$$= -\,\Delta H^\circ_{\text{vap}}(\text{acetone}) \;= -29\,\text{kJ mol}^{-1}$$

$$C_2H_6CO\,(g) \rightarrow C_2H_6CO\,(l) \qquad \text{...(7.29)}$$

Adding Eqs. 7.28 and 7.29,

$$3H_2\,(g) + 3C(\text{graphite}) + \tfrac{1}{2}O_2\,(g) \rightarrow C_2H_6CO\,(l)$$

Hence, $\Delta_f H^\circ(\text{acetone}\ (l)) = \Delta_f H^\circ\,(\text{acetone}\ (g)) - \Delta H^\circ_{\text{vap}}$ (acetone). So, the standard enthalpy of formation of liquid acetone is −234 kJ mol^{-1}. Using the above principles, answer the following SAQ.

SAQ 6

Calculate the standard enthalpy of formation of hydrogen chloride gas. Use Table 7.2.

....

....

....

7.9 SUMMARY

In this unit, some of the aspects of thermochemistry have been discussed.

- The relationship between $\Delta_r U$ and $\Delta_r H$ has been derived and its use in the calculation of internal energy change and enthalpy change has been indicated.
- Standard enthalpy of formation has been defined; the relationship between standard enthalpies of formation of substances and standard enthalpies of reactions has been explained with an example.
- Hess's law of constant heat summation has been stated and, its use in thermochemical calculations explained.
- Kirchhoff's equation has been derived and used in the calculation of $\Delta_r H$ at a given temperature knowing its value at any other temperature.
- Bond enthalpy values have been used in the calculation of standard enthalpies of formation.

7.10 TERMINAL QUESTIONS

1. For the reaction
   $Fe_2O_3\,(s) + 3H_2\,(g) \rightarrow 2Fe\,(s) + 3H_2O\,(l)$
   $\Delta_r H$ at 298 K is -35.1 kJ. What will be the enthalpy of reaction at 375 K, if the difference between the sum of the C_p's of the products and that of the reactants is 85.7 J K^{-1} and, it is independent of temperature?
2. Using Table 7.1 for the standard enthalpies of formation for $CO_2(g)$ and $H_2O(l)$, calculate the standard enthalpy of formation for naphthalene, if its standard enthalpy of combustion is -5153 kJ mol^{-1}.
3. The standard enthalpy of formation of $H_2O(l)$ at 298 K is -285.8 kJ mol^{-1}. Calculate the standard internal energy change $[\Delta_f U^\circ(H_2O)]$ for the formation of water at 298 K.
4. Calculate the standard enthalpy of formation of $PCl_5(s)$, using the following data:
   $P(s) + 1.5\,Cl_2\,(g) \rightarrow PCl_3\,(l) \qquad \Delta_r H^\circ = -318\,kJ$
   $PCl_3\,(l) + Cl_2\,(g) \rightarrow PCl_5\,(s) \qquad \Delta_r H^\circ = -137\,kJ$
5. Using the C_p data given in SAQ 5, calculate $\Delta_r H$ at 1000 K for the reaction:
   $C\,(graphite) + H_2O(g) \rightarrow CO(g) + H_2(g)$
   $\Delta_r H$ at 298 K is 131.2 kJ. Use the integration formulae given in Sec 6.6 of Unit 6.

7.11 ANSWERS

Self assessment Questions

1. (i) 1 (ii) 0

2. $\Delta_r H^\circ = 2\,\Delta_f H^\circ(CO_2) + 3\Delta_f H^\circ(H_2O) - \Delta_f H^\circ(C_2H_6) - \frac{7}{2}\,\Delta_f H^\circ(O_2)$

3. $C\,(graphite) + O_2\,(g) \xrightarrow{(1)} CO_2(g) \qquad \Delta_r H^\circ = -393.5\,kJ$

   $CO(g) + \frac{1}{2}\,O_2\,(g) \xrightarrow{(2)} CO_2\,(g) \qquad \Delta_r H^\circ = -283.5\,kJ$

   Subtracting (2) from (1) and rearranging, we get

   $C\,(graphite) + \frac{1}{2}\,O_2\,(g) \rightarrow CO\,(g)$
   $\Delta_r H^\circ = (-393.5 + 283.5)\,kJ$
   $\Delta_r H^\circ = -110\,kJ$

4. $\frac{1}{2}N_2(g) + O_2(g) \xrightarrow{(1)} NO_2(g) \qquad \Delta_f H^\circ = 33.2\,\text{kJ mol}^{-1}$

$N_2(g) + 2O_2(g) \xrightarrow{(2)} N_2O_4(g) \qquad \Delta_f H^\circ = 9.2\,\text{kJ mol}^{-1}$

(1) × 2−(2), gives $N_2(g)+2O_2(g)-N_2(g)-2O_2(g) \rightarrow 2NO_2(g)-N_2O_4(g)$

i.e., $N_2O_4(g) \rightarrow 2NO_2(g)$

and $\Delta_r H^\circ = ((2\times 33.2)-9.2)$ kJ

$= 57.2$ kJ

5. $\Delta C_p = C_p(CO) + C_p(H_2) - C_p\,(\text{graphite}) - C_p(H_2O)$

$= (9.58-9.60\times 10^{-3}T + 23.09\times 10^{-7}\,T^2)\ \text{J K}^{-1}$

6. $\frac{1}{2}H_2(g) + \frac{1}{2}2Cl_2(g) \rightarrow HCl(g)$

$\Delta_f H^\circ(HCl) = \frac{1}{2}B(H-H) + \frac{1}{2}B(Cl-Cl) - B(H-Cl)$

$= (\frac{1}{2}(436) + \frac{1}{2}(242) - 431)\ \text{kJ mol}^{-1}$

$= -92\ \text{kJ mol}^{-1}$

Terminal Questions

1. ΔC_p is independent of temperature; hence, we have to use Eq. 7.26 to calculate $\Delta_r H$ at 375 K.

   $\Delta_r H(375\text{ K}) = \Delta_r H(298\text{ K}) + \Delta C_p\,(375-298) = -28.5$ kJ

2. $C_{10}H_8(s) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(l)$

   $\Delta_C H^\circ = -5153\ \text{kJ mol}^{-1}$

   $\Delta_C H^\circ\left(C_{10}H_8\right) = 10\,\Delta_f H^\circ\left(CO_2\right) + 4\,\Delta_f H^\circ\left(H_2O\right) - \Delta_f H^\circ\left(C_{10}H_8\right)$ (because $\Delta_f H^\circ\left(O_2\right) = 0$)

   Rearranging the above equation and substituting the values we get,

   $\Delta_f H^\circ\left(C_{10}H_8\right) = 74.8$ kJ

3. $\Delta n_g = -1.5$ mol, R=8.314 J mol^{-1} K^{-1} and T=298 K;

   $\Delta n_g RT$ is to be divided by 1000 to get the final value in kJ mol^{-1}

   Using Eq. 7.15 we get,

   $\Delta_f U^\circ(H_2O) = -282.1\ \text{kJ mol}^{-1}$

4. Adding the two equations given, we get

   $P(s) + \frac{5}{2}Cl_2(g) \rightarrow PCl_5(s)$

   $\Delta_f H^\circ\left(PCl_5\right) = -455\ \text{kJ mol}^{-1}$

5. Using ΔC_p value (calculated in SAQ 5) in Eq. 7.24,

$$\Delta_r H(1000\text{ K}) = \Delta_r H(298\text{ K}) + \int_{298}^{1000} \Delta C_p \mathrm{d}T$$

$$= \left[\ 131.2 + \frac{1}{1000}\int_{298}^{1000}(9.58-9.60\times 10^{-3}T+23.09\times 10^{-7}T^2)\mathrm{d}T\ \right]\text{kJ}$$

(ΔC_p is divided by 1000 to obtain the value in kJ K^{-1} units)

$$= \left[\ 131.2 + \frac{1}{1000}\left(9.58\int_{298}^{1000}\mathrm{d}T - 9.60\times 10^{-3}\int_{298}^{1000}T\mathrm{d}T + 23.09\times 10^{-7}\int_{298}^{1000}T^2\mathrm{d}T\right)\right]\text{kJ}$$

$$= \left[\ 131.2 + \frac{1}{1000}\left(9.58\,(1000-298) - \frac{9.60}{2}\times 10^{-3}(1000^2-298^2) + \frac{23.09\times 10^{-7}}{3}\times(1000^3-298^3)\right)\right]\text{kJ}$$

$= [131.2 + 3.1]$ kJ $= 134.3$ kJ

UNIT 8 THE SECOND LAW OF THERMODYNAMICS

Structure

8.1 INTRODUCTION

It was seen in Unit 6 that transfer of energy between a system and its surroundings takes place through heat and work. This is governed by the first law of thermodynamics which says that increase in the energy of a system must be accompanied by an equal decrease in the energy of the surroundings and *vice versa*. However, it does not tell us anything about the feasibility and direction of flow of energy. According to the first law of thermodynamics, all processes in which energy is conserved are possible. For example, if a cup of hot tea is left on a table then according to the first law, it may be cooled by transferring energy to the surroundings or be heated by absorbing energy from the surroundings. But we all know from daily experience that the cup of tea will always cool till it acquires the temperature of the surroundings. Similarly, if a bottle of perfume is opened in a room, the perfume spreads throughout the room. The reverse process in which all the perfume vapours are collected in the bottle does not take place. These are examples of what are known as spontaneous processes which are irreversible and proceed only in one direction. Again, according to the first law, there exists a direct relationship between heat and work. But it does not tell us whether heat can be completely transformed into work and if so, what is the effect on the system and the surroundings. These aspects are discussed in this unit.

We shall start this unit with the description of Carnot cycle and calculate the efficiency of Carnot engine. This discussion helps us in arriving at the concept of entropy and thermodynamic scale of temperature. We will also show how entropy changes can be used to distinguish between reversible and irreversible cyclic processes. Based on this discussion, the statements of the second law of thermodynamics will be given. The expressions useful in calculating the entropy changes under different conditions will then be derived. We shall finally discuss the physical meaning of entropy. Based on this unit, we can conclude that all spontaneous changes must be accompanied by entropy increase. In the next unit, we shall examine this aspect in a more detailed way.

Objectives

After studying this unit, you should be able to

- differentiate between reversible and irreversible processes based on the value of q,
- describe Carnot cycle and derive an expression useful in calculating the efficiency of a Carnot engine,
- discuss thermodynamic temperature scale,
- define the term entropy,
- state the second law of thermodynamics,

- calculate the entropy changes for isothermal and nonisothermal processes.
- derive an expression useful in calculating entropy of mixing,
- calculate the entropy changes in phase transitions and chemical reactions, and
- explain the physical meaning of entropy.

8.2 REVERSIBLE, IRREVERSIBLE AND CYCLIC PROCESSES

As already mentioned in Unit 6, all thermodynamic properties are state functions and are independent of the path adopted by the system. Also, the internal energy change of a system is given by Eq. 6.8 as $\Delta U = q + w$. Here ΔU is independent of the path chosen but q and w certainly depend upon it. Thus for the same ΔU, different values of q and w are possible by bringing about the process in different ways. It was also mentioned that the work done by a system is maximum if a reversible path is adopted and this maximum work can be determined from the initial and final states of the system. Let us consider a reversible and an irreversible process in which ΔU is same. No matter how we carry out the process (reversible or irreversible), ΔU depends only upon the initial and final states of the system. Thus

The work done on the system is given the symbol, w. Since work done by the system is obtained by reversing the sign of the work done on the system, work done by the system $= -w$

Work done by the system under reversible conditions $= -w_{rev}$

Work done by the system under irreversible conditions $= -w_{irrev}$

$\Delta U = q_{rev} + w_{rev}$ for reversible process ... (8.1)

and $\Delta U = q_{irrev} + w_{irrev}$ for irreversible process ... (8.2)

and so $q_{rev} + w_{rev} = q_{irrev} + w_{irrev}$ ... (8.3)

We know that the work done **by** a system **under reversible conditions** $(-w_{rev})$ is larger than the work done **by** a system **under irreversible conditions** $(-w_{irrev})$.

i.e., $-w_{rev} > -w_{irrev}$ ... (8.4)

Hence, $w_{rev} < w_{irrev}$ ... (8.5)

The transformation of Eq. 8.4 to Eq. 8.5 becomes clear once we understand the following relationship between numbers:

$-3 > -4$ and
$3 < 4$

This is true when we compare the work done on the system under reversible and irreversible conditions. Let us assume that the driving forces under the two conditions mentioned above are fairly different. Also, let us assume that the processes are not adiabatic so that q_{rev} or q_{irrev} is not equal to zero. Using Eqs. 8.3 and 8.5, we can write,

$q_{rev} > q_{irrev}$ ... (8.6)

This means that in a nonadiabatic process, heat absorbed by a system from the surroundings is more under reversible conditions than under irreversible conditions. This relationship will be used by us in Sec. 8.6 while calculating the entropy changes of isolated systems.

Now let us consider ΔU, q and w values of a system in a cyclic process. As defined in Sec. 6.5 of Unit 6, a cyclic process is one in which the system after undergoing any number of processes returns to its initial state. This means that $\Delta U = 0$; hence, the work done by the system during all these processes should be equal to the heat absorbed by the system.

i.e., $q = q_1 + q_2 + \ldots = -(w_1 + w_2 + \ldots) = -w$ ... (8.7)

where q and w are the heat absorbed and work done on the system in the entire cyclic process consisting of several processes; in the individual processes, q_1, q_2 .... etc., are the heat absorbed by the system and, w_1, w_2 .... etc., are the work done on the system.

Using Example 1 discussed below. you can understand the validity of Eqs. 8.5 and 8.6.

Example 1

1.00×10^2 mol of an ideal gas at 3.00×10^2 K temperature and 6.00×10^6 Pa pressure occupies 4.16×10^{-2} m^3 space initially. Calculate the work done on the gas and the heat absorbed by the gas if it undergoes expansion under the following conditions such that the final volume and pressure are 0.832 m^3 and 3.00×10^5 Pa:

(a) Isothermal reversible conditions (b) isothermal irreversible conditions.

Solution

In an isothermal process, for an ideal gas, $\Delta U = 0$

Hence, using Eq. 6.8, $q = -w$

i.e., Heat absorbed by the gas $= -$(work done on the gas)

This equation is applied for both the processes discussed below.

(a) Let us first calculate q_{rev} and w_{rev} using Eq. 6.18 for the isothermal reversible expansion.

$$q_{rev} = -w_{rev} = -2.303\,nRT\log\frac{V_1}{V_2}$$

$$= 2.303\,nRT\log\frac{V_2}{V_1}$$

$$= 2.303\times1.00\times10^2\,\text{mol}\times8.314\,\text{J mol}^{-1}\,\text{K}^{-1}\times3.00\times10^2\,\text{K}\log\frac{0.832\,\text{m}^3}{4.16\times10^{-2}\,\text{m}^3}$$

$$= 7.47\times10^5\,\text{J}$$

Hence, the heat absorbed by the gas during isothermal reversible expansion (q_{rev}) $= 7.47\times10^5$ J

and the work done on the gas (w_{rev}) $= -7.47\times10^5$ J

(b) Let us calculate q_{irrev} and w_{irrev} for the isothermal irreversible process using Eq. 6.13; in this process, the final pressure of the gas is equal to the external pressure (p_{ext}).

Hence, using Eq. 6.13,

$$\begin{aligned} q_{irrev} = -w_{irrev} &= p_{ext}(V_2-V_1) \\ &= 3.00\times10^5\,\text{Pa}\,(0.832\,\text{m}^3-0.0416\,\text{m}^3) \\ &= 3.00\times10^5\times0.7904\,\text{J} \\ &= 2.37\times10^5\,\text{J} \end{aligned}$$

You can compare q and w values in the above two cases to verify the validity of Eqs. 8.5 and 8.6.

$w_{rev} = -7.47\times10^5$ J; $w_{irrev} = -2.37\times10^5$ J

Hence, $w_{rev} < w_{irrev}$ as per Eq. 8.5.

$q_{rev} = 7.47\times10^5$ J; $q_{irrev} = 2.37\times10^5$ J

Hence, $q_{rev} > q_{irrev}$ as per Eq. 8.6.

8.3 THE CARNOT CYCLE

Carnot analysed the functioning of an engine with the following features:

- The engine works in cycles.
- It absorbs heat from a reservoir known as source.
- It does some work out of the heat absorbed.
- It returns the unused part of the heat to another reservoir, known as sink.
- Finally it returns to its original state.

Such an engine is known as Carnot engine. The temperature of the source (T_H) is higher than that of the sink (T_C). The source and the sink are assumed to be of infinite heat capacity; that is, the temperatures of the source and the sink are not affected by small amounts of heat exchange.

Carnot showed that the entire amount of the heat absorbed cannot be converted into work in a cyclic process, no matter how ideal the heat engine is. He deduced that only a fraction of the total heat absorbed is converted into work and this fraction is known as the efficiency of the Carnot engine. Let us now derive an equation useful in calculating its efficiency.

For the sake of simplicity, let us assume that the engine consists of a cylinder and a piston containing one mole of an ideal gas in between the two. The cylinder has perfectly insulated walls and a perfectly conducting base; the piston is frictionless. It is only for the sake of convenience that we have considered that the engine has ideal gas; actually there can be any suitable fluid. We make use of the following expressions from Unit 6 (for one mole of the gas) in this section.

$$w_{isothermal} = RT\ \ln\frac{V_{initial}}{V_{final}} \qquad \text{(Eq. 6.17)}$$

$$w_{adiabatic} = \bar{C}_V\,(T_{final}-T_{initial}) \qquad \text{(Eq. 6.53)}$$

where w is the work done on the system and $\bar{C}_V$ is the molar heat capacity of the gas.

The plot of the pressure-volume data is shown in Fig. 8.1.

In our discussion on expansion or contraction process, w is the work done on the system and q is the heat absorbed by the system.

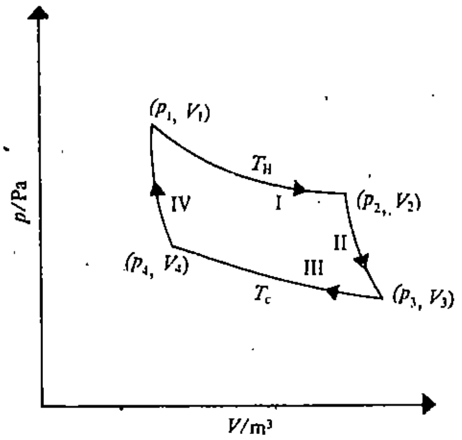


Fig. 8.1 : Carnot cycle.

The Carnot cycle operation can be described by the following four steps: (1) Isothermal expansion (2) Adiabatic expansion (3) Isothermal compression and (4) Adiabatic compression. Let us discuss them one by one.

Step I: Isothermal Expansion

$$T_H \quad \begin{array}{cc} p_1 & V_1 \\ \downarrow & \downarrow \\ p_2 & V_2 \end{array}$$

Initially the gas has pressure p_1 and volume V_1. The cylinder is placed on a heat source maintained at the temperature T_H. The gas is isothermally and reversibly expanded to a volume V_2 and pressure p_2. Let the work done on the gas be w_1 and the heat absorbed from the source be q_H. In an isothermal process, $\Delta U=0$.

Hence, using Eqs. 6.8 and 6.17

$$w_1 = -q_H = RT_H \ \ln \frac{V_1}{V_2} \qquad \text{...(8.8)}$$

$$\text{or} \qquad q_H = RT_H \ \ln \frac{V_2}{V_1} \qquad \text{...(8.9)}$$

The second term on the right hand side of Eq. 8.18 and also the right hand side expressions of Eqs. 8.9, 8.12 and 8.19 are obtained through the transformation based on the general formula:

$$ln \ \frac{a}{b} = -\ln \frac{b}{a}$$

Step II: Adiabatic Expansion

$$\begin{array}{ccc} p_2 & V_2 & T_H \\ \downarrow & \downarrow & \downarrow \\ p_3 & V_3 & T_C \end{array}$$

The cylinder is now placed on a thermally insulated stand and the gas is adiabatically and reversibly expanded till it attains a pressure p_3, volume V_3 and temperature T_C. During this period, no heat is absorbed by the system. The work done on the gas, w_2, as the gas gets cooled from T_H to T_C is given by using Eq. 6.53 as,

$$w_2 = \bar{C}_V (T_C - T_H) \qquad \text{... (8.10)}$$

Step III : Isothermal Compression

$$T_c \quad \begin{array}{cc} p_3 & V_3 \\ \downarrow & \downarrow \\ p_4 & V_4 \end{array}$$

The cylinder is now placed on a sink at temperature T_C and the gas is isothermally and reversibly compressed to a volume V_4 at pressure p_4. During the process the work done on the gas is w_3 and the heat evolved to the sink is $-q_c$ (or q_c is the heat absorbed from the sink).

Using Eqs. 6.8 and 6.17, $w_3 = -q_c = RT_C \ \ln \ V_3 / V_4$ ...(8.11)

$$\text{or } q_c = \ RT_C \ \ln \ \frac{V_4}{V_3} \qquad \text{... (8.12)}$$

Step IV : Adiabatic Compression

$$\begin{array}{ccc} p_4 & V_4 & T_C \\ \downarrow & \downarrow & \downarrow \\ p_1 & V_1 & T_H \end{array}$$

In the last step, the cylinder is again placed on an insulating stand and the gas is adiabatically and reversibly compressed until it reaches its initial state of volume V_1, pressure p_1 and temperature T_H. Hence the work done on the gas, w_4 is given by Eq. 6.53 as,

$$w_4 = \bar{C}_V (T_H - T_C) \qquad \text{...(8.13)}$$

The net work done on the system

$$w. \ = w_1 + w_2 + w_3 + w_4 \qquad \text{...(8.14)}$$

$$\text{or } w \ = RT_H \ln V_1/V_2 + \bar{C}_V (T_C - T_H) + RT_C \ln V_3/V_4 + \ \bar{C}_V (T_H - T_C) \qquad \text{...(8.15)}$$

$$\text{i.e. } w \ = RT_H \ln V_1/V_2 + RT_C \ln V_3/V_4 \qquad \text{...(8.16)}$$

Eq. 6.48 of Unit 6 can be applied to relate the initial and final values of volume and temperature of the two adiabatic processes described in steps II and IV.

Applying Eq. 6.48 to Step II we get,

$$\frac{T_C}{T_H} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

Similarly applying Eq. 6.48 to Step IV, we get,

$$\frac{T_H}{T_C} = \left(\frac{V_4}{V_1}\right)^{\gamma-1} \quad \text{or} \quad \frac{T_C}{T_H} = \left(\frac{V_1}{V_4}\right)^{\gamma-1}$$

Hence, $$\left(\frac{V_2}{V_3}\right)^{\gamma-1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1}$$

i.e., $$\frac{V_2}{V_3} = \frac{V_1}{V_4} \qquad \text{... (8.17)}$$

or $$\frac{V_3}{V_4} = \frac{V_2}{V_1}$$

Using this in Eq. 8.16, $w = RT_H \ln \frac{V_1}{V_2} + RT_C \ln \frac{V_2}{V_1}$

$w = RT_H \ln V_1/V_2 - RT_C \ln V_1/V_2$ ... (8.18)

Hence, total work done on the system $= w = R\,(T_H - T_C) \ln V_1/V_2$

or total work done by the system, $w' = -w = R\,(T_H - T_C) \ln V_2/V_1$ ...(8.19)

since work done by the system $=$ −(work done on the system)

We know that the heat exchange between the gas and the source or sink takes place only in isothermal processes (steps 1 and 3); in adiabatic processes (steps 2 and 4), there is no heat exchange. Again, q_H is the heat absorbed from the source in step 1 and q_C is the heat absorbed from the sink in step 3.

The total heat absorbed by the system is,

$$q = q_H + q_C \qquad \text{... (8.20)}$$

As expected, q turns out to be equal to $-w$ or w' since for the overall cyclic process, $\Delta U = 0$.

Hence, $q = q_H + q_C = w' = -w = R\,(T_H - T_C) \ln V_2/V_1$ ... (8.21)

It may however be noted that out of the heat q_H ($= RT_H \ln V_2/V_1$ as per Eq. 8.9) absorbed from the source, only some of it is converted into useful work and the rest is lost to the sink. Let us now calculate w'/q_H, i.e., the ratio between the total work done by the system during one cycle and the heat absorbed in the first step. This quantity is called the efficiency 'η' of a Carnot engine.

$$\text{Efficiency } (\eta) = \frac{\text{Total work done by the system}}{\text{(Heat absorbed from the source at higher temperature)}} = \frac{w'}{q_H} \qquad \text{... (8.22)}$$

Using Eqs. 8.9 and 8.21,

$$\eta = \frac{q_H + q_C}{q_H} = \frac{R\,(T_H - T_C) \ln V_2/V_1}{R\,T_H \ln V_2/V_1} \qquad \text{...(8.23)}$$

$$\eta = \frac{q_H + q_C}{q_H} = \frac{T_H - T_C}{T_H} \qquad \text{... (8.24)}$$

Since T_C and T_H are always positive and T_C/T_H is less than one, Eq. 8.24 can be rearranged as follows :

$$\eta = 1 - \frac{T_C}{T_H} = 1 + \frac{q_C}{q_H} < 1 \qquad \text{... (8.25)}$$

Since q_C is negative and q_H is positive, $\frac{q_C}{q_H}$ is a negative quantity; $1 + \frac{q_C}{q_H}$ is also less than one.

This means that efficiency is always less than one, i.e., all the heat absorbed at a higher temperature is not converted into work. It is also clear that efficiency will be more if the ratio T_C/T_H is small. Thus, for efficient working of the engine, it should absorb heat at as high a temperature as possible and reject it at as low a temperature as possible. It should also be noted that efficiency is independent of the nature of the fluid. This is called Carnot theorem which can also be stated as:

In all cyclic engines working between the same temperatures of the source and the sink, the efficiency is same.

It must be pointed out that in the Carnot cycle, all processes have been carried out reversibly. Hence, maximum and minimum amount of work are involved in expansion and compression, respectively; this implies that there cannot be any engine more efficient than Carnot engine. In actual engines, there is irreversibility due to sudden expansion and compression and also due to the friction of the piston.

Let us work out an example to show the use of Eq. 8.24.

Example 2
A Carnot engine works between 3.00×10^2 K and 4.00×10^2 K. Calculate its efficiency.

Solution

$$T_H = 4.00 \times 10^2 \text{ K} \qquad T_C = 3.00 \times 10^2 \text{ K}$$

$$\text{Using Eq. 8.24, } \eta = \frac{T_H - T_C}{T_H} = \frac{(4.00 \times 10^2 - 3.00 \times 10^2)\text{ K}}{4.00 \times 10^2 \text{ K}}$$

$$= 0.250$$

Using the data given in this example, answer the following SAQ.

SAQ 1
If the Carnot engine mentioned in Example 2 absorbs 8.00×10^2 J heat from the source, calculate the work done by the engine and the heat rejected to the sink.

8.4 THERMODYNAMIC TEMPERATURE SCALE

For an engine of the type discussed above, both the efficiency and the ratio q_C/q_H can be easily calculated by measurement of the work and heat changes involved. The ratio, q_C/q_H, as shown above, depends only on the temperatures T_C and T_H and are completely independent of the properties of any particular substance. Thus, it is possible to establish a scale of temperature — the absolute or thermodynamic scale — which is not dependent on any particular substance.

We can see from Eq. 8.25, that if $T_C = 0$, $\eta = 1$. We can now define absolute zero as that temperature of the sink at which the efficiency of a Carnot engine will be unity. The size of the degree on this scale is the same as that on the centigrade scale. The kelvin unit is named in honour of Lord Kelvin, who arrived at the thermodynamic scale of temperature based on the properties of reversible heat engines.

8.5 ENTROPY

The efficiency of an engine working on the principle of Carnot cycle is of immense use to engineers; but, its major use in physics and chemistry is in the discussion and understanding of the second law of thermodynamics. It leads to the definition of an important thermodynamic function called **entropy**.

If in a Carnot engine, heat q_2 is absorbed at the higher temperature T_2 and q_1 is absorbed at the lower temperature T_1 (actually q_1 will be a negative quantity since heat is rejected) then, according to Eq. 8.24,

$$\frac{q_2 + q_1}{q_2} = \frac{T_2 - T_1}{T_2} \qquad \ldots (8.26)$$

The following comparison may help you in understanding the transformation of Eq. 8.24 into Eq. 8.26 :

Eq. 8.24	Eq. 8.26
q_H	q_2
q_C	q_1
T_H	T_2
T_C	T_1
$\left(\frac{q_H + q_C}{q_H}\right) = \left(\frac{T_H - T_C}{T_H}\right)$	$\left(\frac{q_2 + q_1}{q_2}\right) = \left(\frac{T_2 - T_1}{T_2}\right)$

or $1+q_1/q_2=1-T_1/T_2$ ... (8.27)

i.e., $q_1/T_1=-q_2/T_2$ ... (8.28)

Hence,

$$\frac{q_1}{T_1}+\frac{q_2}{T_2}=0 \qquad \text{... (8.29)}$$

Thus, the sum of such quantities as obtained by dividing the heat absorbed reversibly by the temperature is zero over a complete Carnot cycle.

Any reversible cyclic process can be broken into a large number of infinitesimal Carnot cycles (as in Fig. 8.2). If in each such small Carnot cycle, heat dq_1 is absorbed at temperature T_1' and dq_2 absorbed at T_2', then for each small Carnot cycle,

$$dq_1/T_1' + dq_2/T_2'=0 \qquad \text{... (8.30)}$$

Summing these over all the cycles we can write in general, sum of $\frac{dq_i}{T_i}$ terms over all the cycles = 0 ...(8.31)

where 'i' stands for an individual process of expansion or contraction in each cycle. Since the summation is continuous, we can replace the summation by integration and have,

$$\oint dq_{rev}/T=0 \qquad \text{... (8.32)}$$

where dq_{rev} is the heat absorbed reversibly at a temperature in an infinitesimal step in the cyclic process and $\oint$ is the integral over a whole cycle.

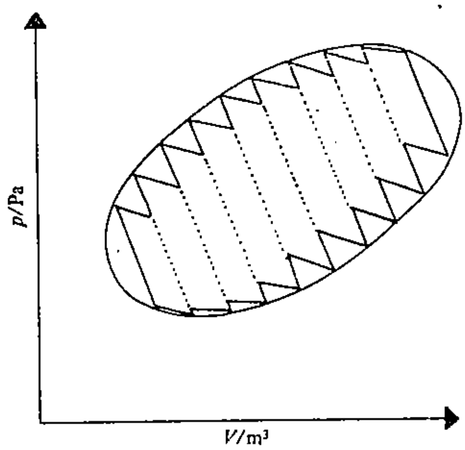


Fig. 8 2 : Infinitesimal Carnot cycles.

Now consider a system going in a reversible manner from an initial state A to an intermediate state B and then back to A via another path (Fig. 8.3). This cyclic process can be broken up into a large number of Carnot cycles. Starting from A and following all these cycles we may reach A once again. The paths inside the figure cancel out each other and only a zigzag path is left. The larger the number of Carnot cycles, the closer will be the resemblance between this zigzag path and the overall path ABA.

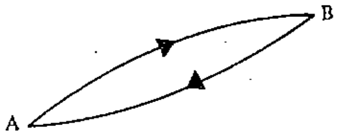


Fig. 8.3 : The cyclic change ABA.

Hence, in the entire cycle,

sum of dq_{rev}/T terms $= \sum dq_{rev}/T = 0$ ... (8.33) where once again dq_{rev} is the heat absorbed reversibly at temperature T in an infinitesimal process. We can break this up into two parts, i.e., one in which we go from A to B and the other in which we go from B to A. Thus,

$$\sum_{\text{Cycle}} dq_{rev}/T = \sum_{A\to B} dq_{rev}/T + \sum_{B\to A} dq_{rev}/T = 0 \qquad \dots (8.34)$$

Or in terms of integrals,

$$\int dq_{rev}/T = \int_A^B dq_{rev}/T + \int_B^A dq_{rev}/T = 0 \qquad \dots (8.35)$$

The symbol, $\sum_{\text{cycle}} \frac{dq_{rev}}{T}$, means summation of $\frac{dq_{rev}}{T}$ terms over the entire circle.

The term $\sum_{A\to B} dq_{rev}/T$ means summation of the $\frac{dq_{rev}}{T}$ terms for the change from A to B.

and so

$$\int_A^B dq_{rev}/T = -\int_B^A dq_{rev}/T \qquad \dots (8.36)$$

Thus, the quantity $\int_A^B dq_{rev}/T$ is not dependent on the path chosen and is only dependent on the initial and final states of the system. This means that it represents a change in some thermodynamic property. This property is called entropy (S), and we write,

$$dq_{rev}/T = dS \qquad \dots (8.37)$$

Thus, $\int dS = 0 \qquad \dots (8.38)$

Also if we represent the entropy of the initial state A as S_A and that of the final state B as S_B, then

$$\Delta S = S_B - S_A = \int_A^B dq_{rev}/T \qquad \dots (8.39)$$

Let us relate the changes in internal energy and enthalpy to entropy change.

If we now put $dq = TdS$ (from Eq. 8.37), $dU = nC_VdT$ (from Eq. 6.26) and $dw = -pdV$ (from Eq. 6.12) in Eq. 6.7, we get Eq. 8.40.

$$dU = dq + dw \qquad \dots (6.7)$$

Hence,

$$dU = n\bar{C}_VdT = TdS - pdV \qquad \dots (8.40)$$

As per Eq. 6.29 of Unit 6,

$$H = U + pV$$

Differentiation of this gives,

$dH = dU + pdV + Vdp$

using Eq. 8.40, $dH = TdS - pdV + pdV + Vdp = TdS + Vdp \qquad \dots (8.41)$

Eqs. 8.40 and 8.41 are the combined mathematical statements of the first and second laws of thermodynamics. The first law of thermodynamics is concerned with the conservation of energy and the second law of thermodynamics introduces the concept of entropy.

It is worth mentioning that the entropy change in a system is given by,

$$dS = \frac{dq_{rev}}{T} \qquad \dots (8.42)$$

This means that the entropy change in a system is to be calculated assuming the process to be reversible, irrespective of the fact that the process is reversible or not. This fact will be highlighted in the next section.

On the basis of the above ideas, answer the following SAQ.

SAQ 2

Calculate the change of entropy when 2.40×10^4 J of heat is transferred reversibly and isothermally to a system at 3.00×10^2 K.

8.6 ENTROPY CHANGES IN ISOLATED SYSTEMS

We are now interested in estimating the entropy change in an isolated system where cyclic processes of isothermal expansion and compression take place. Such cyclic processes can occur in two ways; one in which both expansion and compression are reversible and, another, in which one is irreversible while the other is reversible. Let us consider an isolated system consisting of a cylinder which contains a gas between it and a smooth air tight piston and is placed in a heat reservoir.

Isothermal Reversible Expansion and Reversible Compression
Let the gas (system) undergo isothermal reversible expansion from volume V_1 to V_2 at a temperature T. In this reversible process, the gas absorbs heat, q_{rev}, from the reservoir; the entropy change of the system, ΔS_1, is given by,

$$\Delta S_1 = \frac{q_{rev}}{T} \qquad \ldots (8.43)$$

Since the reservoir also loses heat q_{rev} in a reversible way, the entropy change, ΔS_2, of the reservoir is given by,

$$\Delta S_2 = \frac{-q_{rev}}{T} \qquad \ldots (8.44)$$

The total entropy change of the isolated system, ΔS_a, in this reversible expansion process is given by,

$$\Delta S_a = \Delta S_1 + \Delta S_2 = \frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0 \qquad \ldots (8.45)$$

Let the gas undergo isothermal reversible compression back to its original state. Assume that during this compression, heat lost from the system and the heat gained v the reservoir are both reversible. Then, the total entropy change (ΔS_b) of the 'ated system mentioned above, during reversible compression, is also equal to ro.

$$\Delta S_b = 0 \qquad \ldots (8.46)$$

Hence, ΔS in this cyclic process $= \Delta S_a + \Delta S_b = 0$ ... (8.47)

This means that the total entropy change in a reversible cycle is zero. Let us now see how the entropy changes in a cyclic process involving an irreversible stage.

Isothermal Irreversible Expansion and Reversible Compression
Let the gas undergo isothermal irreversible expansion from a volume V_1 to V_2 at a temperature T. In this process, let us assume that the gas absorbs heat q irreversibly whereas the reservoir loses the same heat reversibly. However, the entropy change of the system (ΔS_1) is still given by Eq. 8.43 as per definition.

The entropy change in a process is calculated by dividing the heat change under reversible condition by temperature, whether or not the process is reversible.

$$\Delta S_1 = \frac{q_{rev}}{T} \qquad \ldots (8.48)$$

But since the reservoir loses heat q reversibly, the entropy change of the reservoir, ΔS_2, is given by,

$$\Delta S_2 = \frac{-q}{T} \qquad \ldots (8.49)$$

Hence the total entropy change of the isolated system, ΔS_a, in this irreversible expansion process is given by,

$$\Delta S_a = \Delta S_1 + \Delta S_2 = \frac{q_{rev}}{T} - \frac{q}{T} > 0 \qquad \ldots (8.50)$$

Since $q_{rev} > q$ as per Eq. 8.6.

Let the gas now undergo isothermal reversible compression such that the heat loss by the system and the heat gain by the surroundings are both reversible. The total entropy change of the isolated system, ΔS_b, in this reversible compression process is given by,

$$\Delta S_b = 0 \qquad \ldots (8.51)$$

Hence, the total entropy change of the isolated system over the whole cycle $= \Delta S_a + \Delta S_b > 0$ ... (8.52)

Hence for any reversible process or cycle $\Delta S_{total} = 0$ ... (8.53)

For any irreversible process or cycle $\Delta S_{total} > 0$ ... (8.54)

In other words, the second law of thermodynamics suggests that the entropy must increase in an irreversible or a spontaneous process. Since all natural processes are irreversible, the entropy of the universe is continuously increasing. The first and the second laws of thermodynamics can be summed up as follows:

The first law	:	Energy of the universe is constant.
The second law	:	Entropy of the universe is tending to a maximum.

The fact that the entropy of an isolated system increases in an irreversible process can be illustrated using Example 3.

Example 3

Assume than an ideal gas undergoes isothermal irreversible expansion and is in contact with a heat reservoir inside an isolated system. Using the data given in Example 1, calculate the entropy change of (a) the gas, (b) the heat reservoir and (c) the isolated system as a whole.

Solution

It is true that the gas expands irreversibly and absorbs heat irreversibly from the heat reservoir. But the heat reservoir (or as a rule, the surroundings always) would lose (or gain) the heat reversibly.

As per Example 1 (b), the heat absorbed by the gas under isothermal irreversible conditions $= 2.37 \times 10^5$ J.

That is, the gas absorbs 2.37×10^5 J **irreversibly** from the heat reservoir. But the heat reservoir loses 2.37×10^5 J **reversibly.**

It is to be remembered that the entropy is a state function and its value is given by dividing the heat change under reversible conditions by temperature.

a) To calculate the entropy change of the gas, we have to consider the heat absorbed if the gas were to expand reversibly. Hence, from Example 1, for q value of the gas, we should use 7.47×10^5 J, which is the heat absorbed under reversible conditions but not 2.37×10^5 J. The temperature of the gas is 3.00×10^2 K.

   Using Eq. 8.43, the entropy change of the gas (ΔS_{gas})

$$= \frac{\text{Heat change under reversible conditions}}{\text{Temperature}}$$

$$= \frac{7.47 \times 10^5 \text{ J}}{3.00 \times 10^2 \text{ K}}$$

$$= 2490 \text{ J K}^{-1}$$

b) The heat reservoir loses 2.37×10^5 J heat reversibly.

   Using Eq. 8.37, the entropy change of the heat reservoir ($\Delta S_{reservoir}$)

$$= \frac{-2.37 \times 10^5 \text{ J}}{3.00 \times 10^2 \text{ K}}$$

$$= -790 \text{ J K}^{-1}$$

   The negative sign is due to loss of heat from the heat reservoir.

c) The total entropy change of the isolated system

$$= \Delta S_{gas} + \Delta S_{reservoir}$$

$$= [(2490) + (-790)] \text{ J K}^{-1}$$

$$= 1700 \text{ J K}^{-1}$$

Hence the entropy of the isolated system increases by 1700 J K^{-1} in this irreversible expansion.

To calculate the entropy change in the universe for a particular process, we should know the entropy change of the system and of the surroundings. We shall study in Secs. 8.8 to 8.11 the ways of calculating the entropy changes in the system. Let us now see how to calculate the entropy change of the surroundings in any particular process.

The surroundings of a system constitute a huge heat reservoir. Hence, the heat loss or gain from the surroundings (q^{surr}) is always considered reversible; this is true whether the system behaves reversibly or irreversibly. Let the temperature of the surroundings be T^{surr}.

$$\left.\begin{array}{l}\text{Hence, the entropy change of the}\\ \text{surroundings}\end{array}\right\} = \frac{q^{surr}}{T^{surr}}$$

This is true for all types of processes.

If a chemical reaction takes place at constant pressure with an enthalpy change, ΔH, then $q^{surr} = -\Delta H$

$$\left.\begin{array}{l}\text{Hence, the entropy change of the}\\ \text{surroundings}\end{array}\right\} = \frac{q^{surr}}{T^{surr}} = \frac{-\Delta H}{T^{surr}}$$

SAQ 3
Calculate the entropy change in the surroundings in the formation of one mole of water from its elements in their standard state at 298.15 K. The standard enthalpy of formation of water is -285.8 kJ mol^{-1}

(**Caution:** This entropy change in the surroundings is not related to the entropy of water or entropy of formation of water; see Example 7 in this unit.)

8.7 STATEMENTS OF THE SECOND LAW OF THERMODYNAMICS

What we have studied so far in this unit can be generalised to obtain the statements of the second law of thermodynamics. Three such statements are given below:

1. The entropy of an isolated system tends to increase and reaches a maximum. This implies that the most stable state of an isolated system is the state of maximum entropy. Since the universe may be considered as an isolated system, it follows that the entropy of the universe always increases.
2. It is impossible to transfer heat from a cold body to a hotter body without doing some work. This was postulated by Clausius.
3. According to Kelvin, it is not possible to take heat from a source (i.e., a hot reservoir) and convert all of it into work by a cyclic process without losing some of it to a colder reservoir.

8.8 ENTROPY CHANGES DURING EXPANSION AND COMPRESSION

In general, the entropy change of the system is defined by the entropy of the final state (B) minus the entropy of the initial state (A). This is equivalent to $\int_A^B \mathrm{d}q_{rev}/T$ which at constant temperature can be written as $\frac{1}{T}\int_A^B \mathrm{d}q_{rev} = q_{rev}/T$, where q_{rev} is the total amount of the heat absorbed reversibly in the process.

Entropy Change in the Isothermal Expansion of an Ideal Gas
If n mol of an ideal gas is isothermally and reversibly expanded from an initial state in which it has pressure p_1 and volume V_1 to the final state of volume V_2 and pressure p_2, then as shown earlier,

$$q_{rev} = -w = nRT \ln V_2/V_1 = nRT \ln p_1/p_2 \quad \ldots (8.55)$$

$$\left.\begin{aligned}\text{and hence, } \Delta S &= q_{rev}/T = nR \ln V_2/V_1 = nR \ln p_1/p_2\\ &= 2.303\, nR \log V_2/V_1 = 2.303\, nR \log p_1/p_2\end{aligned}\right\} \quad \ldots (8.56)$$

Hence, to calculate the entropy change of an ideal gas during isothermal expansion or compression, n, V_1 and V_2 or p_1 and p_2 must be known.

Example 4
1.00 mol of an ideal gas is compressed isothermally and reversibly from 1.00×10^{-2} m^3 to 1.00×10^{-3} m^3. Calculate the entropy change.

Solution

The numerator and denominator in Eq. 8.56 are interchanged along with a sign change, since $V_2 < V_1$.

$$
\begin{aligned}
\text{Using Eq. 8.56, } \Delta S &= -2.303\ nR \log V_1/V_2 \\
&= -2.303 \times 1.00\,\text{mol} \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \log \frac{1.00\times 10^{-2}\,\text{m}^3}{1.00\times 10^{-3}\,\text{m}^3} \\
&= -19.2\,\text{J K}^{-1}
\end{aligned}
$$

Entropy Change During Adiabatic Expansion

An adiabatic expansion involves no heat change which means $\Delta S = 0$ for the system.

Entropy Change of an Ideal Gas when it is Expanded Under Conditions which are not Isothermal

Let n mol of an ideal gas be expanded from an initial state of V_1 and T_1 to a final state of V_2 and T_2. Then according to the first law of thermodynamics (Eq. 6.22),

$$dq_{\text{rev}} = dU + pdV \qquad \ldots (8.57)$$

Using Eq. 6.26, $dU = n\bar{C}_V dT$

Where $\bar{C}_V$ is the molar heat capacity of the gas under constant volume conditions.

According to ideal gas equation, $p = \frac{nRT}{V}$

Using the above two expressions in Eq. 8.57,

$$dq_{\text{rev}} = n\bar{C}_V dT + nRT\, dV/V \qquad \ldots (8.58)$$

$$\text{or } TdS = n\bar{C}_V dT + nRTdV/V$$

$$\text{Hence, } dS = 1/T \left[\, n\bar{C}_V dT + nRT \frac{dV}{V} \,\right] \qquad \ldots (8.59)$$

$$= n\bar{C}_V dT/T + nRdV/V \qquad \ldots (8.60)$$

On integration between the limits $T_1 \rightarrow T_2$, $V_1 \rightarrow V_2$ and $S_1 \rightarrow S_2$,

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} n\bar{C}_V dT/T + \int_{V_1}^{V_2} nRdV/V \qquad \ldots (8.61)$$

Assuming that $\bar{C}_V$ is independent of temperature, we have

$$
\left.
\begin{aligned}
S_2 - S_1 = \Delta S &= n\bar{C}_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \\
&= 2.303\, n \left(\bar{C}_V \log \frac{T_2}{T_1} + R \log \frac{V_2}{V_1}\right)
\end{aligned}
\right\} \qquad \ldots (8.62)
$$

This is the case when we take T and V to be the variable quantities. Since for an ideal gas p, V and T are related by the ideal gas equation, only two of these are independent variables.

Now suppose we consider T and p as the variables. Let them change from T_1 to T_2 and p_1 to p_2 during the process. Then these are related to the initial and final volumes V_1 and V_2 as

$$V_2/V_1 = T_2 p_1 / T_1 p_2 \qquad \ldots (8.63)$$

Hence, from Eq. 8.62, we have

$$
\begin{aligned}
\Delta S &= n\bar{C}_V \ln T_2/T_1 + nR \ln T_2 p_1/T_1 p_2 && \ldots (8.64) \\
\Delta S &= n\bar{C}_V \ln T_2/T_1 + nR \ln T_2/T_1 + nR \ln p_1/p_2 && \ldots (8.65) \\
&= (\bar{C}_V + R)n \ln T_2/T_1 + nR \ln p_1/p_2 && \ldots (8.66)
\end{aligned}
$$

$$\text{Since } \bar{C}_p - \bar{C}_V = R,\ \bar{C}_p = R + \bar{C}_V \qquad \ldots (8.67)$$

$$
\left.
\begin{aligned}
\Delta S &= n\bar{C}_p \ln T_2/T_1 + nR \ln p_1/p_2 \\
&= 2.303\ n(\bar{C}_p \log T_2/T_1 + R \log p_1/p_2)
\end{aligned}
\right\} \qquad \ldots (8.68)
$$

Hence, using Eq. 8.62 or 8.68, we can calculate the entropy change of an ideal gas when its pressure or volume changes due to temperature change. Let us work out an example.

Example 5

1.00 mol of a monoatomic gas initially at 3.00×10^2 K and occupying 2.00×10^{-3} m^3 is heated to 3.25×10^2 K and the final volume is 4.00×10^{-3} m^3. Assuming ideal behaviour, calculate the entropy change for the process.

Solution

For a monoatomic gas $\bar{C}_V = 3/2\,R \;= 3/2 \times 8.314$ J mol^{-1} K^{-1}

$= 12.47$ J mol^{-1} K^{-1}

Using Eq. 8.62, $\Delta S = 2.303\, n(\bar{C}_V \log T_2/T_1 + R \log V_2/V_1)$

$$= 2.303 \times 1.00\,(12.47 \log \frac{3.25\times10^2}{3.00\times10^2} + 8.314 \log \frac{4.00\times10^{-3}}{2.00\times10^{-3}})\ \text{J K}^{-1}$$

$= 6.76$ J K^{-1}.

SAQ 4

Show that under isothermal conditions, Eqs. 8.62 and 8.68 reduce to the form of Eq. 8.56.

8.9 ENTROPY OF MIXING

Suppose that n_1 mol of an ideal gas initially present at pressure p and n_2 mol of another ideal gas also at the same initial pressure p are mixed at a constant temperature so that the total pressure is also p. This is possible by using a vessel of suitable volume. Let the partial pressure of the first gas in the mixture be p_1 and the partial pressure of the other gas be p_2. Then the change in entropy for the first gas from Eq. 8.56 is

$$\Delta S_1 = n_1 R \ln p/p_1 \quad \text{... (8.69)}$$

Similarly for the other gas,

$$\Delta S_2 = n_2 R \ln p/p_2 \quad \text{... (8.70)}$$

The total entropy of mixing, ΔS_{mix}, is hence

$$\Delta S_{mix} = \Delta S_1 + \Delta S_2 = n_1 R \ln p/p_1 + n_2 R \ln p/p_2 \quad \text{... (8.71)}$$

If the mole fractions of the gases in the mixture are x_1 and x_2 respectively, then according to Dalton's law of partial pressures,

Partial pressure of a gas = Total pressure × mole fraction of the gas

Hence, $p_1 = px_1$ and $p_2 = px_2$

$$\Delta S_{mix} = n_1 R \ln p/x_1 p + n_2 R \ln p/x_2 p \quad \text{... (8.72)}$$

$$\Delta S_{mix} = n_1 R \ln 1/x_1 + n_2 R \ln 1/x_2 \quad \text{... (8.73)}$$

$$= 2.303\, n_1 R \log 1/x_1 + 2.303 n_2 R \log 1/x_2$$

$$\text{Hence, } \left.\begin{aligned}\Delta S_{mix} &= 2.303\, R\,(n_1 \log 1/x_1 + n_2 \log 1/x_2)\\ &= -2.303\, R\,(n_1 \log x_1 + n_2 \log x_2)\end{aligned}\right\} \quad \text{... (8.74)}$$

If we know n_1 and n_2, ΔS_{mix} can be calculated. The mole fractions x_1 and x_2 are less than one, since $x_1+x_2 = 1$; as a result of this, $\log 1/x_1$ and $\log 1/x_2$ are positive. Hence, ΔS_{mix} is positive.

Example 6

Calculate the entropy of mixing of 1.00 mol of H_2 with 2.00 mol of O_2 assuming that no chemical reaction occurs.

Solution

$$n_{H_2} = 1.00 \text{ mol}; \quad n_{O_2} = 2.00 \text{ mol}$$

$$x_{H_2} = \frac{n_{H_2}}{n_{H_2}+n_{O_2}} = \frac{1.00 \text{ mol}}{3.00 \text{ mol}} = 0.333$$

Similarly,

$$x_{O_2} = \frac{2.00 \text{ mol}}{3.00 \text{ mol}} = 0.667$$

Using Eq. 8.74, $\Delta S_{\text{mix}} = 2.303\,R\,(n_{H_2} \log \frac{1}{x_{H_2}} + n_{O_2} \log \frac{1}{x_{O_2}})$

$$= 2.303 \times 8.314\,(1.00 \log \frac{1}{0.333} + 2.00 \log \frac{1}{0.667})\,\text{J K}^{-1}$$

$$= 15.88\ \text{J K}^{-1}.$$

On the basis of what you have studied in this section, answer the following SAQ.

SAQ 5

Does the entropy of mixing of ideal gases depend on temperature?
(**Hint:** Examine Eq. 8.74.)

8.10 ENTROPY CHANGES IN PHASE TRANSITIONS

The change of matter from one phase (solid, liquid, gas, allotropic form) into another is called phase transition. Such changes take place at definite temperatures called transition temperatures (melting points, boiling points etc.) at a given pressure. These transitions are accompanied by absorption or evolution of heat (called latent heat). Since absorption or evolution of heat at constant temperature leads to an entropy change, the entropy of transition is given as,

$$\Delta S_{\text{trans}} = q_{\text{rev}}/T = \Delta H_{\text{trans}}/T \qquad \dots (8.75)$$

Eq. 8.75 is valid only when the transition takes place in a reversible manner, i.e., when the two phases are in equilibrium.

Thus, when one mole of a solid melts to the liquid phase, the entropy of fusion is given by

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_f}$$

where T_f is the melting point and ΔH_{fus} is the molar enthalpy of fusion. Similarly,

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_B} \qquad \dots (8.77)$$

where T_B is the boiling point and ΔH_{vap} is the molar enthalpy of vaporization.

It is obvious that the entropy of freezing and condensation (vapour into liquid) will be equal to $-\Delta S_{\text{fus}}$ and $-\Delta S_{\text{vap}}$, respectively.

In a similar manner, we can define the entropy change accompanying the transition of a substance from an allotropic form to another. If such a transition takes place at a temperature T_{trans} and, ΔH_{trans} is the molar enthalpy of transition, then the entropy change accompanying the transition is,

$$\Delta S_{\text{trans}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}} \qquad \dots (8.78)$$

Thus, in phase transitions, ΔS values can be calculated from the corresponding ΔH values.

Using the material given above, answer the following SAQ.

SAQ 6

Calculate the entropy of fusion of benzene solid, if its melting point is 279 K and its enthalpy of fusion is 10.6 kJ mol^{-1}.

8.11 ENTROPY CHANGES IN CHEMICAL REACTIONS

Let us now calculate the entropy change accompanying a general chemical reaction of the type,

$$aA + bB + \dots \rightarrow cC + dD + \dots \qquad \dots (8.79)$$

We define the entropy change for a reaction ($\Delta_r S$) as the difference between the total entropy of the products and the total entropy of the reactants. Thus, if S_A,

S_B....are the entropies of one mole of reactants, A, B, etc., and S_C, S_D...., of the products, C, D, etc., then

$$\Delta_r S = (cS_C + dS_D + \ldots) - (aS_A + bS_B + \ldots) \qquad \ldots (8.80)$$

where c, d, a, b,...etc., are the stoichiometric coefficients in Eq. 8.79.

The variation of entropy change for a reaction with temperature can be readily deduced from Eq. 8.80 by differentiating with respect to temperature at constant pressure. Hence,

$$\left[\frac{\partial(\Delta_r S)}{\partial T}\right]_p = \left[c\left(\frac{\partial S_C}{\partial T}\right)_p + d\left(\frac{\partial S_D}{\partial T}\right)_p + \ldots\right]$$

$$- \left[a\left(\frac{\partial S_A}{\partial T}\right)_p + b\left(\frac{\partial S_B}{\partial T}\right)_p + \ldots\right] \qquad \ldots (8.81)$$

According to Eq. 8.41,

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$$

or

$$\bar{C}_p \mathrm{d}T = T\mathrm{d}S + V\mathrm{d}p$$

At constant pressure ($\mathrm{d}p=0$),

$$\bar{C}_p \mathrm{d}T = T\mathrm{d}S_p$$

or

$$\frac{\mathrm{d}S_p}{\mathrm{d}T} = \frac{\bar{C}_p}{T}$$

or

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{\bar{C}_p}{T}$$

$\bar{C}_p$ is the molar heat capacity of a substance at constant pressure.

Using the above result in Eq. 8.81,

$$\left[\frac{\partial(\Delta_r S)}{\partial T}\right]_p = \frac{[c\bar{C}_p(\mathrm{C}) + d\bar{C}_p(\mathrm{D}) + \ldots] - [a\bar{C}_p(\mathrm{A}) + b\bar{C}_p(\mathrm{B})\ldots]}{T} \qquad \ldots (8.82)$$

$$\left[\frac{\partial(\Delta_r S)}{\partial T}\right]_p = \Delta C_p / T \qquad \ldots (8.83)$$

where ΔC_p is the difference between the heat capacities of the products and reactants at constant pressure.

or

$$\mathrm{d}(\Delta_r S) = \Delta C_p \frac{\mathrm{d}T}{T} \qquad \ldots (8.84)$$

Assume that $\Delta_r S_1$ and $\Delta_r S_2$ are the entropy changes at temperatures T_1 and T_2 and, ΔC_p is independent of temperature. Then Eq. 8.84 on intagration gives,

$$\int_{\Delta_r S_1}^{\Delta_r S_2} d(\Delta_r S) = \Delta C_p \int_{T_1}^{T_2} \frac{\mathrm{d}T}{T} \qquad \ldots (8.85)$$

or

$$\Delta_r S_2 - \Delta_r S_1 = \Delta C_p \ln T_2/T_1 \qquad \ldots (8.86)$$

Eq. 8.86 is useful in determining $\Delta_r S$ value of a reaction at any particular temperature, if it is known at any other temperature along with C_p values.

The standard states of the substances will be defined in the next unit.

Entropy values of substances can be determined using the third law of thermodynamics; we shall study this in the next unit. The entropy values of some of the substances in their standard states at 298.15 K are given in Table 8.1. These are known as standard entropy ($S°$) values. Similar to the calculation of $\Delta_r S$ as per Eq. 8.80, we can calculate $\Delta_r S°$ from the standard entropy values of the reactants and the products.

Table 8.1 : Standard Entropy (S°) values at 298.15 K

Substance	S°/J K^{-1}mol^{-1}	Substance	S°/J K^{-1}mol^{-1}
C(graphite)	5.7	$C_6H_6(l)$	173.3
C(diamond)	2.4	He(g)	126.2
AgCl(S)	96.2	$H_2(g)$	130.7
AgBr(s)	107.1	$Cl_2(g)$	223.1
Ag(s)	42.6	$CO_2(g)$	213.7
Hg(l)	76.0	$O_2(g)$	205.1
$Br_2(l)$	152.2	$CH_4(g)$	186.3
$H_2O(l)$	69.9		

Example 7

Calculate the standard entropy of formation of $H_2O(l)$ at 298.15 K using Table 8.1.

Solution

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$

The standard entropy of formation of water ($\Delta_f S^\circ$ (H_2O)) can be calculated using Eq. 8.80. Note that the substances are in their standard states at 298.15 K; hence S° values are used instead of S.

$$\begin{aligned}\Delta_f S^\circ (H_2O) &= S^\circ (H_2O)-(S^\circ (H_2) + \tfrac{1}{2} S^\circ (O_2))\\ &= \left[69.9-(130.7+(\tfrac{1}{2}\times 205.1))\right] \text{J K}^{-1}\end{aligned}$$

Since one mole of water is formed,

$$\Delta_f S^\circ (H_2O) = -163.4 \text{ J mol}^{-1} \text{ K}^{-1}$$

SAQ 7

i) Calculate the entropy change of the system for the combustion of one mole of methane gas at 298.15 K; use Table 8.1.

ii) Calculate the entropy change of the surroundings for the combustion of one mole of methane gas at 298.15 K, if the molar enthalpy of combustion of methane is -8.90×10^5 J mol^{-1}.

8.12 PHYSICAL MEANING OF ENTROPY

From the macroscopic point of view, the definition of entropy as per the second law of thermodynamics is enough to define the direction in which a system will move in a spontaneous process. However, we are now interested in knowing what exactly goes on the microscopic level within the system. Let us look into the total internal energy of a system. This internal energy is, no doubt, the sum of the kinetic energies (translational, vibrational and rotational) and potential energies of all the molecules in the system. For a given total energy of a system in a definite macroscopic state, however, there can be a large number of microscopic states (Ω), each corresponding to a different distribution of the same amount of energy amongst molecules. Then entropy is quantitatively related to Ω as follows:

$$S=k \ln \Omega \qquad \text{... (8.87)}$$

where k is the Boltzmann constant. Obviously, larger the value of Ω, larger will be the entropy of the system. The simplest case will be the one in which all the molecules have zero kinetic energy and are located in a definite orientation in a crystal lattice. Then, there is only one microscopic state and hence, entropy will be zero. This has been found to be so for a large number of substances at the absolute zero of temperature. Exceptions are there in the case of CO and N_2O molecules, as these substances do not have a perfectly crystalline structure at absolute zero of temperature. As the temperature increases, the molecules gain kinetic energy and, a certain amount of disorder or randomness creeps into the system resulting in an increase in Ω and, hence, in the entropy. Thus entropy is related to disorder which, in turn, is defined in terms of Ω.

Such an interpretation of entropy provides a suitable explanation for entropy changes in various processes. In the isothermal expansion of an ideal gas, although the energy remains constant, entropy increases. This is due to more disorder as a result of an increment in the space in which the molecules can move. In a similar way, the mixing of two ideal gases at a given temperature again leads to increase of disorder and hence, the entropy of mixing is positive. Heating a substance increases the range of molecular velocities thereby enhancing disorder. Fusion is associated with the destruction of the highly ordered structure of a solid; the evaporation results in the formation of the highly chaotic gaseous phase. Thus, both these processes involve an increase in the entropy of the system.

An interesting experimental observation is that the entropy of vaporization of a large number of substances is 85 J mol^{-1} K^{-1}. This is known as Trouton's rule (discussed in Sec. 4.6 of Unit 4 of this course). This is understandable because the conversion of liquid into vapour introduces about the same magnitude of disorder. However, Trouton's rule is not perfect since in water, ammonia and acetic acid, the molecules exist in the associated form due to hydrogen bonding in the liquid phase and their conversion into vapour involves a much greater entropy change.

In the next unit, we will describe a procedure under the third law of thermodynamics to calculate the entropy of substances. It is worth relating entropy values to the disorderliness in the molecular arrangement. The magnitudes of entropy values given in Table 8.1 indicate that the entropies of gases (except hydrogen and the noble gases) are generally larger than those of solids or liquids composed of particles of similar size. This is evidently due to the disorderly arrangement of molecules in gases as compared to those in solids or liquids. The metallic bonding in silver and mercury accounts for their low entropy values. The orderly arrangement due to hydrogen bonding can be a responsible factor for the low entropy value of water. The orderly arrangement of carbon atoms in tetrahedral structure in diamond as against the loosely held layers present in graphite explains the lower entropy value of diamond than graphite.

The reaction entropies can also be related to structural changes. In Example 7, we calculated the standard entropy of formation of water to be -163.4 J mol^{-1} K^{-1}. The negative value is due to (i) the formation of a liquid with more orderly structure from the gaseous molecules which are in chaotic motion and (ii) the decrease in the number of molecules as we proceed from the reactants to the products.

8.13 SUMMARY

In this unit, we described the second law of thermodynamics and the concept of entropy. We started the unit indicating the main aspects of reversible, irreversible and cyclic processes. We then described Carnot cycle and derived an equation for calculating its efficiency. Using this equation, the concept of entropy was arrived at. The expressions were derived for calculating the entropy changes in different physical processes. The method of calculation of entropy changes in chemical reactions was indicated towards the end of the unit. Also, the physical meaning of entropy was discussed.

8.14 TERMINAL QUESTIONS

1. If the efficiency of a Carnot engine is 20% and the temperature of the sink is 3.00×10^2 K, calculate the temperature of the source.

2. A Carnot engine works between 5.00×10^2 K and 3.00×10^2 K. Calculate the minimum amount of heat that must be absorbed by the engine from the source at 5.00×10^2 K in order to obtain 1.50 kJ of work.

3. (a) 2.80×10^{-2} kg of nitrogen at 415 K has an initial pressure of 1.50×10^6 Pa. It is isothermally and reversibly expanded such that its final pressure is 1.00×10^5 Pa. Calculate the entropy change in the process.

   (b) Also, assuming that the process is irreversible calculate the entropy change.

(**Hint:** Assume that the gas expands against an external pressure of 1×10^5 Pa.)

4. Assuming that air is made up of 80% nitrogen and 20% oxygen only, calculate the entropy of mixing of nitrogen and oxygen to form two moles of air at 298 K.

5. Calculate the standard entropy of formation of $CO_2(g)$ at 298.15 K. Use Table 8.1.

6. Calculate the entropy of vaporization of water at 373 K, if the molar enthalpy of vaporization of water is 40.6 kJ mol^{-1}. Does it follow Trouton's rule?

8.15 ANSWERS

Self Assessment Questions

1. Using Eq. 8.22, work done by the engine = Efficiency of the engine × heat absorbed from the source

$$= (0.250\times 8.00\times 10^2)\ \mathrm{J}$$
$$= 2.00\times 10^2\ \mathrm{J}$$

Heat rejected to the sink ($-q_C$) can be calculated using Eq. 8.25.

$$\eta = 0.250 = 1 + \frac{q_C}{q_H}$$
$$\therefore \frac{q_C}{q_H} = -0.75$$
$$q_C = -0.75\, q_H = -0.75\times 8.00\times 10^2\ \mathrm{J}$$
$$= -6.00\times 10^2\ \mathrm{J}$$
$$\text{Heat rejected to the sink} = -q_C = 6.00\times 10^2\ \mathrm{J}$$

2. Using Eq. 8.42, entropy change

$$= \frac{\text{Heat transferred reversibly}}{\text{Temperature}}$$
$$= \frac{2.40\times 10^4\ \mathrm{J}}{3.00\times 10^2\ \mathrm{K}} = 80\ \mathrm{J\,K^{-1}}$$

3. $\Delta H = \Delta_f H^\circ\ (H_2O) = -285.8$ kJ mol^{-1}; hence for one mole of water, $\Delta H = -285.8$ kJ
$q^{surr} = -\Delta H = 285.8$ kJ

$$\text{Hence, } \Delta S \text{ for the surroundings} = \frac{q^{surr}}{T^{surr}} = \frac{285.8\times 10^3\ \mathrm{J}}{298.15\ \mathrm{K}}$$
$$= 958.6\ \mathrm{J\,K^{-1}}$$

4. Under isothermal conditions, $T_1 = T_2$; hence $\log T_2/T_1 = 0$. The first term in the right hand side of Eqs. 8.62 and 8.68 becomes zero. Hence, under isothermal conditions, Eqs. 8.62 and 8.68 take the form of Eq. 8.56.

5. The entropy of mixing of ideal gases does not depend on temperature; Eq. 8.74 does not have a temperature term.

6. Using Eq. 8.76, ΔS_{fus}

$$= \frac{\Delta H_{fus}}{T_f} = \frac{10600\ \mathrm{J\,mol^{-1}}}{279\ \mathrm{K}}$$
$$= 38.0\ \mathrm{J\,mol^{-1}\,K^{-1}}$$

7. (i) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Standard entropy change for the combustion of methane

$$= S^\circ(CO_2) + 2S^\circ(H_2O) - (S^\circ(CH_4) + 2S^\circ(O_2))$$
$$= [213.7 + (2\times 69.9) - (186.3 + (2\times 205.1))]\ \mathrm{J\,K^{-1}}$$
$$= -243\ \mathrm{J\,K^{-1}}$$

Hence, entropy change of the system

$$= \Delta_r S^\circ \text{ for the combustion of methane}$$
$$= -243\ \mathrm{J\,K^{-1}}$$

(ii) Entropy change of the surroundings

$$= \frac{q^{\text{surr}}}{T^{\text{surr}}}$$

But $q^{\text{surr}} = -(\Delta H$ for the combustion of one mole of methane)
$= 8.90\times10^5$ J

$$\text{Hence, } \Delta S \text{ for the surroundings } = \frac{q^{\text{surr}}}{T^{\text{surr}}} = \frac{8.90 \times 10^5 \text{ J}}{298.15 \text{ K}}$$
$$= 2990 \text{ J K}^{-1}$$

Terminal Questions

1. Since the efficiency is 20%, $\eta = 0.2$

   Using Eq. 8.25, $\eta = 1 - \frac{T_C}{T_H} = 0.2$

   $$\frac{T_C}{T_H} = 0.8 \text{ or } T_H = \frac{T_C}{0.8} = \frac{3.00\times10^2 \text{ K}}{0.8}$$
   $$= 375 \text{ K}$$

2. Using Eq. 8.24, $\eta = \frac{T_H - T_C}{T_H} = \frac{(5.00\times10^2 - 3.00\times10^2)\text{K}}{5.00\times10^2 \text{ K}} = 0.400$

   Using Eq. 8.22, heat absorbed from the source $= \frac{\text{Work done}}{\eta}$

   $$= \frac{1.50 \text{ kJ}}{0.4}$$
   $$= 3.75 \text{ kJ}$$

3. a) $n = \frac{\text{Mass of nitrogen}}{\text{Molar mass}} = \frac{2.80 \times 10^{-2} \text{ kg}}{2.80 \times 10^{-2} \text{ kg mol}^{-1}} = 1.00 \text{ mol}$

   Using Eq. 8.56, $\Delta S = 2.303\times1.00 \text{ mol}\times8.314 \text{ J mol}^{-1} \text{ K}^{-1} \log\frac{1.50\times10^6 \text{ Pa}}{1.00 \times 10^5 \text{ Pa}}$

   Hence, ΔS for the reversible process $= 22.5$ J K^{-1}

   b) Whether the process is conducted reversibly or irreversibly, the entropy change is same, since entropy is a state property.
   Hence, ΔS for the irreversible process $= 22.5$ J K^{-1}

4. Total number of moles of air = 2
   Hence $n_{N_2} = 2.0\times0.8 \text{ mol} = 1.6 \text{ mol}$
   $n_{O_2} = 2.0 \times 0.2 \text{ mol} = 0.4 \text{ mol}$
   $x_{N_2} = 0.8$ and $x_{O_2} = 0.2$

   Using Eq. 8.74, $\Delta S_{\text{mix}} = 2.303 \times 8.314 \left(1.6 \log\frac{1}{0.8} + 0.4 \log\frac{1}{0.2}\right) \text{ J K}^{-1}$

   $$= 8.3 \text{ J K}^{-1}$$

5. C (graphite) + O_2 (g) → CO_2 (g)

   $\Delta_f S^\circ (CO_2) = S^\circ (CO_2) - \left[S^\circ \text{(graphite)} + S^\circ (O_2)\right]$

   $= \left\{213.7 - \left[5.7 + 205.1\right]\right\} \text{ J K}^{-1} \text{ mol}^{-1}$

   $= 2.9 \text{ J K}^{-1} \text{ mol}^{-1}.$

6. $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_B} = \frac{40.6\times10^3 \text{ J mol}^{-1}}{373 \text{ K}}$
   $= 109 \text{ J mol}^{-1} \text{ K}^{-1}.$

ΔS_{vap} for water is more than that predicted by Trouton's rule. As compared to other liquids, the increase in disorderliness is more when (hydrogen bonded) water molecules are vaporized.

UNIT 9 FREE ENERGY FUNCTIONS

Structure

9.1 INTRODUCTION

In Units 6 and 7, we studied the application of the first law of thermodynamics in calculating the enthalpy and internal energy changes of the reactions. Such energy calculations do not tell us whether a given reaction is feasible or not. In Unit 8, the concept of entropy was introduced through the second law of thermodynamics; we studied that the total entropy value of the system and the surroundings can help us in deciding the spontaneity of a reaction. But the main difficulty is that it is not always possible to estimate the entropy change of the surroundings.

In this unit, we will introduce two more thermodynamic quantities known as Gibbs free energy (G) and Helmholtz free energy (A). We shall also discuss the importance of the Gibbs free energy change (ΔG) in predicting whether a given process (physical or chemical) will occur spontaneously or not. We shall derive Maxwell relations and state their applications. We shall then arrive at Gibbs-Helmholtz equation and Clausius-Clapeyron equation. We shall also explain the applications of these two equations. We shall then examine the criteria for spontaneity. We shall illustrate the utility of the Gibbs free energy of formation of substances in calculating the reaction free energies. We shall study at length the chemical potential and other partial molar quantities. Finally we shall explain the third law of thermodynamics and discuss its application in calculating the entropies of the substances.

Objectives

After studying this unit, you should be able to:

- distinguish between spontaneous and nonspontaneous processes,
- define Helmholtz free energy (A) and Gibbs free energy (G),
- Calculate ΔA and ΔG for different processes,
- derive Maxwell relations,
- derive Gibbs-Helmholtz equation,
- explain the significance of Clausius-Clapeyron equation,
- explain the criteria for spontaneity,
- define chemical potential and other partial molar quantities,
- derive Gibbs-Duhem equation, and,
- state and explain the third law of thermodynamics.

9.2 SPONTANEOUS AND NONSPONTANEOUS PROCESSES

In this section, we will explain how spontaneous and nonspontaneous processes differ. Let us try to understand what a spontaneous process is. We know that

i) water flows down the hill spontaneously

ii) a gas expands spontaneously into vacuum

iii) heat is conducted spontaneously from the hot end of a metal bar to the colder end until the temperature of the bar is same throughout

iv) a gas diffuses spontaneously into another gas.

Any process which can take place without the application of external force is a spontaneous process. All natural processes are spontaneous. Thermodynamic definition of a spontaneous process is given in Sec. 9.8.

But the reverse of the above changes does not occur spontaneously. All natural processes occur spontaneously. Thus we can define that a spontaneous or a natural process occurs in a system by itself. No external force is required to make the process continue. On the other hand a nonspontaneous process will not occur unless some external force is continuously applied. A chemist is always interested to know whether, under a given set of conditions, a reaction or a process is feasible or not. According to the second law of thermodynamics, $\mathrm{d}S \geqslant \frac{\mathrm{d}q}{T}$, in which the equality refers to a system undergoing a reversible process and the inequality refers to an irreversible process. For an isolated system for which $\mathrm{d}q = 0$, the above equation is reduced to $\mathrm{d}S \geqslant 0$. In an isolated system, an irreversible change is always spontaneous. This is because in such systems, no external force can interact with the system. Thus, the tendency of entropy of an isolated system to increase can be used as a criterion for a spontaneous change. Is this always true? Let us examine this question. Water freezes to crystalline ice spontaneously at 263 K. Ice is in a more ordered state than water and the entropy decreases in freezing. How do we explain the above process? The answer to this question lies in the fact that we must always consider the total entropy change, *i.e.*, the entropy change of the universe. This entropy change is equal to the sum of the entropy changes of the system and the surroundings.

$$\Delta S_{\text{Total}} = \Delta S_{\text{Universe}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}} \quad \text{.... (9.1)}$$

Eq. 9.1 is very difficult to apply for testing the spontaneity of a process. This is so since for evaluating the total entropy change, we have to evaluate ΔS for the surroundings also. In many cases, such calculations are extremely difficult and sometimes not even practical. Therefore, it will be advantageous if we can redevelop the criteria for spontaneity in such a manner that only changes in the properties of the system are considered. For this purpose, we define two energy functions called Helmholtz free energy and Gibbs free energy in the next section.

SAQ 1

Explain why the change in entropy in a system is not always a suitable criterion for spontaneous change?

9.3 HELMHOLTZ FREE ENERGY AND GIBBS FREE ENERGY

Helmholtz free energy (A) and Gibbs free energy (G) are defined by the expressions:

$$A = U - TS \quad \text{... (9.2)}$$

and $$G = H - TS \quad \text{... (9.3)}$$

since $$H = U + pV$$

$$G = U + pV - TS \quad \text{... (9.4)}$$

A (denoting Helmholtz free energy) comes from the German word, *Arbeit*, which means work.

Since U, H, p, S, V and T are state functions, A and G are also dependent only on the state of the system. In simpler words, a system in a given state has definite values of A and G. In the next section we shall derive equations useful in calculating changes in A and G at constant temperature.

Physical significance of A and G

Differentiating Eq. 9.2, we obtain

$$dA = dU - TdS - SdT \quad \ldots (9.5)$$

At constant temperature ($dT = 0$), we have

$$dA = dU - TdS \quad \ldots (9.6)$$

We know (from Unit 8, Eq. 8.37) that for a reversible process

$$TdS = dq_{rev}$$

Also Eq. 6.7 for a reversible process gives

$$dU = dq_{rev} + dw_{rev}$$

Substituting the values for TdS and dU in Eq. 9.6, we obtain,

$$dA = (dq_{rev} + dw_{rev}) - dq_{rev}$$

or $$dA = dw_{rev} \quad \ldots (9.7)$$

or $$-dA = -dw_{rev} \quad \ldots (9.8)$$

Since the process is carried out reversibly, $-dw_{rev}$ represents the maximum work done by the system. This is an important conclusion which states that the change in Helmholtz free energy is equal to the amount of reversible work done on the system, or decrease in Helmholtz free energy ($-dA$) is the maximum amount of work that can be obtained from the system ($-dw_{rev}$) during the given change. As a result, the function A is sometimes also referred to as the work function.

In a similar way, the differentiation of Eq. 9.4 yields,

$$dG = dU + pdV + Vdp - SdT - TdS \quad \ldots (9.9)$$

At constant temperature ($dT = 0$) and pressure ($dp = 0$), Eq. 9.9 is reduced to

$$dG = dU + pdV - TdS \quad \ldots (9.10)$$

Once again if the process is carried out reversibly, using Eq. 6.7 ($dU = dq_{rev} + dw_{rev}$) and $TdS = dq_{rev}$, we obtain from Eq. 9.10

$$dG = dq_{rev} + dw_{rev} + pdV - dq_{rev}$$

or $$dG = dw_{rev} + pdV \quad \ldots (9.11)$$

Now dw_{rev} consists of expansion work ($-pdV$) and some other kind of work called the useful or the net work dw_{net} done on the system. Replacing dw_{rev} by $-pdV + dw_{net}$ in Eq. 9.11, we obtain,

$$dG = -pdV + dw_{net} + pdV$$

or $$dG = dw_{net} \quad \ldots (9.12)$$

or $$-dG = -dw_{net} \quad \ldots (9.13)$$

Thus decrease in Gibbs free energy ($-dG$) is a measure of the maximum useful work that can be obtained from the system at constant temperature and pressure. Most experiments in the laboratory are carried out under such conditions. So the property G or the change associated with it (ΔG) is very important.

SAQ 2

What is the physical significance of decrease in Gibbs free energy?

9.4 CHANGES IN A AND G

When a system goes from state 1 to state 2 at constant temperature, the change in A can be obtained from Eq. 9.6 by integration between the limits $A_1 \rightarrow A_2$, $U_1 \rightarrow U_2$ and $S_1 \rightarrow S_2$.

$$\int_{A_1}^{A_2} dA = \int_{U_1}^{U_2} dU - T\int_{S_1}^{S_2} dS$$

or $$A_2 - A_1 = U_2 - U_1 - T(S_2 - S_1)$$

or $$\Delta A = \Delta U - T\Delta S \quad \ldots (9.14)$$

The change in G when a system goes from a state 1 to state 2 can be obtained by integrating Eq. 9.10 at constant temperature and pressure between the limits $G_1 \rightarrow G_2$, $U_1 \rightarrow U_2$, $V_1 \rightarrow V_2$ and $S_1 \rightarrow S_2$.

$$\int_{G_1}^{G_2} dG = \int_{U_1}^{U_2} dU + p\int_{V_1}^{V_2} dV - T\int_{S_1}^{S_2} dS$$

or $$G_2-G_1 = U_2-U_1 + p(V_2-V_1) - T(S_2-S_1)$$

or $$\Delta G = \Delta U + p\Delta V - T\Delta S$$

We know that at constant pressure, $\Delta U + p\Delta V = \Delta H$ (Eq. 6.32)

Hence, $$\Delta G = \Delta H - T\Delta S \quad \ldots (9.15)$$

Example 1

For the reaction,

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Calculate ΔG at 7.00×10^2 K. The entropy and enthalpy changes at 7.00×10^2 K are respectively, -1.45×10^2 J mol^{-1} K^{-1} and -1.13×10^2 kJ mol^{-1}

Solution

$$\begin{aligned}
\Delta H &= -1.13\times10^2 \text{ kJ mol}^{-1} \\
\Delta S &= -1.45 \times 10^2 \text{ J K}^{-1}\text{ mol}^{-1} = -1.45\times10^2 \times 10^{-3} \text{ kJ K}^{-1}\text{ mol}^{-1} \\
&= -1.45 \times 10^{-1} \text{ kJ K}^{-1}\text{ mol}^{-1} \\
T &= 7.00 \times 10^2 \text{ K} \\
\Delta G &= \Delta H - T\Delta S \\
\text{or} \quad \Delta G &= (-1.13\times10^2 \text{ kJ mol}^{-1}) - 7.00\times10^2 \text{ K} (-1.45\times10^{-1} \text{ kJ K}^{-1}\text{ mol}^{-1}) \\
&= -1.13 \times 10^2 \text{ kJ mol}^{-1} + 1.015 \times 10^2 \text{ kJ mol}^{-1} \\
&= -0.115 \times 10^2 \text{ kJ mol}^{-1} \\
&= -11.5 \text{ kJ mol}^{-1}
\end{aligned}$$

Variation of *A* and *G* with Temperature

From Eq. 9.5,

$$dA = dU - TdS - SdT$$

Since $TdS = dq$

$$dA = dU - SdT - dq \quad \ldots (9.16)$$

Substituting from the first law of thermodynamics,

$dU = dq - pdV$ in Eq. 9.16, we have

$$dA = dq - pdV - SdT - dq$$

or $$dA = -pdV - SdT \quad \ldots (9.17)$$

From Eq. 9.17 at constant volume ($dV=0$), we have

$$(\partial A)_V = -S(\partial T)_V$$

or $$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \ldots (9.18)$$

At constant temperature ($dT=0$), Eq. 9.17 is reduced to

$$(\partial A)_T = -p(\partial V)_T$$

or $$\left(\frac{\partial A}{\partial V}\right)_T = -p \quad \ldots (9.19)$$

Equations similar to Eqs. 9.18 and 9.19 can be obtained in the case of Gibbs free energy. From Eq. 9.9 we have

$$dG = dU + pdV + Vdp - SdT - TdS$$

Since $dq = TdS$ from second law of thermodynamics and $dU = dq - pdV$ from first law of thermodynamics,

$$dG = dq - pdV + pdV + Vdp - SdT - dq$$

or $$dG = Vdp - SdT \quad \ldots (9.20)$$

At constant pressure ($dp=0$), Eq. 9.20 is reduced to

$$(\partial G)_p = -S(\partial T)_p$$

or $$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \ldots (9.21)$$

At constant temperature ($dT=0$), we have from Eq. 9.20,

$$(\partial G)_T = V(\partial p)_T \quad \ldots (9.22)$$

or $$\left(\frac{\partial G}{\partial p}\right)_T = V \quad \ldots (9.23)$$

If G_1 and G_2 are the free energies of the system in the initial and the final states, respectively, then at constant temperature, the free energy change (ΔG) is given by integrating Eq. 9.22.

$$\Delta G = \int_{G_1}^{G_2} dG = \int_{p_1}^{p_2} V dp$$

Where p_1 and p_2 are the initial and the final pressures, respectively.

For n mol of an ideal gas

$$pV = nRT \text{ or } \quad V = \frac{nRT}{p}$$

$$\therefore \Delta G = \int_{p_1}^{p_2} nRT \frac{dp}{p} = nRT \int_{p_1}^{p_2} \frac{dp}{p} \quad \dots (9.24)$$

$$= nRT \ln \frac{p_2}{p_1} = 2.303\, nRT \log \frac{p_2}{p_1}$$

Since pressure is inversely proportional to volume for an ideal gas at constant temperature, we have,

$$\therefore \Delta G = 2.303\, nRT \log \frac{p_2}{p_1} = 2.303\, nRT \log \frac{V_1}{V_2} \quad \dots (9.25)$$

Example 2

Calculate the free energy change which occurs when 1.00 mol of an ideal gas expands reversibly and isothermally at 3.10×10^2 K from an initial volume of 5.00×10^{-2} m^3 to 1.00 m^3.

Solution

$n = 1.00$ mol $\quad T = 3.10 \times 10^2$ K

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

$V_1 = 5.00 \times 10^{-2}$ m^3 $\quad V_2 = 1.00$ m^3

$$\Delta G = 2.303\, nRT \log \frac{V_1}{V_2}$$

$$= 2.303 \times 1.00 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.10 \times 10^2 \text{ K} \log \frac{5.00\times10^{-2} \text{ m}^3}{1.00 \text{ m}^3}$$

$$= (5.94 \times 10^3 \log \frac{1}{20}) \text{ J}$$

$$= -(5.94\times10^3 \log 20) \text{ J}$$

$$= -7.72 \text{ kJ}$$

SAQ 3

From the first and second laws of thermodynamics derive the following relations:

i) $\left(\frac{\partial A}{\partial T}\right)_V = -S$

ii) $\left(\frac{\partial G}{\partial p}\right)_T = V$

A state function depends only on the state of the system. It does not depend on the history of the system or how that state has been achieved.

$dU = dq - pdV$
For a reversible process,
$dq = TdS$
Hence, $dU = TdS - pdV$

9.5 THE MAXWELL RELATIONS

So far we have learnt about the five functions U, H, S, A and G which are state functions and extensive variables. The various expressions useful in estimating the changes in the above functions in a closed system in terms of temperature, pressure, volume and entropy may be written as

$$dU = TdS - pdV \quad \dots (8.40)$$

$$dH = TdS + Vdp \quad \dots (8.41)$$

$$dA = -SdT - pdV \quad \text{from Eq. 9.17}$$

$$dG = -SdT + Vdp \qquad \text{from Eq. 9.20}$$

At constant volume ($dV = 0$), Eq. 8.40 becomes

$$(\partial U)_V = T\,(\partial S)_V$$

$$\text{or } \left(\frac{\partial U}{\partial S}\right)_V = T \qquad \ldots (9.26)$$

and at constant entropy ($dS = 0$), Eq. 8.40 becomes

$$(\partial U)_S = -p\,(\partial V)_S$$

$$\text{or } \left(\frac{\partial U}{\partial V}\right)_S = -p \qquad \ldots (9.27)$$

$H = U + pV$,
$dH = dU + pdV + Vdp$
But $dU + pdV = dq = TdS$
Hence, $dH = TdS + Vdp$

Differentiating Eq. 9.26 with respect to volume at constant entropy and Eq. 9.27 with respect to entropy at constant volume, we get

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_S$$

$$\text{and } \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial p}{\partial S}\right)_V$$

Since U is a state function, it follows that

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$$

$$\text{or } \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad \ldots (9.28)$$

U is a thermodynamic function and dU is a total differential (see the Appendix for the explanation). The change in U with respect to both V and S is same whether we change U with respect to V first, keeping S constant and then with respect to S, keeping V constant, or vice versa. Also see Eqs. 9.77 and 9.78 in sec. 9.10.

Following the same mathematical procedure as described above, the following expressions can be easily derived:

$$\text{From Eq. 8.41, } \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \qquad \ldots (9.29)$$

$$\text{From Eq. 9.17, } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \ldots (9.30)$$

$$\text{From Eq. 9.20, } \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad \ldots (9.31)$$

Eqs. 9.28 to 9.31 are known as Maxwell relations. The Maxwell relations are important because they equate the rate of change of a particular quantity (which cannot be determined experimentally) with the rate of change of volume, pressure or temperature (which can be determined experimentally).

9.6 GIBBS-HELMHOLTZ EQUATION

The dependence of Gibbs free energy on temperature can be expressed in several ways. Starting from the definition (Eq. 9.3),

$$G = H - TS$$

$$\text{or} \qquad -S = \frac{G-H}{T}$$

Substituting the expression for $-S$ in Eq. 9.21, we obtain,

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G-H}{T} \qquad \ldots (9.32)$$

Sometimes it is important to know the variation of G/T on temperature. By differentiating G/T with temperature at constant pressure, we obtain

$$\left[\frac{\partial (G/T)}{\partial T}\right]_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{1}{T^2}G \qquad \ldots (9.33)$$

Substituting the value of $\left(\frac{\partial G}{\partial T}\right)_p$ from Eq. 9.32 into Eq. 9.33, we get

$$\left[\frac{\partial(G/T)}{\partial T}\right]_p = \frac{G-H}{T^2} - \frac{1}{T^2}G$$

Hence, $$\left[\frac{\partial(G/T)}{\partial T}\right]_p = \frac{G-H-G}{T^2}$$

or $$\left[\frac{\partial(G/T)}{\partial T}\right]_p = -\frac{H}{T^2} \qquad \dots (9.34)$$

Eq. 9.34 is known as Gibbs-Helmholtz equation and it can be put in another form by remembering that $d(1/T) = -(\frac{1}{T^2})\,dT$; so on replacing ∂T in Eq. 9.34 by $-T^2\,\partial\,(\frac{1}{T})$, we have

$$\left[\frac{\partial(G/T)}{-T^2\partial(1/T)}\right]_p = -\frac{H}{T^2}$$

or $$\left[\frac{\partial(G/T)}{\partial\,(1/T)}\right]_p = H \qquad \dots (9.35)$$

Similar equation for Helmholtz free energy can also be derived in the form

$$\left[\frac{\partial\,(A/T)}{\partial T}\right]_V = -\frac{U}{T^2} \qquad \dots (9.36)$$

and $$\left[\frac{\partial(A/T)}{\partial\,(1/T)}\right]_V = U \qquad \dots (9.37)$$

The dependence of Gibbs free energy on temperature can be expressed in another way also. Suppose that G_1 is the Gibbs free energy for a system in the initial state and at temperature T. Let the temperature change to $T + dT$ and the corresponding value of free energy to $G_1 + dG_1$.

The terms, $\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$ and $\left[\frac{\partial(\Delta A)}{\partial T}\right]_V$, are the temperature coefficients of ΔG and ΔA at constant pressure and volume, respectively. The temperature coefficient of a particular parameter tells us how that parameter varies with respect to temperature.

If $\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$, for example, is

(i) positive, it means ΔG increases with increasing temperature; and
(ii) negative, it means ΔG decreases with increasing temperature.

Also, $$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = \left[\frac{\Delta G_2-\Delta G_1}{T_2-T_1}\right]_p$$

where ΔG_2 and ΔG_1 are the free energy changes at temperatures, T_2 and T_1.

Similarly for the final state of the system, let the Gibbs free energies be G_2 and $G_2 + dG_2$ at temperatures T and $T + dT$, respectively. At constant pressure, Eq. 9.20 reduces to

$$(\partial G)_p = -S(\partial T)_p \qquad \dots (9.38)$$

and so $$(\partial G_1)_p = -S_1(\partial T)_p \qquad \dots (9.39)$$

and $$(\partial G_2)_p = -S_2(\partial T)_p \qquad \dots (9.40)$$

Where S_1 and S_2 are the entropies of the system in the initial and the final states, respectively. Subtraction of Eq. 9.39 from Eq. 9.40 gives

$$(\partial G_2-\partial G_1)_p = -S_2\,(\partial T)_p-(-S_1\,(\partial T)_p)$$

or $$[\partial(G_2-G_1)]_p = -(S_2-S_1)(\partial T)_p$$

or $$[\partial(\Delta G)]_p = -\Delta S\,(\partial T)_p \qquad \dots (9.41)$$

i.e., $$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = -\Delta S \qquad \dots (9.42)$$

As per Eq. 9.15

$$\Delta G = \Delta H - T\,\Delta S = \Delta H + T\,(-\Delta S) \qquad \dots (9.15)$$

Substituting Eq. 9.42 in Eq. 9.15 we have

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p \qquad \dots (9.43)$$

Eq. 9.43 is also known as Gibbs-Helmholtz equation and is applicable for any process, reversible or irreversible, since the values of ΔG and ΔH depend only on the initial and final states of the system. For a reaction at constant volume, similar equation for Helmholtz free energy can be derived in the form

$$\Delta A = \Delta U + T\left[\frac{\partial(\Delta A)}{\partial T}\right]_V \qquad \dots (9.44)$$

The Gibbs-Helmholtz equation permits the calculation of ΔU or ΔH provided ΔA or ΔG and their respective temperature coefficients,

$$\left[\frac{\partial(\Delta A)}{\partial T}\right]_V \quad \text{or} \quad \left[\frac{\partial(\Delta G)}{\partial T}\right]_p \quad \text{are known}$$

Example 3

The free energy change ΔG for a particular process is -121.00 kJ mol^{-1} at 298 K and 117.00 kJ mol^{-1} at 308 K. Calculate the enthalpy change for the process at 303 K.

Solution

$$\Delta G \text{ at } 298 \text{ K} = -121.00 \text{ kJ mol}^{-1}$$

$$\Delta G \text{ at } 308 \text{ K} = -117.00 \text{ kJ mol}^{-1}$$

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = \frac{(\Delta G_{308} - \Delta G_{298})}{(308-298)\text{ K}} = \frac{[(-117.00 \text{ kJ mol}^{-1}) - (-121.00 \text{ kJ mol}^{-1})]}{(308-298)\text{ K}}$$

$$= \frac{+4.00 \text{ kJ mol}^{-1}}{10 \text{ K}} = 4.00 \times 10^{-1} \text{ kJ mol}^{-1} \text{ K}^{-1}$$

At 303 K, the value of ΔG may be taken as the average of the values at 298 K and 308 K.

$$\text{Hence, } \Delta G \text{ at } 303 \text{ K} = \frac{-117.00 \text{ kJ mol}^{-1} - 121.00 \text{ kJ mol}^{-1}}{2}$$

$$= -119.00 \text{ kJ mol}^{-1}$$

Substituting the values in the Gibbs-Helmholtz equation

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$$

$$-119.00 \text{ kJ mol}^{-1} = \Delta H + 303 \text{ K} \times 4.00 \times 10^{-1} \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$= \Delta H + 121.20 \text{ kJ mol}^{-1}$$

$$\Delta H = -121.20 \text{ kJ mol}^{-1} - 119.00 \text{ kJ mol}^{-1} = -240.20 \text{ kJ mol}^{-1}$$

When applied to chemical reactions, the Gibbs-Helmholtz equation will take the following form:

Initial state (Reactants) → Final state (Products)

Free energy $\quad G_i \quad\quad G_f$

Eq. 9.34 applies to both the initial and final states, i.e.,

$$\left[\frac{\partial(G_i/T)}{\partial T}\right]_p = -\frac{H_i}{T^2} \quad \text{and} \quad \left[\frac{\partial(G_f/T)}{\partial T}\right]_p = -\frac{H_f}{T^2}$$

Subtracting we get,

$$\left[\frac{\partial}{\partial T}\left(\frac{G_f}{T} - \frac{G_i}{T}\right)\right]_p = -\left(\frac{H_f}{T^2} - \frac{H_i}{T^2}\right)$$

$$\text{or} \quad \left[\frac{\partial(\Delta G/T)}{\partial T}\right]_p = -\frac{\Delta H}{T^2} \qquad \dots (9.45)$$

The above equation is important because from the knowledge of enthalpy of reactions we can predict whether increase in temperature will favour the reaction in one direction or other.

9.7 CLAUSIUS-CLAPEYRON EQUATION

From Eq. 9.30 we have

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

The above equation can be applied to any closed system consisting of two phases of the same substance in equilibrium with each other. Let us consider a closed system in which a pure liquid and its vapour are in equilibrium with each other.

$$\text{A (liquid)} \rightleftharpoons \text{A (vapour)}$$

The vapour pressure of the liquid (A) depends upon the temperature but is independent of the volume of the liquid and the vapour.
Hence,

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\mathrm{d}p}{\mathrm{d}T} \qquad \dots (9.46)$$

When one mole of the liquid is vaporized isothermally and reversibly in such a way that during the process, the liquid and the vapour remain in equilibrium, the increase in enthalpy is equal to the molar enthalpy of vaporization (ΔH_{vap}). Since the process is reversible, it follows from Eq. 8.77,

$$\Delta S = \frac{\Delta H_{\text{vap}}}{T} \qquad \dots (9.47)$$

where T is temperature.

Let the increase in volume and entropy during the vaporization of one mole of liquid be ΔV and ΔS, respectively. Then we have at constant temperature (using Eq. 9.47),

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\Delta S}{\Delta V} = \frac{\Delta H_{\text{vap}}}{T\Delta V} \qquad \dots (9.48)$$

Comparing Eqs. 9.30, 9.46 and 9.48, we have

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\text{vap}}}{T\Delta V} \qquad \dots (9.49)$$

Eq. 9.49 was first deduced by Clapeyron (1834) and is known as Clapeyron equation. It was later extended by Clausius (1850). Eq. 9.49 was derived for a system consisting of liquid and vapour in equilibrium. The same equation can, however, be derived for equilibrium between any two phases such as, solid and liquid, solid and vapour, two crystalline forms of the same substance etc. For a system consisting of water in the two phases, liquid and vapour, in equilibrium with each other,

$$\text{Water (liquid)} \rightleftharpoons \text{Water (vapour)}$$

Eq. 9.49 can be written as,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\text{vap}}}{T(V_g - V_l)} \qquad \dots (9.50)$$

Where

ΔH_{vap} = Molar enthalpy of vaporization of water
V_g = Molar volume of water vapour at temperature T
V_l = Molar volume of liquid water at temperature T

For a system consisting of ice at its melting point, the two phases in equilibrium are ice and liquid water.

$$\text{Water (ice)} \rightleftharpoons \text{Water (liquid)}$$

Eq. 9.49 may be written as

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\text{fus}}}{T(V_l - V_s)} \qquad \dots (9.51)$$

Where

ΔH_{fus} = Molar enthalpy of fusion of ice
V_s = Molar volume of water in the solid (ice) state
V_l = Molar volume of water in the liquid state

In the liquid $\rightleftharpoons$ vapour equilibrium, Clausius assumed that the molar volume of a liquid is much less than the molar volume of its vapour; hence $V_g - V_l$ can be ta approximately as V_g. Eq. 9.50 may be written as,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\text{vap}}}{TV_g} \qquad \dots (9.52)$$

Assuming that the vapour behaves ideally,

$$V_g = RT/p \qquad \dots (9.53)$$

Substituting for the volume V_g in Eq. 9.52, we have

$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{T} \times \frac{p}{RT} = \frac{\Delta H_{vap}\, p}{RT^2} \qquad \dots (9.54)$$

Eq. 9.54 is known as Clausius-Clapeyron equation and can be rewritten as,

$$\frac{dp}{p} = \frac{\Delta H_{vap}}{R} \times \frac{dT}{T^2} \qquad \dots (9.55)$$

Eq. 9.55 can be integrated between limits $p_1 \rightarrow p_2$ and $T_1 \rightarrow T_2$, assuming that ΔH_{vap} remains constant over a small range of temperature.

$$\int_{p_1}^{p_2} \frac{dp}{p} = \frac{\Delta H_{vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \qquad \dots (9.56)$$

$$\text{or} \quad \ln \frac{p_2}{p_1} = \frac{-\Delta H_{vap}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \qquad \dots (9.57)$$

$$\text{or} \quad 2.303 \log \frac{p_2}{p_1} = \frac{\Delta H_{vap}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \qquad \dots (9.58)$$

$$\text{or} \quad \log \frac{p_2}{p_1} = \frac{\Delta H_{vap}}{2.303\, R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \qquad \dots (9.59)$$

This is the integrated form of Clausius-Clapeyron equation.

The left hand side of Eq. 9.56 is integrated using formula 2 of Sec. 6.6 of Unit 6. The right hand side of Eq. 9.56 is integrated using formula 1 of Sec. 6.6. Substitute, $x_1 = T_1$, $x_2 = T_2$, $x = T$, $m = -2$ and $a = \frac{\Delta H_{vap}}{R}$ in that formula.

$$\frac{\Delta H_{vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} = \frac{\Delta H_{vap}}{R} \int_{T_1}^{T_2} T^{-2}\, dT$$

$$= \frac{\Delta H_{vap}}{R} \left[-T^{-1} \right]_{T_1}^{T_2}$$

$$= \frac{-\Delta H_{vap}}{R} \left[\frac{1}{T} \right]_{T_1}^{T_2}$$

$$= \frac{-\Delta H_{vap}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

The applications of Clausius-Clapeyron equation are given below:

1. If the vapour pressures of a liquid at two different temperatures are known, then its molar enthalpy of vaporization can be calculated using Eq. 9.59.
2. If the vapour pressure of a liquid at any one temperature is known, then that at another temperature can be calculated using Eq. 9.59.
3. Eq. 9.59 can also be used for calculating the effect of pressure on the boiling point of a liquid.

Example 4

Calculate the vapour pressure of water at 298 K. Molar enthalpy of vaporization of water at its normal boiling point is 4.10×10^4 J mol^{-1}.

Solution

The standard pressure is 1.00×10^5 pa and the boiling point of water at this pressure (known as its normal boiling point) is 373 K.

$p_1 = ?$
$T_1 = 298$ K
$R = 8.314$ J mol^{-1} K^{-1}
$\Delta H_{vap} = 4.10 \times 10^4$ J mol^{-1}

$p_2 = 1.00 \times 10^5$ pa
$T_2 = 373$ K

Substituting these values in Clausius-Clapeyron equation (Eq. 9.59).

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{vap}}{2.303\, R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{1.00 \times 10^5 \text{ Pa}}{p_1} = \frac{4.10 \times 10^4 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \frac{(373 \text{ K} - 298 \text{ K})}{373 \text{ K} \times 298 \text{ K}}$$
$$= 1.445$$

or $\log 1.00 \times 10^5 - \log p_1 = 1.445$
or $5.00 - \log p_1 = 1.445$
or $\log p_1 = 5.00 - 1.445 = 3.555$
or p_1 = Antilog of $3.555 = 3.59 \times 10^3$ Pa

SAQ 4

Ether boils at 306 K at 1.00×10^5 Pa pressure. At what temperature will it boil at a pressure of 9.85×10^3 Pa? Given that the molar enthalpy of vaporization of ether is 2.74×10^4 J mol^{-1}.

9.8 CRITERIA FOR SPONTANEITY

We have seen in Sec. 9.2 that entropy can be used as a criterion for determining the spontaneity of a process. We can also express the criteria for spontaneity in terms of other thermodynamic properties, namely U, H, A and G.

Internal Energy Change as a Criterion for Spontaneity

From the first law of thermodynamics, we know

$dq = dU - dw$ (true for irreversible or reversible process)

and since $dq_{rev} = TdS$ (as per Eq. 8.37)

$TdS = dU - dw$ (for a reversible process)

For an irreversible process, $dq_{irrev} < dq_{rev}$ (as per Eq. 8.6)

Hence, $dq_{irrev} < TdS$.

So, for an irreversible process, $dU - dw < TdS$

or $TdS > dU - dw$

Thus for any process.

$TdS \geqslant dU - dw$

or $TdS \geqslant dU + (-dw)$

If we consider only the pressure-volume work ($dw = -pdV$), then

$TdS \geqslant dU + pdV$

Subtracting TdS from both sides, $0 \geqslant dU + pdV - TdS$

or $dU + pdV - TdS \leqslant 0$ ... (9.60)

i.e., for a process to be feasible, the condition given in Eq. 9.60 must hold good. At constant volume ($dV = 0$) and entropy ($dS = 0$), Eq. 9.60 thus reduces to

$(\partial U)_{V,S} \leqslant 0$ ... (9.61)

According to Eq. 9.61 when the volume and entropy remain constant, the internal energy of a system remains constant in a reversible process $[(\partial U)_{v,s} = 0]$, whereas in an irreversible process the internal energy decreases $[(\partial U)_{V,S} < 0]$.

Enthalpy Change as a Criterion for Spontaneity

We know that $H = U + pV$

Differentiating the above expression, we get

$dH = dU + pdV + Vdp$

Since from first law, $dU = dq + dw$

$dH = dq + dw + pdV + Vdp$

Considering only pressure-volume work done on the system, we can write as per Eq. 6.14, $dw = -pdV$; we then have

$dH = dq - pdV + pdV + Vdp$

or $dH = dq + Vdp$

or $dH - Vdp = dq$ (true for both reversible and irreversible processes). For a reversible process $dq_{rev} = TdS$ and, for an irreversible process $dq_{irrev} < TdS$.

Thus we have for any process

$dH - Vdp \leqslant TdS$ ... (9.62)

At constant pressure ($dp = 0$) and constant entropy ($dS = 0$)

Eq. 9.62 reduces to

$(\partial H)_{p,S} \leqslant 0$ ... (9.63)

According to Eq. 9.63, when the pressure and entropy remain constant, the enthalpy of a system remains constant in a reversible process $[(\partial H)_{p,S} = 0]$, whereas in an irreversible process the enthalpy decreases $[(\partial H)_{p,S} < 0]$.

Helmholtz Free Energy change as a Criterion for Spontaneity

From $A = U - TS$ we have

$dA = dU - TdS - SdT$

Since $dU = dq + dw$

$dA = dq + dw - TdS - SdT$

$dA - dw + TdS + SdT = dq$ (true for both reversible and irreversible processes)

Since $dq_{rev} = TdS$ and $dq_{irrev} < TdS$

$dA - dw + TdS + SdT \leqslant TdS$

or $dA - dw + SdT \leqslant 0$ (cancelling TdS from both the sides)

Considering only pressure-volume work done on the system, ($dw=-pdV$), we have

or $dA+pdV+SdT \leqslant 0$

At constant volume ($dV=0$) and constant temperature ($dT=0$), the above form reduces to,

$$(\partial A)_{T,V} \leqslant 0 \qquad \dots (9.64)$$

According to Eq. 9.64, when the temperature and volume remain constant, the Helmholtz free energy of a system remains constant in a reversible process $[(\partial A)_{T,V}=0]$, whereas in an irreversible process the Helmholtz free energy decreases $[(\partial A)_{T,V} < 0]$.

Gibbs Free Energy change as a Criterion for Spontaneity

$$G=H-TS=U+pV-TS$$

or $dG=dU+pdV+Vdp-TdS-SdT$

Since $dU=dq+dw$

$dG=dq+dw+pdV+Vdp-TdS-SdT$

or $dG-dw-pdV-Vdp+TdS+SdT=dq$ (true for reversible and irreversible processes)

Since, $dq_{rev}=TdS$ and $dq_{irrev} < TdS$

$$dG-dw-pdV-Vdp+TdS+SdT \leqslant TdS$$

or $dG-dw-pdV-Vdp+SdT \leqslant 0$ (cancelling TdS terms both sides)

If only pressure-volume work is done ($dw=-pdV$), we have

$$dG+pdV-pdV-Vdp+SdT \leqslant 0$$

or $dG-Vdp+SdT \leqslant 0$

At constant temperature ($dT=0$) and constant pressure ($dp=0$), the above equation reduces to

$$(\partial G)_{T,p} \leqslant 0 \qquad \dots (9.65)$$

According to Eq. 9.65, when the pressure and temperature remain constant, the Gibbs free energy of a system remains constant in a reversible process $[(\partial G)_{p,T} = 0]$, whereas in an irreversible process, Gibbs free energy decreases $[(\partial G)_{p,T}<0]$. Thus the criterion for spontaneity in terms of Gibbs free energy is that the process would be feasible if ΔG is negative.

By combining Eqs. 9.15 and 9.65, we can draw some useful conclusions. From Eq. 9.15 we have

$$\Delta G=\Delta H-T\Delta S$$

It can be seen from Eqs. 9.15 and 9.65 that

1. If ΔH is negative and ΔS is positive, ΔG will be negative at all temperatures; hence, the process would be spontaneous at all temperatures.
2. If ΔH is positive and ΔS is negative, ΔG will be positive at all temperatures; hence, the process would not be feasible at any temperature.
3. If ΔH and ΔS are both positive or negative, ΔG will be positive or negative depending upon the temperature.

There are four possibilities for ΔG based on the signs of ΔH and ΔS. These are outlined in Table 9.1.

Table 9.1: Criterion for Spontaneous Change

Case	ΔH	ΔS	ΔG	Result
1	−	+	−	spontaneous at all temperatures
2	−	−	− +	spontaneous at low temperatures nonspontaneous at high temperatures
3	+	+	+ −	nonspontaneous at low temperatures spontaneous at high temperatures
4	+	−	+	nonspontaneous at all temperatures

SAQ 5

Under what conditions, would you expect the following reactions to occur spontaneously

a) $N_2(g)+3H_2(g) \rightarrow 2NH_3(g)$ (The reaction is exothermic)

b) $O_2(g) \rightarrow 2O(g)$ (The reaction is endothermic)

9.9 THE GIBBS FREE ENERGY OF FORMATION

The term fugacity comes from the Latin word for "fleetness" (meaning : to move rapidly). The fugacity is a measure of the molar Gibbs energy of a real gas. The fugacity has the same units as pressure and approaches the pressure (value) as pressure approaches zero.

It is obvious from the definition of Gibbs free energy (Eqs. 9.3 and 9.4) that the absolute value of G is not determinable since the absolute values of U and H are unknown. However, in most cases, this is not a handicap as we require only changes in Gibbs free energy for a given process. In this section, we are interested in showing the method of calculation of standard Gibbs free energy of a reaction. Before that, let us define the standard states of the substances.

The standard states of solids and liquids correspond to their most stable form at 1 bar pressure and the specified temperature. For a gas, the standard state is pure gas at unit fugacity. For ideal gas, fugacity is unity when pressure is 1 bar at a specified temperature. In all these cases, the most stable form has the lowest free energy. The standard state convention may be summarized as given below:

Ideal solution will be defined in Unit 10 of this course.

For a solid : The pure substance at 1 bar external presssure and at a specified temperature.

For a liquid : The pure substance at 1 bar external pressure and at a specified temperature.

For a gas : An ideal gas at 1 bar partial pressure and at a specified temperature.

For a solute : An ideal solution at one molar concentration and at a specified temperature.

The standard Gibbs free energy of formation, $\Delta_f G°$, of a substance is defined as the change in the Gibbs free energy that accompanies the formation of one mole of the substance in its standard state from the elements in their standard states. Just like $\Delta_f H°$, the standard Gibbs free energy of formation of all elements by definition is zero. Thus $\Delta_f G°(CO_2)$ is the Gibbs free energy for the reaction,

$$C\ (\text{graphite})+O_2(g) \rightarrow CO_2(g) \qquad \Delta_r G° = -394.4\ \text{kJ mol}^{-1}$$

It may be mentioned that $\Delta_f G°$ can be defined at any temperature but generally these values are tabulated at 298.15 K. The values of $\Delta_f G°$ for some selected substances at 298.15 K are given in Table 9.2.

Table 9.2 : Standard Gibbs Free Energies of Formation at 298.15 K of some Selected Substances

Substance	$\Delta_f G°/(\text{kJ mol}^{-1})$	Substance	$\Delta_f G°/(\text{kJ mol}^{-1})$
$H(g)$	203.3	$NH_3(g)$	−16.5
$O(g)$	230.1	$CH_4\ (g)$	−50.8
$Cl\ (g)$	105.4	$C_2H_6\ (g)$	−32.9
$Br\ (g)$	82.4	$C_2H_4\ (g)$	68.1
$Br_2\ (g)$	3.1	$C_2H_2\ (g)$	209.2
$I\ (g)$	70.3	Benzene (*l*)	124.3
$I_2\ (g)$	19.3	Methanol (*l*)	−166.4
$H_2O\ (g)$	−228.6	Ethanol (*l*)	−174.1
$H_2O\ (l)$	−237.2		
$HF\ (g)$	−273.2		
$HCl\ (g)$	−95.3		
$HBr\ (g)$	−53.4		
$HI\ (g)$	1.7		
$CO\ (g)$	−137.2		
$CO_2\ (g)$	−394.4		

The table of standard Gibbs free energies of formation can be very useful for calculating the standard Gibbs free energy of a reaction. This is defined as the change in Gibbs free energy that accompanies the conversion of reactants in their standard states to products in their standard states. In other words,

$$\left\{\begin{array}{l}\text{Standard Gibbs free}\\ \text{energy for a reaction}\end{array}\right\} = \Delta_r G^\circ = \left\{\begin{array}{l}(\text{sum of } \Delta_f G^\circ \text{ values of products}) -\\ (\text{sum of } \Delta_f G^\circ \text{ values of reactants})\end{array}\right\} \quad \ldots (9.66)$$

Example 5

Using the data in Table 9.2 calculate the standard Gibbs free energy for the reaction.

$$H(g) + Br_2(g) \rightarrow HBr(g) + Br(g)$$

Solution

$$\begin{aligned}\Delta_r G^\circ &= [\Delta_f G^\circ(\text{HBr}) + \Delta_f G^\circ(\text{Br})] - [\Delta_f G^\circ(\text{H}) + \Delta_f G^\circ(\text{Br}_2)]\\ &= \{[-53.4+82.4]-[203.3+3.1]\}\ \text{kJ mol}^{-1}\\ &= -177.4\ \text{kJ mol}^{-1}\end{aligned}$$

Hence, hydrogen atom can spontaneously react with bromine gas to give hydrogen bromide.

SAQ 6

Why are the values of $\Delta_f G^\circ$ of some of the elements given in Table 9.2 different from zero?

9.10 PARTIAL MOLAR QUANTITIES AND CHEMICAL POTENTIAL

The enthalpy change involved in the dissolution of a solute in a solvent is very much dependent on the amounts of the solute and solvent present. Similarly, other thermodynamic properties like volume, internal energy, Helmholtz free energy and Gibbs free energy also depend on the composition of the system. Until now, however, we have considered only the closed system in which the amounts of the reactants and the products are fixed. We shall now consider open system in which the amounts of the components may vary.

Molar volume of water

$$= \frac{\text{Molar mass of water}}{\text{Density of water}} = \frac{1.8\times10^{-2}\ \text{kg}}{1.0\times10^{3}\ \text{kg m}^{-3}}$$

$= 1.8\times10^{-5}\ \text{m}^3$

$= 18\ \text{cm}^3$ (since $1\ \text{cm}^3 = 10^{-6}\ \text{m}^3$)

If we consider a single homogeneous phase consisting of only one component, then the value of an extensive property divided by the amount of the substance becomes the molar property. These molar properties are indicated by putting a bar above the symbols.

Thus, $\bar{V} = \dfrac{V}{n}$ and $\bar{H} = \dfrac{H}{n}$, where n is the amount (the number of moles) of the single component. V and H are the volume and the enthalpy of n mol of a substance. $\bar{V}$ and $\bar{H}$ are the molar volume and the molar enthalpy of the substance. However, if the system is a phase consisting of several components, then the addition of one mole of any pure substance in the mixture does not necessarily mean that it increases the value of the extensive property by the molar quantity. Thus, in a mixture of water and alcohol, if one mole of water is added, then the increase in volume is not equal to 18 cm^3 but depends on the composition of the mixture. Thus we introduce the concept of partial molar quantities. These are of particular use in the case of solutions of two or more components. The partial molar quantity of a component is defined as the change in the extensive property of a mixture when one mole of the pure component is added in such a way that there is no change in temperature ($dT=0$), pressure ($dp=0$) and composition ($dN=0$). This is possible if we consider the system to be very large.

When the composition of the system varies, then for a small change of temperature, pressure and the amounts of the constituents, the change in Gibbs free energy for a two component system is given by.

$$G = f(T, p, n_1, n_2) \quad \ldots (9.67)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,N} dT + \left(\frac{\partial G}{\partial p}\right)_{T,N} dp + \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1} dn_2 \quad \ldots (9.68)$$

Eq. 9.67 is to be read as follows:

G is a function of T, P, n_1 and n_2.

This means that the free energy of a two component system depends on the pressure, temperature and the amounts of the components 1 and 2.

Eq. 9.68 is written from Eq. 9.67, since dG is a perfect or total differential. The value of a total differential (such as dG) depends only on the values of the variables (such p, T, n_1 and n_2) and not on the type of the process which the system may adopt. For a better understanding of the total differential, see the Appendix at the end of this unit.

where n_1 and n_2 are the number of moles of components 1 and 2 and $N=n_1+n_2$=total number of moles of components.

The subscripts p and N in the first term of the right hand side denote the fact that the pressure and composition are kept constant while noting the change in G with respect to temperature. Similarly the subscripts T, N or T, p, n_2 or T, p, n_1 signify the parameters kept constant while G is varied with respect to a parameter not mentioned as a subscript outside the bracket.

The partial derivative $\left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2}$ represents the rate of change in free energy per mole of component 1 added to the system, when temperature, pressure and the amount of component 2 are constant. It is also called the partial molar free energy ($\bar{G}_1$) or simply chemical potential (μ_1) of the component 1. The chemical potentials of the two components are defined as,

$$\left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2} = \mu_1 \text{ and } \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1} = \mu_2 \quad \ldots (9.69)$$

At constant temperature ($dT=0$) and constant pressure, ($dp=0$), Eq. 9.68 may be written as,

$$dG_{T,p} = \mu_1 dn_1+\mu_2 dn_2 \quad \ldots (9.70)$$

It is possible to define chemical potential in terms of other thermodynamic functions also; but we consider it in terms of Gibbs free energy only.

If a system has definite composition having n_1 and n_2 moles of the respective components, then on integrating Eq. 9.70, we have.

$$G_{T,p} = \mu_1 n_1+\mu_2 n_2 \quad \ldots (9.71)$$

Eq. 9.71 describes the free energy of a system of two components in terms of the partial molar free energies of the components. Similar expressions can be written for other thermodynamic quantities of the system also in terms of the partial molar quantities.

The reason, as to why the increase in volume on the addition of one mole of water to a large volume of ethanol, is not equal to the molar volume of water will be seen in Unit 10 of this course.

The importance of partial molar quantities can be understood from the following example. When one mole of water is added to a sufficiently large volume of ethanol, it is found that the increase in volume is not equal to the molar volume of water ($18\ cm^3$) but only $14\ cm^3$. The quantity, $14\ cm^3 mol^{-1}$, is the partial molar volume of water in a large volume of ethanol. Thus the partial molar volume of a substance in a mixture of defined composition is the increase in volume that occurs when a substance is added to a sufficiently large sample of the solution. In general, when n_A mol of A is mixed with n_B mol of B, the total volume (V) of the mixture can be obtained from Eq. 9.72 which is written similar to Eq. 9.71.

$$V=n_A\bar{V}_A+n_B\bar{V}_B \quad \ldots (9.72)$$

Where $\bar{V}_A$ and $\bar{V}_B$ are the partial molar volumes of A and B, respectively.

Example 6

What is the total volume of the solution, when 3.80 mol of water is mixed with 0.500 mol of ethanol? The partial molar volumes of water and ethanol at this composition are $1.80 \times 10^{-5} m^3\ mol^{-1}$ and $5.34 \times 10^{-5} m^3 mol^{-1}$, respectively.

Solution

$n(H_2O) = 3.80$ mol $\qquad \bar{V}(H_2O)=1.80\times10^{-5}\ m^3\ mol^{-1}$

$n(C_2H_5OH) = 0.500$ mol $\qquad \bar{V}(C_2H_5OH)=5.34\times10^{-5}\ m^3\ mol^{-1}$

Applying Eq. 9.72,

$$\begin{aligned} V &= (3.80\ mol)\times(1.80\times10^{-5}\ m^3\ mol^{-1}) + \\ &\quad (0.500\ mol)\times(5.34\times10^{-5}\ m^3\ mol^{-1}) \\ &= 6.84\times10^{-5}\ m^3+2.67\times10^{-5}\ m^3 \\ &= 9.51\times10^{-5}\ m^3 \end{aligned}$$

Let us now see how Eq. 9.71 can be used to derive an important relationship (known as Gibbs-Duhem Equation) between the changes in the chemical potentials of the two components present in a solution.

Gibbs-Duhem Equation

According to Eq. 9.71 at a given temperature and pressure, the total Gibbs free energy for a homogeneous phase is equal to the sum of the products of the chemical potentials and the number of moles of each component. Hence, the Gibbs free energy of the system can change either by the change of chemical potential of a component or its amount in the system. A general expression for change in G at the given temperature and pressure can be obtained by differentiating Eq. 9.71, i.e.,

$$dG_{T,\,p}=\mu_1 dn_1+n_1 d\mu_1+\mu_2 dn_2+n_2 d\mu_2 \qquad \ldots(9.73)$$

Comparing this equation with 9.70 we obtain,

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \qquad \ldots(9.74)$$

This equation is known as Gibbs-Duhem equation.

$$\text{or } d\mu_1 = -(n_2/n_1)d\mu_2 \qquad \ldots(9.75)$$

which means that the chemical potentials for components 1 and 2 cannot be varied independently. If μ_2 increases, then μ_1 will decrease by a definite amount. This equation finds extensive applications in liquid-vapour, liquid-solid and liquid-liquid equilibrium of binary mixtures.

Let us now see how the chemical potential varies with temperature and pressure.

Dependence of Chemical Potential on Temperature and Pressure

From Eq. 9.20, $dG=Vdp-SdT$

$$\text{Hence,}\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \ldots(9.21)$$

$$\text{and}\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \ldots(9.23)$$

We know that the chemical potential of the component i (μ_i) is given by,

$$\mu_i =\left(\frac{\partial G}{\partial n_i}\right)_{T,\,p,\,n_j} \qquad \ldots(9.76)$$

where j=all the components except i. Note that the subscript n_j means that the amounts of all the components except i are kept constant.

Differentiating μ_i (given in Eq. 9.76) with respect to temperature at constant pressure and composition, we have

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\,N} = \frac{\partial^2 G}{\partial T \partial n_i}$$

Since G is a state function,

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\,N} = \frac{\partial^2 G}{\partial T \partial n_i} = \left[\frac{\partial}{\partial n_i}\left[\frac{\partial G}{\partial T}\right]_{p,\,N}\right]_{T,\,p,\,n_j}$$

From Eq. 9.21, $\left(\frac{\partial G}{\partial T}\right)_p = -S$

$$\text{Hence,}\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\,N} = \left[\frac{\partial}{\partial n_i}(-S)\right]_{T,\,p,\,n_j} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,\,p,\,n_j} = -\bar{S}_i \qquad \ldots(9.77)$$

Where $\bar{S}_i$ is the partial molar entropy of the ith component. Since the entropy of a substance is always positive, its chemical potential or Gibbs free energy would decrease with increase in temperature. Eq. 9.77 describes the dependence of μ_i on temperature at constant pressure and composition. Let us now derive an expression useful in describing the dependence of μ_i on pressure.

Eqs. 9.77 and 9.78 are obtained from Eq. 9.76 using one of the properties of total differentials. Since dG is a total differential, the second order differentials of G with respect to T and n_i taken in any order are the same.

$$\text{i.e.,} \frac{\partial^2 G}{\partial T \partial n_i} = \frac{\partial^2 G}{\partial n_i \partial T}$$

Also the second order differentials of G with respect to p and n_i taken in any order are the same.

$$\frac{\partial^2 G}{\partial p \partial n_i} = \frac{\partial^2 G}{\partial n_i \partial p}$$

Since G is a thermodynamic property, the change in G depends on the changes in the values of the variables such as T, n_i or p, n_i etc. at any particular instant, but not on the way or the sequence by which such variables are changed.

Differentiating μ_i (given in Eq. 9.76) with respect to pressure at constant temperature and composition, we have,

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\,N} = \frac{\partial^2 G}{\partial p \partial n_i}$$

$$= \left[\frac{\partial}{\partial n_i}\left[\frac{\partial G}{\partial p}\right]_{T,\,N}\right]_{T,\,p,\,n_j}$$

From Eq. 9.23, $\left(\frac{\partial G}{\partial p}\right)_T = V$

Hence, $\left(\frac{\partial \mu_i}{\partial p}\right)_{T,N} = \left[\frac{\partial}{\partial n_i}(V)\right]_{T,p,n_j} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_j} = \bar{V}_i$ ... (9.78)

where $\bar{V}_i$ is the partial molar volume of the component i. Eq. 9.78 defines the dependence of μ_i on pressure at constant temperature and composition.

Chemical Potential of Ideal Gases

The chemical potential of the components in a mixture of ideal gases can be expressed in three possible ways. First let us derive an expression for the chemical potential of a component in terms of its partial pressure.

For an ideal gas, $pV=nRT$ ... (9.79)

Let us consider an ideal gas mixture at temperature T, total pressure p and volume V. Let the number of moles of each component be $n_1, n_2, \ldots n_i \ldots$, and the partial pressure of each component be $p_1, p_2, \ldots p_i, \ldots$ respectively.

Then from Eq. 9.79, we have

$$V = \frac{nRT}{p} = (n_1+n_2+\ldots+n_i+\ldots)\frac{RT}{p} = n_t\frac{RT}{p}$$

Where n_t is the total number of moles of all the components. Differentiating V in the above equation with respect to n_i at constant temperature and pressure, we have

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_j} = \bar{V}_i = \frac{RT}{p}$$

Note that the subscript n_j denotes that the amounts of all other components except i are kept constant. But from Eq. 9.78,

$$\bar{V}_i = \left(\frac{\partial \mu_i}{\partial p}\right)_{T,N}$$

$$\text{Hence, } \left(\frac{\partial \mu_i}{\partial p}\right)_{T,N} = \frac{RT}{p} \qquad \ldots (9.80)$$

$$\text{or} \quad \partial\mu_i = RT\frac{dp}{p} = RT\,d\ln p \qquad \ldots (9.81)$$

If p_i is the partial pressure of the component i and p is the total pressure of the mixture of gases, then according to Dalton's law of partial pressures,

$$p_i = \frac{n_i}{n_t}p = x_i p,$$

where x_i is the mole fraction of the component i. Taking logarithms both sides, $\ln p_i = \ln x_i + \ln p_i$.

If x_i is constant, we can write on differentiation of $\ln p_i$,
$d\ln p_i = d\ln p$

This means that in a gaseous mixture of constant composition, the partial pressure of a component varies as the total pressure.

Substituting for $d\ln p$ in Eq. 9.81, we have
$d\mu_i = RT\, d\ln p_i$

Integrating between the limits $\mu_i(1) \rightarrow \mu_i(p_i)$ and $1 \rightarrow p_i$ we have,

$$\int_{\mu_i(1)}^{\mu_i(p_i)} d\mu_i = RT \int_1^{p_i} d\ln p_i$$

$$[\mu_i]_{\mu_i(1)}^{\mu_i(p_i)} = RT\,[\ln p_i]_1^{p_i}$$

or $\mu_i(p_i) - \mu_i(1) = RT\ln p_i - RT\ln 1$

i.e., $\mu_i(p_i) - \mu_i(1) = RT\ln p_i$ [since $\ln 1 = 0$]

or $\mu_i(p_i)=\mu_i(1)+RT\ln p_i$ ... (9.82)

In Eq. 9.82, $\mu_i(p_i)$ is the chemical potential of the i th component at temperature T when its partial pressure is p_i, and $\mu_i(1)$ is the chemical potential at the same temperature but at a partial pressure of unity. Hence, $\mu_i(1)$ is equal to $\mu_i(p_i)$ when $p_i=1$ bar; i.e., $\mu_i(1)$ is the chemical potential under standard state at 1 bar. Thus in general, we may write Eq. 9.82 in the form,

$$\mu_i(p_i) = \mu_i^\circ(p) + RT\ln p_i \qquad \text{... (9.83)}$$

where $\mu_i(p_i)$ is the chemical potential of the i^th^component at a partial pressure p_i and $\mu_i^\circ(p)$ is its standard chemical potential. Eq. 9.83 gives the chemical potential of an ideal gas i in terms of its partial pressure in a mixture. Let us now derive an expression for the chemical potential of an ideal gas in terms of its concentration in a mixture.

In order to transform Eq. 9.83 in terms of concentration, we use the ideal gas law and substitute $p_i = \frac{n_i}{V}RT = c_iRT$ where c_i is the concentration of the i^th^ component. Let $\mu_i(c_i)$ be the chemical potential of the i th component when its concentration is c_i in the mixture of ideal gases.

$$\begin{aligned} \text{So, } \mu_i(c_i) &= \mu_i(p_i) = \mu_i^\circ(p_i)+RT\ln p_i \\ &= \mu_i^\circ(p)+RT\ln c_i+RT\ln RT \\ \text{or } \mu_i(c_i) &= \mu_i^\circ(c)+RT\ln c_i \qquad \text{... (9.84)} \end{aligned}$$

Here $\mu_i^\circ(c)=\mu_i^\circ(p)+RT\ln RT$ and is equal to the chemical potential of the i^th^ component under standard state (when c_i is unity).

A similar expression can be derived in terms of the mole fraction (x_i) of the i^th^ component. For this purpose, we make use of Dalton's law of partial pressures, $p_i=x_i\,p$ where p_i is the partial pressure of the i^th^component and p is the total pressure of the mixture of ideal gases.

Let us assume that $\mu_i(x_i)$ is the chemical potential of the i^th^ component in terms of its mole fraction in the mixture.

$$\begin{aligned} \text{Using Eq. 9.83, } \mu_i(x_i) &= \mu_i(p_i) = \mu_i^\circ(p)+RT\ln p_i \\ &= \mu_i^\circ(p)+RT\ln x_i+RT\ln p \\ \text{Hence, } \quad \mu_i(x_i) &= \mu_i^\circ(x) + RT\ln x_i \qquad \text{... (9.85)} \end{aligned}$$

where $\mu_i^\circ(x)=\mu_i^\circ(p)+RT\ln p$ and is equal to the chemical potential of the component i under standard state (when $x_i=1$). Eqs. 9.83, 9.84 and 9.85 are applicable to ideal systems only. When a system exhibits deviation from ideal behaviour, modified forms of these equations are to be used.

In the next section, we study the third law of thermodynamics and its application in calculating the entropy of the substances.

9.11 THE THIRD LAW OF THERMODYNAMICS

The second law of thermodynamics has been used to calculate entropy changes in various chemical and physical processes. However, the absolute values of entropy have so far remained uncalculable. We now try to devise a scale of standard entropies so that we can associate definite entropies with different states of a given system.

The Nernst Heat Theorem

We start with Gibbs-Helmholtz equation (Eq. 9.43)

$$\Delta G=\Delta H+T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p \qquad \text{... (9.43)}$$

In Sec. 9.6 we mentioned that it is possible to calculate ΔH by knowing ΔG at two different temperatures. A question which remained unanswered was whether we can calculate ΔG from ΔH data. One thing which is clear from Eq. 9.43 is that as we approach the absolute zero of temperature, ΔG and ΔH must be equal unless

$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$ assumes an infinite value. Richards, however, found, during his studies on the electromotive force values of cells, that the quantity $\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$ actually decreases as temperature is lowered. This observation prompted Nernst to conclude that $\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$ decreases in such a way that it reaches zero value gradually at absolute zero. This implies that ΔG and ΔH not only approach each other near absolute zero, but do so assymptotically (i.e. in such a manner that their curves overlap at this point as in Fig. 9.1)

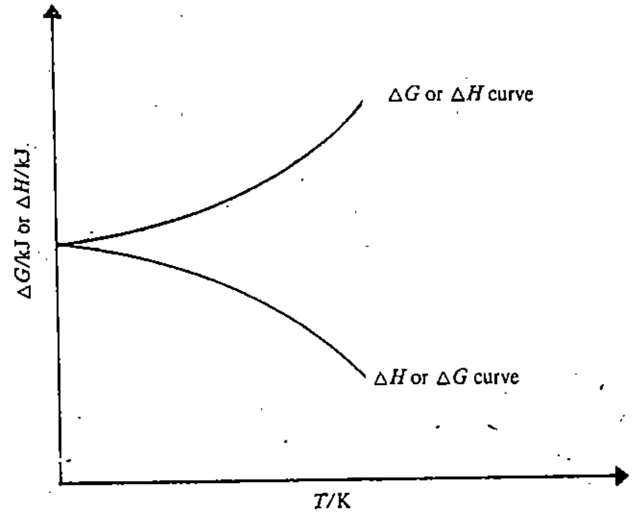


Fig. 9.1: ΔG and ΔH variation with temperature.

$T \xrightarrow{\text{Lt}} 0$ means temperature is near about absolute zero.

Mathematically this statement is equivalent to

$$T \xrightarrow{\text{Lt}} 0 \quad \frac{d(\Delta G)}{dT} = T \xrightarrow{\text{Lt}} 0 \quad \frac{d(\Delta H)}{dT} = 0 \qquad \ldots (9.86)$$

This is known as Nernst Heat Theorem and it is strictly applicable only to pure solids and not to liquids and gases which are not capable of existence at absolute zero.

As per Eq. 7.23 of Unit 7,

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_p = \Delta C_p$$

and again, according to Eq. 9.42,

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = -\Delta S$$

Here ΔS represents the change in entropy accompanying a reaction and ΔC_p is the difference between the total heat capacities of the products and those of the reactants at constant pressure. We can put Eq. 9.86 in the form,

$$T \xrightarrow{\text{Lt}} 0 \quad \Delta S = T \xrightarrow{\text{Lt}} 0 \quad \Delta C_p = 0 \qquad \ldots (9.87)$$

In other words, at absolute zero, there is no difference between the heat capacities of the reactants and the products at constant pressure; this imples that the C_p values of all substances at 0 K are same. Later studies have shown that at the absolute zero of temperature, the heat capacity of a solid should be zero.

i.e., at 0 K, $C_p = 0$ ... (9.8

A similar argument for the entropy change accompanying a reaction leads to the conclusion that all solids have the same entropy at absolute zero and , according to Max Planck, this value of entropy is zero.

The results so far discussed can be stated as the Third Law of Thermodynamics: "The entropy of a pure, perfectly crystalline solid approaches zero, as temperature approaches absolute zero."

The zero entropy of such solids can be readily understood since a perfectly crystalline solid implies a perfectly ordered arrangement of atoms, molecules and ions; or at absolute zero of temperature, number of microscopic states (Ω) of Eq: 8.87 (of Unit 8) is equal to unity and the entropy of the substance is zero.

$$S = k \ln \Omega = k \ln 1 = 0 \qquad \text{... (8.87)}$$

In case, the solid is not perfectly crystalline in nature, then its absolute entropy at 0 K is not zero, This has been discussed in Sec. 8.12 of Unit 8.

In Eq. 8.87, Ω stands for the number of microscopic states or modes of arrangement of the species. At absolute zero, for a perfectly crystalline substance, there is only one mode of arrangement.
i.e., $\Omega = 1$.

Applications of The Third Law of Thermodynamics

A lower limit on entropy enables us to determine the absolute value of the entropy of a system, if we can deduce an expression for the variation of entropy with temperature. Let us begin with the familiar relations, $T\mathrm{d}S = \mathrm{d}q$ (Eq. 8.37 of Unit 8) and $\mathrm{d}q_p = C_p\mathrm{d}T$ (Eq. 6.3 of Unit 6).

Hence at constant pressure, $T\mathrm{d}S = C_p\mathrm{d}T$

i.e.,
$$\mathrm{d}S = C_p\frac{\mathrm{d}T}{T} \qquad \text{... (9.89)}$$

If we integrate Eq. 9.89 between the temperature limits 0 and T and entropy limits 0 and S, we have,

$$\int_0^S dS = \int_0^T C_p \frac{dT}{T} \qquad \text{... (9.90)}$$

Where S is the entropy at temperature T and by the third law, entropy at 0 K (S_o) is zero.

$$\text{Hence, } S_T - S_o = S_T = \int_0^T C_p \frac{dT}{T} = \int_0^T C_p \mathrm{d}\ln T \qquad \text{... (9.91)}$$

To calculate the value of S_T, the heat capacity of the substance should be known from 0 K to the temperature at which the entropy is to be calculated. The heat capacities of solids are known upto about 10 K to 15 K. Below this temperature, the heat capacities of solids are determined using the Debye equation,

$$C_p \approx C_v = aT^3 \qquad \text{... (9.92)}$$

where a is constant; the value of a is determined from the value of C_p at some low temperature. This temperature is denoted as T_{min}; it is the lowest temperature at which C_p of the solid can be measured conveniently. Eq. 9.92 is valid for crystalline solids at low temperatures near 0 K. Eq. 9.91 may be written as,

$$S_T = \int_0^{T_{\text{min}}} C_p\frac{\mathrm{d}T}{T} + \int_{T_{\text{min}}}^T C_p\frac{\mathrm{d}T}{T} = \int_0^{T_{\text{min}}} aT^3\frac{\mathrm{d}T}{T} + \int_{T_{\text{min}}}^T C_p \,\mathrm{d}\ln T \qquad \text{...(9.93)}$$

The first integral is evaluated using the Debye equation (Eq. 9.92). The second integral is evaluated by plotting C_p vs $\ln T$ (Fig. 9.2); the shaded area under the curve is equal to the value of the second integral.

Eq. 9.93 can be simplified as follows:

$$S_T = \int_0^{T_{\text{min}}} aT^3\frac{\mathrm{d}T}{T} + \int_{T_{\text{min}}}^T C_p \,\mathrm{d}\ln T$$

$$S_T = a\int_0^{T_{\min}} T^2 \mathrm{d}T + \int_{T_{\min}}^{T} C_p \mathrm{d}\ln T \text{ (since } a \text{ is constant)}$$

$$= a\left[\frac{T^3}{3}\right]_0^{T_{\min}} + \int_{T_{\min}}^{T} C_p \,\mathrm{d}\ln T$$

$$\text{Hence, } S_T = \frac{a}{3} T^3_{\min} + \int_{T_{\min}}^{T} C_p \,\mathrm{d}\ln T$$

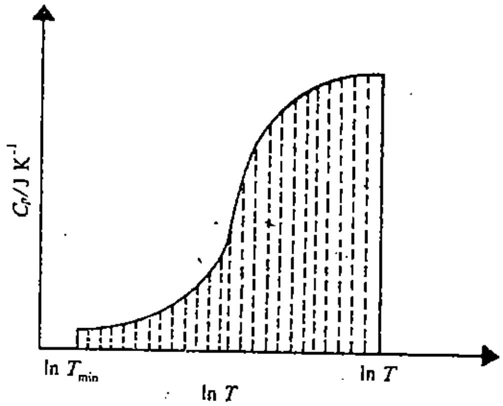


Fig. 9.2 : C_p vs ln T plot

While using this method, it must be remembered that any phase change taking place between the temperatures zero kelvin (0 K) and T K, also contributes towards the absolute entropy. The entropy of phase change. ΔS_{trans}, is given by Eq. 8.75 of Unit 8.

$$\Delta S_{\text{trans}} = \frac{\Delta H_{\text{trans}}}{T} \qquad \text{... (8.75)}$$

where ΔH_{trans} and T are the enthalpy and transition temperature, respectively for the phase transition. The phase transition includes changes such as solid to liquid, liquid to vapour and one allotropic form to another.

Let us now calculate the absolute molar entropy of a substance in the vapour phase at T K. This absolute molar entropy will be given by the sum of the entropy changes involved in various stages as given below:

$$\left.\begin{array}{ll}
S = \dfrac{a}{3} T^3_{\min} & \text{(entropy change for bringing the temperature of the solid from 0 K to } T_{\min}) \\
+ \displaystyle\int_{T_{\min}}^{T_f} \bar{C}_p(s) \,\mathrm{d}\ln T & \text{(entropy change for heating the solid from } T_{\min} \text{ to its melting point)} \\
+ \dfrac{\Delta H_{\text{fus}}}{T_f} & \text{(entropy change for the fusion of the solid into liquid)} \\
+ \displaystyle\int_{T_f}^{T_B} \bar{C}_p(l) \,\mathrm{d}\ln T & \text{(entropy change for heating the substance (in the liquid state) from its melting point to the boiling point)} \\
+ \dfrac{\Delta H_{\text{vap}}}{T_B} & \text{(entropy change for the vaporization of the liquid)} \\
+ \displaystyle\int_{T_B}^{T} \bar{C}_p(g) \,\mathrm{d}\ln T & \text{(entropy change for heating the vapour from the boiling point to the temperature } T)
\end{array}\right\} \text{... (9.95)}$$

If a substance exists in different allotropic modifications, then ΔS_{trans} of the allotropic transition as given by Eq. 8.75 also must be added while calculating the absolute molar entropy of a substance.

where $\bar{C}_p(s)$, $\bar{C}_p(l)$ and $\bar{C}_p(g)$ are the molar heat capacities of the solid, liquid and gaseous phases, respectively; T_f and T_B are the melting and boiling points and ΔH_{fus} and ΔH_{vap} are the molar enthalpies of fusion and vaporization, respectively. Hence, by substituting in Eq. 9.95, the values of the molar heat capacities, the molar enthalpies and the temperatures, the absolute molar entropy of a substance can be calculated.

9.12 SUMMARY

For a spontaneous change, the total entropy of the system and the surroundings must increase. If entropy is used as a criterion for spontaneity, it is necessary to determine the entropy change for both the system and the surrroundings. This is inconvenient as one has to consider the changes taking place both in the system and the surroundings. Therefore, a criterion for spontaneity is developed in such a manner that only changes in the properties of the system are considered. For this purpose, two more state functions called, Helmholtz free energy (A) and Gibbs free energy (G) are defined. Decrease in Helmholtz free energy is equal to the maximum amount of work that can be obtained from the system during a given change. The decrease in Gibbs free energy is a measure of maximum useful work that can be obtained from the system at constant temperature and pressure. The Gibbs free energy change (given by the relation $\Delta G = \Delta H - T\Delta S$) of a physical or a chemical process is a criterion for spontaneity of a process. ΔG has a negative value for a spontaneous process.

Maxwell relations equate the rate of change of a quantity (which cannot be determined experimentally) with the rate of change of volume, pressure or temperature. Gibbs-Helmholtz equation permits the calculation of ΔU *or* ΔH provided ΔA or ΔG at two temperatures are known. Clausius–Clapeyron equation is useful for calculating the molar enthalpy of vaporization of liquids if the values of vapour pressure at two different temperatures are known. The standard free energy change, $\Delta_r G^\circ$, is based on the conversion of reactants in their standard states to products in their standard states.

The chemical potential of a given substance is the change in free energy of the system that results on the addition of one mole of that particular substance at a constant temperature and pressure to such a large quantity of the system that there is no appreciable change in the overall composition of the system. Gibbs-Duhem equation shows that variation in chemical potential of one of the components in a binary system affects the value of the chemical potential for another component. According to Nernst heat theorem, ΔG and ΔH not only become equal to each other at absolute zero but also approach each other gradually at temperatures near absolute zero. At the absolute zero of temperature, the entropy of every substance may become zero and it does become zero in the case of a perfectly crystalline substance.

9.13 TERMINAL QUESTIONS

1. Fill in the blanks
   i) The free energy change of a reaction indicates the ———————— in which a reaction occurs.
   ii) For a process to occur spontaneously, the entropy of the ———————— must increase.
   iii) If a reaction has $\Delta H < 0$ and $\Delta S < 0$, the reaction proceeds in the forward direction at ———————— temperatures.
   iv) The entropy of a substance is always ———————— above 0 K.
2. Predict whether the process

$$CCl_4(l) + H_2(g) \rightarrow HCl(g) + CHCl_3(l)$$

is spontaneous at 298 K under standard state conditions. At 298 K, $\Delta_r H^\circ = -91.35$ kJ and $\Delta_r S^\circ = 41.50$ J K^{-1} for this reaction.

3. During a reversible isothermal compression of 1.00 mol of an ideal gas, its pressure increases from 101.3 Pa to 1013 Pa at 3.00×10^2 K. Calculate the change in Gibbs free energy of the gas.

4. The Gibbs free energy change (ΔG) in a process was found to be -140.5 kJ at 303 K and -137.5 kJ at 313K. Calculate the change in enthalpy (ΔH) accompanying the process at 308 K.

5. When 2.00 mol of a substance A and 3.00 mol of a substance B are mixed, the total volume is $2.10 \times 10^{-4} m^3$. If the partial molar volume of A is $2.00 \times 10^{-5} m^3 mol^{-1}$, what is the partial molar volume of B?

6. $\Delta_r G$ for a reaction at 3.00×10^2 K is -121.0 kJ and $\Delta_r H$ for it is -46.0 kJ. Calculate $\Delta_r S$ for the reaction at 3.00×10^2K.

9.14 ANSWERS

Self Assessment Questions

1. We have to take into account the total change in entropy which is equal to the sum of the entropy changes of the system and the surroundings. Generally the entropy change of the surroundings is not easy to calculate.

2. The decrease in Gibbs free energy is equal to the maximum amount of useful work that a system can perform at constant temperature and pressure.

3. See Sec. 9.4.

4. Given that $\Delta H_{vap} = 2.74 \times 10^4$ J.mol^{-1}
$T_2 = 306$ K; $T_1 = ?$
$p_2 = 1.00 \times 10^5$ Pa; $p_1 = 9.85 \times 10^3$ Pa
Substituting the values in Clausius-Clapeyron equation,

It is advisable to denote higher vapour pressure value as p_2 (and the corresponding temperature value as T_2) and the lower vapour pressure value as p_1(and the corresponding temperature as T_1). This will help you in simplifying the logarithmic term.

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{vap}}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{1.00\times10^5 \text{ Pa}}{9.85\times10^3 \text{ Pa}} = \frac{2.74\times10^4 \text{ J mol}^{-1}}{2.303\times8.314 \text{ J mol}^{-1}\text{ K}^{-1}} \quad \frac{(306 - T_1)\text{ K}}{(306\, T_1)\text{ K}^2}$$

$$(5.0000 - 3.9934) = 1.431 \times 10^3 \left(\frac{306 - T_1}{306\, T_1}\right)$$

$$1.0066 = 4.68 \frac{(306 - T_1)}{T_1}$$

$$\text{Hence, } \frac{(306 - T_1)}{T_1} = \frac{1.0066}{4.68}$$

$$= 0.2151$$

$$(306 - T_1) = 0.2151\, T_1$$

$$\text{or } \quad 1.2151\, T_1 = 306 \text{ K or } T_1 = 252 \text{ K}$$

5. (a) The forward reaction is exothermic, i.e. ΔH is negative. For the forward reaction, ΔS is negative as the number of molecules of gaseous products is less than those of gaseous reactants.

$\Delta G = \Delta H - T\Delta S$

Since ΔH is $-$ve and ΔS is $-$ve, the value of ΔG will be negative only at low temperatures, i.e., the reaction would proceed spontaneously at low temperatures.

(b) The reaction being endothermic, ΔH is positive. There is an increase in the number of gaseous species (one molecule giving rise to two atoms). Hence, ΔS is also positive.

$\Delta G = \Delta H - T\Delta S$

when ΔH is +ve and ΔS is +ve, a negative value of ΔG would be obtained only at high temperatures.

6. These elements are not in their most stable state.

Terminal Questions

1 (i) direction (ii) universe (iii) low (iv) positive.

2. $$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$
$$= (-91.35 \text{ kJ}) - (298 \text{ K})\ (41.50 \text{ J K}^{-1}) \frac{1 \text{ kJ}}{1000 \text{ J}}$$
$$= -103.7 \text{ kJ}$$

The negative value of $\Delta_r G^\circ$ indicates that the reaction will be spontaneous at 298 K.

3. Using Eq. 9.25,
$$\Delta G = 2.303 \text{ nRT} \log \frac{p_2}{p_1}$$
$$= 2.303 \times 1.00 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.00 \times 10^2 \text{K} \log \frac{1013 \text{ Pa}}{101.3 \text{ Pa}}$$
$$\Delta G = 5.74 \times 10^3 \text{ J} = 5.74 \text{ kJ}$$

4. $$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = \frac{(-137.5 \text{ kJ} - (-140.5 \text{ kJ}))}{(313 \text{ K} - 303 \text{ K})} = 0.300 \text{ kJ K}^{-1}$$
$$\Delta G \text{ at } 308 \text{ K} = \frac{(-137.5 - 140.5) \text{ kJ}}{2} = -139.0 \text{ kJ}$$
$$\Delta H = \Delta G - T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$$
$$\Delta H = -139.0 \text{ kJ} - (308 \text{ K} \times 0.300 \text{ kJ K}^{-1})$$
$$= -231 \text{ kJ}$$

5. $$V_{\text{Total}} = n_A \bar{V}_A + n_B \bar{V}_B$$
$$2.10 \times 10^{-4} \text{ m}^3 = [(2.00 \times 2.00 \times 10^{-5}) + (3.00 \text{V}_B)] \text{ m}^3$$
$$\bar{V}_B = \frac{(2.10 \times 10^{-4} - 4.00 \times 10^{-5}) \text{ m}^3}{3.00 \text{ mol}} = \frac{1.70 \times 10^{-4}}{3.00} \text{ m}^3 \text{ mol}^{-1}$$
$$= 5.67 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

6. $$\Delta_r G = \Delta_r H - T\Delta_r S$$
$$-121.0 \text{ kJ} = -46.0 \text{ kJ} - T\Delta_r S$$
$$T\Delta_r S = -46.0 \text{ kJ} + 121.0 \text{ kJ} = 75.0 \text{ kJ}$$
$$\Delta_r S = \frac{75.0 \text{ kJ}}{3.00 \times 10^2 \text{ K}} = 0.250 \text{ kJ K}^{-1} = 250 \text{ J K}^{-1}$$

9.15 APPENDIX

Total Differentials

Let us consider a dependent variable, x, such that its value depends on the variables y and z only,

i.e., $x = f(y, z)$ ... (A.1)

For any change in y and z, there will be a change in x also; also if the change in x (i.e., dx) so produced is irrespective of the path followed, then dx is called total differential. The value of dx in terms of changes in y and z can be expressed as follows:

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \qquad \text{... (A.2)}$$

The meaning of this equation is given below:

$$\begin{array}{l}\text{Total change}=\\ \text{in } x\end{array} \left\{ \begin{array}{l} \left[\begin{array}{l}\text{change in } x \text{ due to}\\ \text{change in } y \text{ by one}\\ \text{unit when } z \text{ remains}\\ \text{constant}\end{array} \quad \times \quad \begin{array}{l}\text{actual}\\ \text{infinitesimal}\\ \text{change in } y\end{array}\right] + \\[2ex] \left[\begin{array}{l}\text{Change in } x \text{ due to}\\ \text{change in } z \text{ by one}\\ \text{unit when } y \text{ remains}\\ \text{constant}\end{array} \quad \times \quad \begin{array}{l}\text{actual}\\ \text{infinitesimal}\\ \text{change in } z\end{array}\right] \end{array}\right\}$$

By comparison you can recognise that Eqs. A.1 and 9.67 as well as Eqs. A.2 and 9.68 are similar. The only difference is that x depends on two variables y and z only, whereas G depends on four variables T, p, n_1 and n_2. Consequently Eq. 9.68 contains four terms in the right hand side, each term depicting a change in G due to a given change in a particular variable:

One of the characteristics of a total differential is that the second order differentials of a variable such as x given above are the same.

i.e.,
$$\frac{\partial^2 x}{\partial y \partial z} = \frac{\partial^2 x}{\partial z \partial y} \qquad \text{... (A.3)}$$

This means that the change in x is same, whether it is varied with respect to z first and y next or *vice versa*.

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UGCHE-04
Physical Chemistry

Block

3

SOLUTIONS AND PHASE RULE

UGCHE-04(21A)

SOLUTIONS AND PHASE RULE

In Block 2, we laid the thermodynamic foundation for the study of physical and chemical equilibria. In Block 3, we shall concentrate on some of the aspects of physical equilibria. In Block 4, we shall discuss chemical equilibria.

This block consists of four units. In Unit 10, we shall discuss some aspects of the completely miscible liquid systems. We shall first study how vapour pressures of completely miscible liquids vary with composition. Then we shall study the variation of the boiling points of the completely miscible liquids with composition. In Unit 11, we shall explain the characteristics of partially miscible and completely immiscible liquid systems.

In Unit 12, we shall explain the colligative properties and their importance in the determination of relative molecular masses of non-volatile solutes. In Unit 13, we shall discuss the phase equilibria of one and two component systems.

After studying this block, you should be able to :

- apply Raoult's law to the study of completely miscible liquid mixtures,
- discuss the variation of miscibility of partially miscible liquids with temperature,
- explain the methods of determination of relative molecular masses of non-volatile solutes using colligative properties, and
- apply phase rule to the study of one and two component systems.

UNIT 10 SOLUTIONS—I

Structure

10.1 INTRODUCTION

A solution may be defined as a homogeneous mixture of two or more substances, the composition of which may vary. It consists of two components, solute and solvent. The substance which is present in larger proportion is called the solvent and the substance which is present in smaller proportion is called the solute. Depending upon the number of constituents, a solution may be referred to as binary (two components), ternary (three components) or quaternary (four components). Depending upon the state of the solute and the solvent, there are nine types of solutions. The concentration of a solution could be expressed using different terms, e.g., molarity, molality, mole fraction, etc. The solubility of solids in liquids generally increases with rise in temperature. The solubility of gases in liquids is governed by Henry's law. Liquid solutions obeying Raoult's law are called ideal solutions. Solutions which do not obey Raoult's law are called non-ideal solutions. In this unit, we shall discuss the above aspects and also study fractional distillation of liquids. In the next unit, we shall study partially miscible and completely immiscible liquid pairs.

Objectives

After studying this unit you should be able to :

- define a solution,
- list various types of solutions,
- express concentration of solutions in different ways,
- define solubility,
- explain the solubility curves,
- state Henry's law,
- state Raoult's law,
- distinguish between ideal and non-ideal solutions,
- discuss Raoult's law curves,
- explain the principle of fractional distillation, and
- define the term, azeotrope.

10.2 TYPES OF SOLUTIONS

A solution may exist in solid, liquid or gaseous state. Depending upon the physical state, a solution may be classified into the types shown in Table 10.1.

Table 10.1 : Types of Solutions

Solute	Solvent	Example
Gas	Gas	Mixture of gases (e.g., air)
Gas	Liquid	Aerated water (which is a solution of CO_2 in water under pressure)
Gas	Solid	Gas adsorbed by metals or minerals (e.g., H_2 in palladium)
Liquid	Gas	Moist air
Liquid	Liquid	Alcohol in water
Liquid	Solid	Mercury in zinc (zinc amalgam)
Solid	Gas	Camphor in air
Solid	Liquid	Salt in water
Solid	Solid	Alloys (e.g., brass)

Solutions of substances in water are called aqueous solutions while solutions in other solvents are called nonaqueous solutions.

Solutions of mercury in metals are called amalgams e.g., sodium amalgam, zinc amalgam, etc. Amalgamation modifies the properties of metals. For example, sodium metal is a powerful reducing agent whereas sodium amalgam is a moderate reducing agent.

A solution is always in the same physical state as the solvent. In this unit, we shall study solid-liquid, gas-liquid and liquid-liquid solutions.

SAQ 1

Classify the following into the types of solutions to which they belong :

i) A five rupee coin
ii) Sodium amalgam
iii) Soda water

....

....

....

10.3 DIFFERENT WAYS OF EXPRESSING CONCENTRATION OF SOLUTIONS

The relative amounts of a solute and a solvent in a solution are expressed through concentration terms. Some of the ways of expressing the concentration of a solution are described below :

i) Molarity (M)

Molarity is defined as the number of moles of the solute present in 1 dm^3 (1 L or 10^{-3} m^3) of the solution. When 0.1 mole of a solute is present in one cubic decimeter of the solution, we say that the solution is 0.1 molar (0.1 M).

A solution containing *x* mol of a substance in 1 dm^3 of a solution is called *x* molar or *x* M solution.

$$\text{Molarity (M)} = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution in dm}^3} \quad \ldots (10.1)$$

Note that the volume of the solution should be expressed in dm^3 for expressing the concentration in terms of molarity.

ii) Molality (m)

Molality is defined as the number of moles of a solute present in one kilogram of the solvent. When one mole of a solute is dissolved in one kilogram of water, the concentration of the solution is one molal (1 m).

$$\text{Molality (m)} = \frac{\text{Number of moles of the solute}}{\text{Mass of the solvent in kg}} \quad \ldots (10.2)$$

iii) Normality (N)

The number of gram-equivalents of a solute present in 1 dm^3 of the solution is called its normality. A one normal solution contains one gram-equivalent of a solute in 1 dm^3 of solution and is denoted by 1 N.

$$\text{Normality (N)} = \frac{\text{Strength in g dm}^{-3}}{\text{Equivalent weight}} \quad \ldots (10.3)$$

iv) Mole fraction (x)

The mole fraction of a solute in a solution is the ratio of the number of moles of a solute to the total number of moles of the solute and the solvent in a solution. If n_2 mole of a solute is dissolved in n_1 mole of a solvent, the mole fraction of the solvent and the solute are given by the following expressions :

The sum of the mole fractions of all the components in a solution is always equal to one.

$$\text{Mole fraction of the solvent } (x_1) = \frac{n_1}{n_1 + n_2} \quad \ldots (10.4)$$

$$\text{Mole fraction of the solute } (x_2) = \frac{n_2}{n_1 + n_2} \quad \ldots (10.5)$$

v) Percentage

In terms of percentage, the concentration of a solution may be expressed in four different ways :

10 mL of alcohol present in 100 mL of solution = 10% (*V/V*)
10 g NaCl present in 100 mL of solution = 10% (*W/V*)
10 mL alcohol present in 100 g of solution = 10% (*V/W*)
10 g NaCl present in 100 g of solution = 10% (W/W)

Unless specified, a 10% solution may always be taken as weight by weight (*W/W*).

vi) Parts per million (ppm)

When a solute present in the solution is in very minute amounts, the concentration is usually expressed in parts per million (ppm). For example, the amount of oxygen dissolved in sea water is 5.8 g in 10^6 (1 million) ~~gram~~ of sea water. It means 5.8 parts of oxygen are present in one million parts of sea water. Hence, the concentration of oxygen in sea water is 5.8 ppm. The concentration of gases which pollute the atmosphere is also expressed in ppm.

All concentration units except mole fraction, molality, ppm and percentage (*W/W*), vary with temperature.

$$\text{One ppm} = \frac{\text{Mass of solute (g)}}{\text{Total mass of solution (g)}} \times 10^6 \quad \ldots (10.6)$$

Similar to Eq. 10.6, parts per billion (ppb) may be defined as follows:

$$\text{One ppb} = \frac{\text{Mass of solute (g)}}{\text{Total mass of solution (g)}} \times 10^9$$

Let us work out an example using the molarity expression explained above.

Example 1

Concentrated sulphuric acid contains 98% acid by weight. Its density is 1.85×10^3 kg m^{-3}. Calculate its molarity.

Solution

1 m = 10 dm
1 m^3 = (10 dm)^3
= 10^3 dm^3

$$\text{Molarity of sulphuric acid} = \frac{\text{Number of moles of sulphuric acid}}{\text{Volume in dm}^3}$$

$$= \frac{\text{Mass of sulphuric acid in 1 m}^3}{\text{Molar mass} \times 10^3\ \text{dm}^3}$$

$$= \frac{98 \times 1.85 \times 10^3\ \text{kg}}{100 \times 0.098\ \text{kg mol}^{-1}} \times \frac{1}{10^3 \text{dm}^3}$$

$$= 18.5\ \text{M}.$$

SAQ 2

A solution contains 0.100 kg each of water and ethanol. Find the mole fraction of each component.

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10.4 SOLUTIONS OF SOLIDS IN LIQUIDS

In solutions of solids in liquids, the liquid is referred to as the solvent and, the solid which is dissolved in it, as the solute. When a solid is added gradually to a given amount of a liquid (solvent) at constant temperature, a state is reached when some of the solid remains undissolved. The solution is then said to be saturated. The mass of the solute that can be dissolved in 0.100 kg of a solvent to form a saturated solution at a given temperature is called its **solubility**.

Solubility of a solid in a liquid varies with temperature. The plot of solubility against temperature is called the solubility curve. Some typical solubility curves are shown in Fig. 10.1.

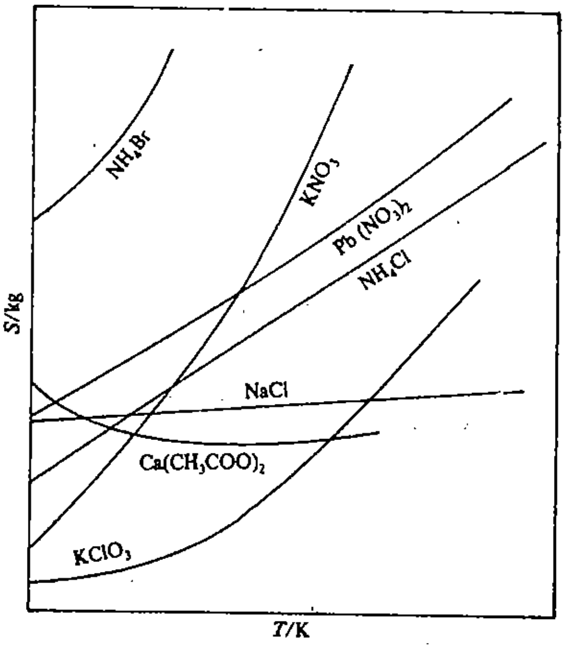

Fig. 10.1 : Solubility curves of different solutes: *S* stands for solubility and *T* for temperature.

The solubilities of many of the ionic substances in water increase with temperature. The solubility of sodium chloride increases to a very small extent with rise in temperature. The solubility of calcium acetate decreases with rise in temperature.

In many cases, when a solute is dissolved in a solvent, heat is absorbed, i.e., cooling results. Then according to Le Chatelier's principle, when the temperature of a saturated solution in contact with the solute is raised, a change will take place such that there is absorption of heat, i.e., along the direction in which cooling takes place. The solubility of the substance will, therefore, increase with rise in temperature.

The dissolution of some salts in water (e.g., calcium salts of organic acids) is accompanied by evolution of heat. Evidently, the solubility of such salts decreases with rise in temperature.

According to Le Chatelier's principle, if a system under equilibrium is subjected to a change of concentration, pressure or temperature, the system shifts in such a way that tends to undo the effect of that change. You will study this principle in detail in Unit 14.

10.5 SOLUTIONS OF GASES IN LIQUIDS

Most of the gases dissolve in water or some other liquids to a greater or less extent. In a gas, the molecules are quite far apart. After dissolution in a liquid solvent, the molecules of the gas are much closer. It is just like saying that before a gas dissolves in a liquid, it must be condensed to give a liquid. The condensation of gas is an exothermic process. The enthalpy of condensation is larger than the enthalpy of solution. Thus the dissolution of a gas is an exothermic process (i.e., heat is evolved). The solubility of a gas in a liquid is measured in terms of absorption coefficient or Bunsen coefficient. This coefficient has been named after the scientist, Bunsen, who introduced it. It is denoted by α. It is defined as the volume of a gas at standard temperature and pressure (273.15 K and 1.013×10^5 Pa) dissolved by unit volume of the solvent at the temperature of the experiment and under a pressure of 1.013×10^5 Pa. The absorption coefficients of some gases are given in Table 10.2.

Table 10.2 : Absorption Coefficients at 293 K

Solvent	Carbon dioxide	Hydrogen	Oxygen	Nitrogen
Water	0.88	0.018	0.028	0.015
Ethanol	3.00	0.081	0.142	0.130
Benzene	—	0.060	0.165	0.105

Factors affecting solubility of gases

The solubility of a gas in a liquid depends upon :

- temperature
- pressure, and
- nature of the gas and the solvent.

We will consider each of these factors separately.

1. Effect of temperature

The dissolution of a gas in a liquid is an exothermic process. Hence, according to Le Chatelier's principle, the solubility of a gas in a liquid decreases with rise in temperature. This behaviour can be seen when bubbles of dissolved air escape on heating water below 373 K.

2. Effect of pressure—Henry's law

The solubility of solids in liquids is not so much affected by pressure as the volume changes are not so high. But the solubility of a gas in a liquid varies considerably with pressure. In 1803, the English Chemist, Henry found that the solubility of a gas increases as the gas pressure is increased at a given temperature. He proposed the generalisation which is known as Henry's law. It may be stated as follows :

At constant temperature, the partial pressure of a gas over a solution is directly proportional to the concentration of the gas in the solution.

For example, doubling the pressure of oxygen, doubles the amount of oxygen that will dissolve in a given amount of the solvent.

Mathematically, Henry's law is expressed as follows:

$$p = Kx \qquad \text{. . . (10.7)}$$

Where p is the partial pressure of the gas over the solution and x is the solubility of the gas in terms of its mole fraction in the solution; K is a constant, characteristic of the specific combination of the solvent and the gas. It is called Henry's law constant. The partial pressure is expressed in terms of pascal (Pa).

From Eq. 10.7, the Henry's law constant is given as

$$K = \frac{p}{x} \qquad \text{. . . (10.8)}$$

K has the dimensions of pressure. K is not constant as expected from Eq. 10.8 because of non-ideality of the solution. Its value is obtained by plotting the ratio p/x vs x and extrapolating to $x = 0$. Such a graph is shown in Fig. 10.2.

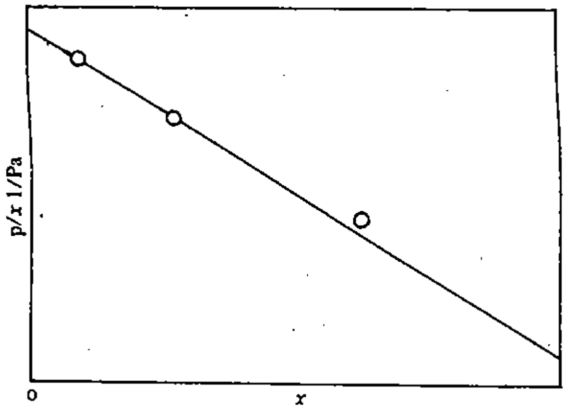

Fig. 10.2: Evaluation of Henry's law constant.

Henry's law constants for some gases are given in Table 10.3:

Table 10.3 : Henry's Law Constants at 298 K

Gas	$K/10^9$ Pa	
	In water	In benzene
H_2	7.12	0.37
N_2	8.68	0.24
O_2	4.40	—
CO	5.80	0.16
CO_2	0.17	0.01

It has been found that Henry's law is followed most closely by dilute solutions of gases that do not react with the solvent. Thus the law is valid for the solubility of hydrogen chloride and ammonia in water. Hydrogen chloride ionises in water and ammonia enters into chemical combination with water.

$$H_2O + HCl \rightleftharpoons H_3O^+ + Cl^-$$
$$H_2O + NH_3 \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

3. Nature of the gas and the solvent

Generally, gases which react chemically with the solvent are more soluble in it than in other solvents. For example, hydrogen chloride gas is more soluble in water than in benzene. Gases which can be easily liquefied are more soluble in common solvents.

Example 2

The Henry's law constant for O_2 is 4.40×10^9 Pa. Calculate the molarity of oxygen in water at 298 K. The partial pressure of oxygen over the solution is 1.00×10^5 Pa. Assume that 1.00 dm³ of the aqueous solution weighs 1.00 kg.

Solution

$K = 4.40 \times 10^9$ Pa
$p = 1.00 \times 10^5$ Pa

Mole fraction of oxygen,

$$x_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}} = \frac{n_{O_2}}{n_{O_2} + (1.00/0.018)\ \text{mol}} \simeq \frac{n_{O_2}}{(1.00/0.018)\ \text{mol}} = \frac{n_{O_2}}{55.6\ \text{mol}}$$

The approximation is done above since the number of moles of O_2 is negligible in comparison to the number of moles of H_2O.

Substituting the values in Eq. 10.8, we get

$$4.40 \times 10^9\ \text{Pa} = \frac{1.00 \times 10^5\ \text{Pa}}{n_{O_2}/55.6\ \text{mol}} = \frac{1.00 \times 10^5\ \text{Pa}}{n_{O_2}} \times 55.6\ \text{mol}$$

$$\text{or } n_{O_2} = \frac{1.00 \times 10^5\ \text{Pa}}{4.40 \times 10^9\ \text{Pa}} \times 55.6\ \text{mol} = 1.26 \times 10^{-3}\ \text{mol.}$$

In other words, the solubility of oxygen in water at 298 K = 1.26×10^{-3} mol dm^{-3} since 1 kg (or 1 dm^3) of the solution contains 1.26×10^{-3} mol of oxygen.

SAQ 3

Why cannot fish live in warm water?

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10.6 SOLUTIONS OF LIQUIDS IN LIQUIDS

In the liquid-liquid type solution, we consider only binary liquid solutions, i.e., solutions containing two liquids. When two liquids A and B are mixed, we can have the following possibilities.

i) liquid A is completely miscible with liquid B in all proportions (e.g., water and ethanol, toluene and benzene, etc.).

ii) liquids A and B are only partially miscible in each other (e.g., water and phenol).

iii) liquids A and B are completely immiscible with each other (e.g., water and carbon tetrachloride). We shall study completely miscible liquid systems in this unit. The other two types will be taken up for study in Unit 11.

Raoult's Law

Consider a binary solution containing two liquids A and B which are completely miscible with each other in all proportions. In such solutions, the terms, solute and solvent, can be interchanged for the two components. In 1880, the French Chemist, Raoult found that when a non-volatile solute is dissolved in a solvent (liquid), the vapour pressure of the solvent decreases. If the solute and the solvent are both volatile, the vapour pressures of both the components are decreased. Based on these observations, he gave the following generalisation which is called **Raoult's law**.

The partial vapour pressure of any volatile component in a solution is equal to the product of the vapour pressure of the pure component and its mole fraction in the solution.

Each component of an ideal solution is present in differing amounts in liquid and vapour phases. Remember that Raoult's law talks about the relationship between the partial pressure of a component and its mole fraction in the liquid phase.

If x_A and x_B are the mole fractions of the components A and B in the liquid solution and p_A and p_B, the vapour pressures of these components, respectively, then according to Raoult's law,

$$p_A = p_A^o x_A \qquad \ldots (10.9)$$

and $$p_B = p_B^o x_B \qquad \ldots (10.10)$$

If the vapours behave like an ideal gas, then according to Dalton's law of partial pressures, the total vapour pressure, p, is given by

$$p = p_A + p_B = p_A^0 x_A + p_B^0 x_B \qquad \ldots (10.11)$$

Ideal Solutions

A solution which obeys Raoult's law at all concentrations and at all temperatures is called an ideal solution. Two liquids A and B on mixing form an ideal solution, if

i) the molecules of A and B have similar structure and polarity, and

ii) the intermolecular attractions between A and A, B and B, and A and B are all alike.

Thermodynamically, ideal solutions are those in which there is no volume change ($\Delta V_{mixing} = 0$) and enthalpy change ($\Delta H_{mixing} = 0$) when two liquids A and B are mixed. Thus the characteristics of an ideal solution are:

i) it must obey Raoult's law

ii) $\Delta H_{mixing} = 0$

iii) $\Delta V_{mixing} = 0$

Some examples of nearly ideal liquid mixtures are :

i) ethylene bromide and ethylene chloride

ii) n-hexane and n-heptane

iii) benzene and toluene

iv) n-butyl chloride and n-butyl bromide

v) carbon tetrachloride and silicon tetrachloride

Non-ideal Solutions

Many of the completely miscible liquid pairs form non-ideal solutions. These solutions do not obey Raoult's law. They either show positive deviation (when the vapour pressure of the solution is higher than that of an ideal solution of the same concentration) or negative deviation (when the vapour pressure of the solution is lower than that of an ideal solution of the same concentration) from Raoult's law. In such solutions

$$p_A \neq p_A^o x_A \qquad \ldots (10.12)$$

and $$p_B \neq p_B^o x_B \qquad \ldots (10.13)$$

When the components of a non-ideal solution are mixed, a considerable change in volume and enthalpy is noticed. Thus the characteristics of non-ideal solutions are as follows :

i) they do not obey Raoult's law

ii) $\Delta H_{mixing} \neq 0$

iii) $\Delta V_{mixing} \neq 0$

Examples of non-ideal solutions showing positive and negative deviations are given in Table 10.4.

Table 10.4 : Liquid pairs showing deviation from Raoult's law

Positive deviation	Negative deviation
$H_2O + C_2H_5OH$	$H_2O + HCl$
$CH_3COCH_3 + C_2H_5OH$	$H_2O + HNO_3$
$C_2H_5OH + C_6H_{12}$	$H_2O + H_2SO_4$
$CH_3COCH_3 + CS_2$	$CH_3COCH_3 + CHCl_3$

Let us work out an example illustrating the application of Raoult's law.

Example 3

Two liquids A and B form an ideal solution at 300 K. The vapour pressure of a solution containing 1.0 mol of A and 2.0 mol of B at 300 K is 2.0×10^5 Pa. When one more mole of B is added to the solution, the vapour pressure of the solution is 2.1×10^5 Pa. Calculate the vapour pressures of A and B in the pure state.

Solution

According to Eq. 10.11, total vapour pressure of the solution is given by,

$$p = p_A^\circ x_A + p_B^\circ x_B$$

Substituting the values, we get

$$2.0 \times 10^5 \text{ Pa} = p_A^\circ \left(\frac{1.0}{1.0 + 2.0}\right) + p_B^\circ \left(\frac{2.0}{1.0 + 2.0}\right)$$

or $2.0 \times 10^5 \text{ Pa} = p_A^\circ/3.0 + 2.0\, p_B^\circ/3.0$

or $p_A^\circ + 2.0\, p_B^\circ = 6.0 \times 10^5 \text{ Pa}$ ... (1)

Also $$2.1 \times 10^5 \text{ Pa} = p_A^\circ \left(\frac{1.0}{1.0 + 3.0}\right) + p_B^\circ \left(\frac{3.0}{1.0 + 3.0}\right)$$

or $p_A^\circ + 3.0\, p_B^\circ = 8.4 \times 10^5 \text{ Pa}$ ... (2)

From (1) and (2),

$p_B^\circ = 2.4 \times 10^5$ Pa

$p_A^\circ = 1.2 \times 10^5$ Pa

SAQ 4

0.100 mol of acetone and 0.100 mol of chloroform are mixed at 308 K. At this temperature, the total vapour pressure of the solution is 3.47×10^4 Pa. The vapour pressures of pure acetone and pure chloroform at 308 K are 4.60×10^4 Pa and 3.92×10^4 Pa, respectively. Verify whether this solution is ideal or not.

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10.7 RAOULT'S LAW CURVES

According to Raoult's law, the partial vapour pressure of each component A and B of an ideal solution is given by Eqs. 10.9 and 10.10. The partial vapour pressure of each component can be plotted against its mole fraction in the liquid phase. Such vapour pressure curves for an ideal solution are shown in Fig. 10.3.

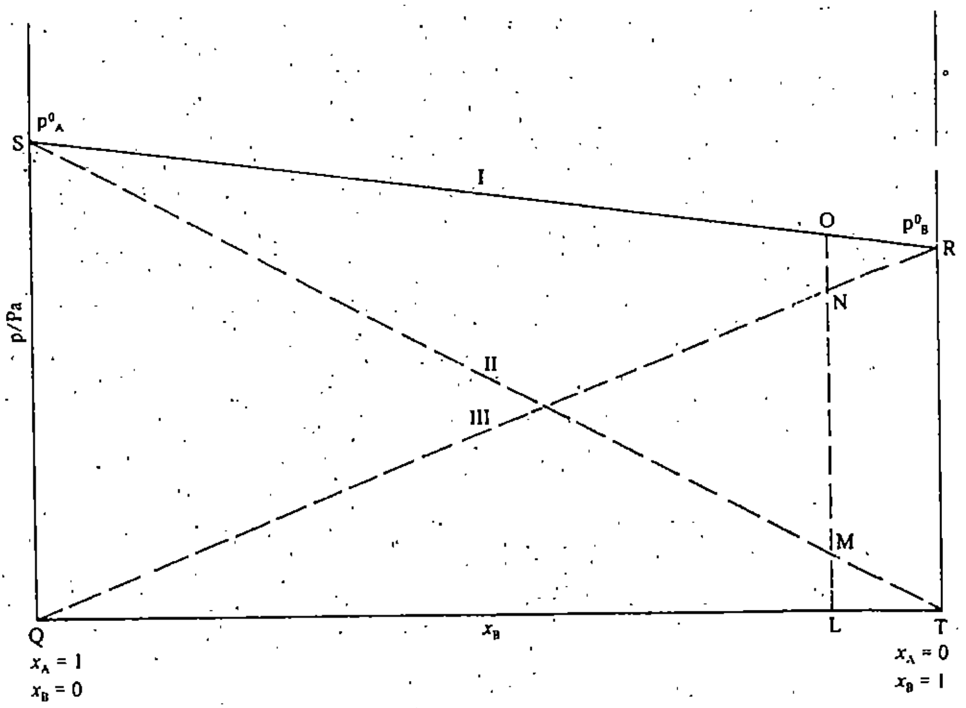

Fig. 10.3 : Vapour pressure curves for ideal solution :
Curve I : Total vapour pressure of solution;
Curve II : Partial vapour pressure of A, $p_A = p^\circ_A x_A$;
Curve III : Partial vapour pressure of B, $p_B = p^\circ_B x_B$

The dotted lines show the variation of vapour pressure of the components A and B with mole fraction in the liquid phase. Thus curve QR (III) indicates the variation of partial vapour pressure of B with its mole fraction in liquid solution and curve ST (II) indicates the variation of partial vapour pressure of A with its mole fraction in the liquid solution. The points, S and R, represent the vapour pressures (p^0_A and p^0_B) of the pure components A and B, respectively. The variation of total vapour pressure with respect to the mole fraction of B in the liquid solution is given by the curve SR (I).

Note that the partial pressure curves II and III of the components A and B pass through the respective origins T and Q (where the mole fraction of a particular component and its partial pressure are zero). This is understandable since the partial pressure of a component, p_i as given by Raoult's law is $p_i = p^\circ_i x_i$. This resembles the equation $y = mx$ that represents a straight line passing through the origin. The curve I representing the total vapour pressure of an ideal solution is a straight line connecting p°_A and p°_B, since the total pressure p as per Eq. 10.11 is given by

$p = p^\circ_A$ when $x_A = 1$ and $x_B = 0$ and $p = p^\circ_B$ when $x_A = 0$ and $x_B = 1$

From Fig. 10.3, it can be seen that the vapour pressure of an ideal solution of composition L is given by the sum of the partial vapour pressure of A and the partial vapour pressure of B (or OL = ML + NL).

Vapour Pressure Curves of Solutions Showing Positive Deviation

If the molecular interactions between A and B are weaker than the A-A or B-B molecular interactions, then the escaping tendency of the molecules of A and B from the solution becomes more than that from the pure liquids. As a result, the vapour pressure of the solution will be greater than that of an ideal solution of the same composition. Such solutions are said to show positive deviation from Raoult's law. Mathematically,

$$p_A > p^\circ_A x_A \qquad \ldots (10.14)$$

$$p_B > p^\circ_B x_B \qquad \ldots (10.15)$$

$$\text{and } p > p^\circ_A x_A + p^\circ_B x_B \qquad \ldots (10.16)$$

In Fig. 10.4, the dotted lines are theoretical curves showing the ideal behaviour; the solid lines are curves drawn as per experimental values and show positive deviation from ideal behaviour. When ethanol and cyclohexane are mixed, the curves as shown in Fig. 10.4 are obtained.

In ethanol, there is a strong intermolecular hydrogen bonding. When cyclohexane is added to it, the cyclohexane molecules get in between the ethanol molecules thereby decreasing the intermolecular interactions. During the formation of such solutions, heat is absorbed and there is a slight increase in volume.

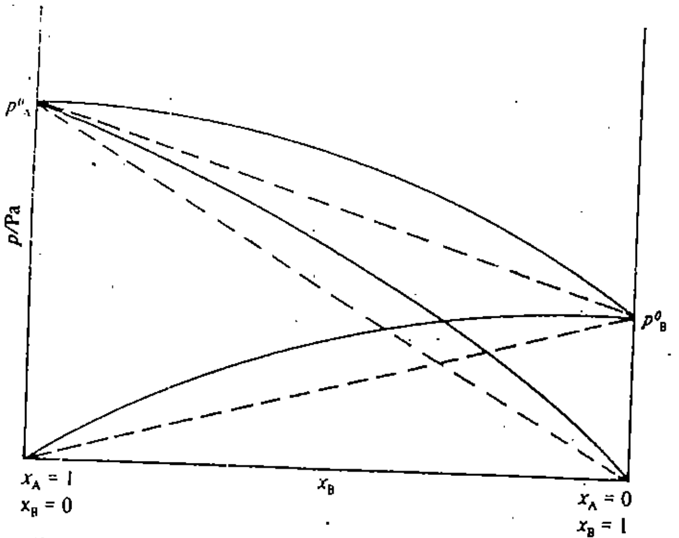

Fig. 10.4 : Curves showing positive deviation from Raoult's law.

Vapour Pressure Curves of Solutions Showing Negative Deviation

If the intermolecular forces between A and B are stronger than those of A-A and B-B, he solution formed by mixing A and B shows negative deviation from Raoult's law. ue to stronger A-B interactions, the escaping tendency of A and B from the solution ecomes less than that from the pure liquids. The vapour pressure of such a solution vill be less than an ideal solution of the same composition. This behaviour is shown n Fig. 10.5.

We have explained in Sec. 4.5 of Unit 4 of this course that increase of molecular attraction causes a decrease in vapour pressure of liquids.

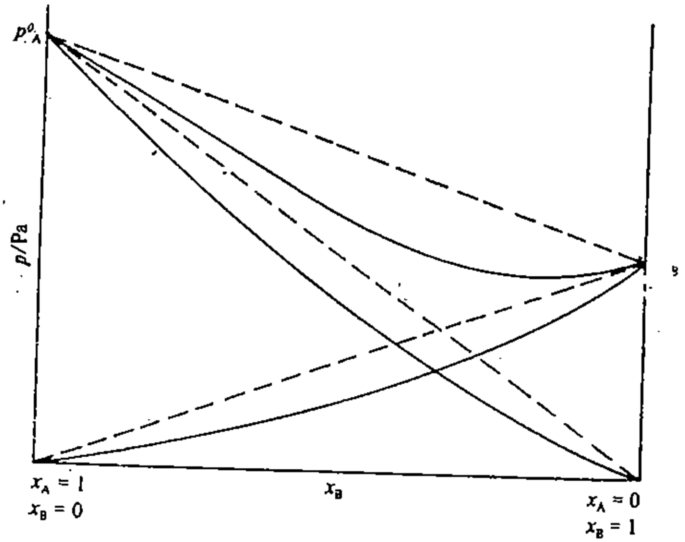

Fig. 10.5 : Curves showing negative deviation from Raoult's law.

e dotted lines are the theoretical curves representing the ideal behaviour, whereas solid lines are the curves drawn as per experimental values and show negative iation from ideal behaviour. When acetone and chloroform are mixed, they form lrogen bonds with each other. As a result, the intermolecular attractions between tone and chloroform become stronger. The tendency of the molecules to escape m the solution thus decreases. The vapour pressure, therefore, decreases. During formation of such solutions, heat is evolved and there is a slight decrease in ume.

.8 VAPOUR PRESSURE VARIATION WITH LIQUID AND VAPOUR COMPOSITION

sider a solution containing one mole of benzene and one mole of toluene so that nole fraction of each component in the solution is 0.5. The vapour pressures of benzene and toluene at 298 K are 1.25×10^4 Pa and 3.70×10^3 Pa, respectively. rding to Raoult's law.

$$p_{C_6H_6} = p^{\circ}_{C_6H_6}\, x_{C_6H_6} = (1.25 \times 10^4 \text{ Pa}) \times 0.5 = 6.25 \times 10^3 \text{Pa}$$

$$p_{C_7H_8} = p^{\circ}_{C_7H_8}\, x_{C_7H_8}$$
$$= (3.70 \times 10^3 \text{ Pa}) \times 0.5$$
$$= 1.85 \times 10^3 \text{ Pa}$$

$$p_{\text{total}} = (6.25 \times 10^3 \text{ Pa}) + (1.85 \times 10^3 \text{ Pa}) = 8.10 \times 10^3 \text{ Pa}$$

Mole fraction of benzene in the vapour phase

$$= \frac{6.25 \times 10^3 \text{ Pa}}{8.10 \times 10^3 \text{ Pa}} = 0.77$$

Mole fraction of toluene in the vapour phase

$$= \frac{1.85 \times 10^3 \text{ Pa}}{8.10 \times 10^3 \text{ Pa}} = 0.23$$

It is quite interesting to compare the mole fractions of benzene in the vapour and liquid phase solutions. From the calculations made above, the mole fraction of benzene (0.77) in the vapour phase is more than that in the liquid phase (0.5). Again, the mole fraction of toluene in the vapour phase (0.23) is less than that in the liquid phase (0.5). Bearing in mind that benzene is more volatile than toluene, we can arrive at the following generalisation which is one of the forms of Konowaloff's rule: The mole fraction of a more volatile component in an ideal solution is more in the vapour phase than in the liquid phase.

For the purpose of comparing the compositions of the solutions in the liquid and the vapour phases at a given total vapour pressure, it is worth drawing curves of the type I and II shown in Fig. 10.6. Curve I shows the variation of total vapour pressure with respect to the mole fraction in the liquid phase. Similarly, curve II shows the variation of the total vapour pressure with respect to the mole fraction in the vapour phase. The line MN is called a **tie line** and it gives us the composition of the solution in the liquid and vapour phases in equilibrium at a particular total vapour pressure.

Note that the vapour phase curve II lies below the liquid phase curve I. This is due to the fact that the vapour phase is richer in the more volatile component than the liquid phase and this has been explained in the beginning of this section.

In Figs. 10.6 to 10.15, *g* and *l* refer to vapour phase and liquid phase curves.

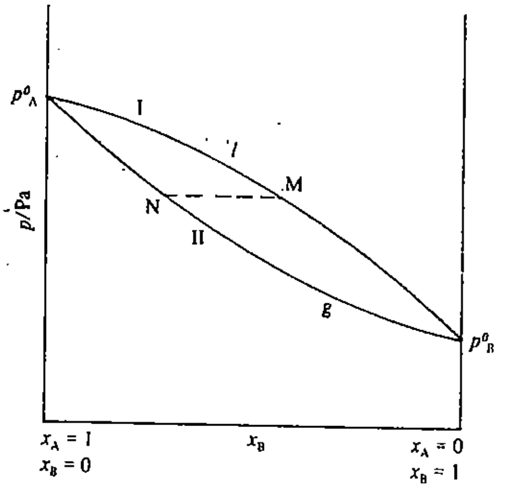

Fig. 10.6: Liquid and vapour composition curves for an ideal solution.

The curves I and II of Fig. 10.6 are obtained in the case of solutions obeying Raoult's law. In the case of solutions showing positive deviation from Raoult's law, the liquid and vapour comporisition curves are of the type shown in Fig. 10.7. Note that there is a maximum point, M, where both the liquid and vapour phases have the same composition.

In the case of a solution showing negative deviation from Raoult's law, the liquid and vapour composition curves are of the type shown in Fig. 10.8. Note that the curves meet at the minimum point M where both the liquid and vapour phases have the same composition.

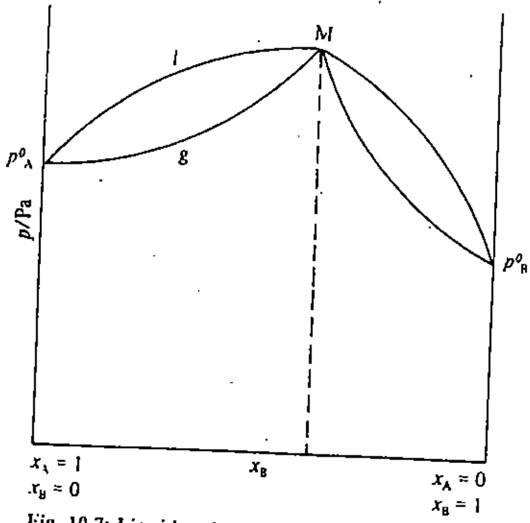

Fig. 10.7: Liquid and vapour composition curves for a liquid mixture showing positive deviation.

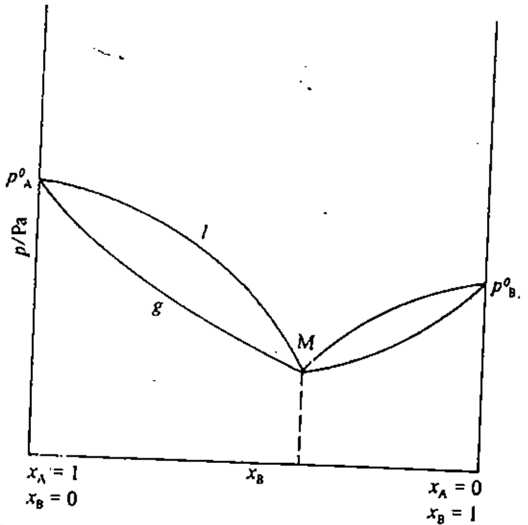

Fig. 10.8: Liquid and vapour composition curves for a liquid mixture showing negative deviation.

The curves in Figs. 10.3 to 10.8 have been drawn for vapour pressure values at constant temperature.

So far we studied the effect of composition on the vapour pressure of the completely miscible liquid system. In the next section, we will study the effect of composition on the boiling points of solutions. Such studies are helpful in understanding some of the aspects of separation of components from a binary liquid mixture. In particular, we will study the principles of fractional distillation and azeotropic distillation.

SAQ 5

In a binary solution obeying Raoult's law, can the liquid and the vapour phases have the same composition?

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10.9 BOILING POINT DIAGRAMS

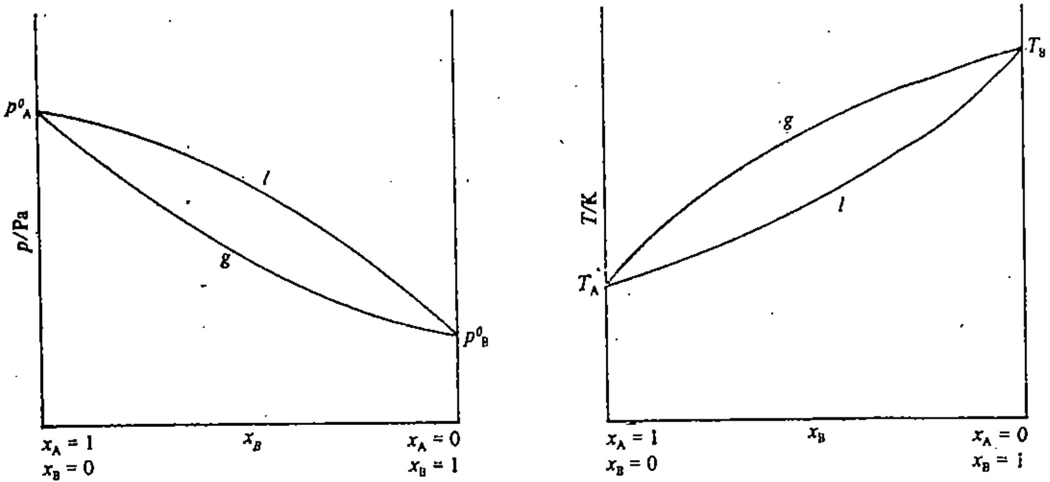
Let us consider a binary mixture consisting of two liquids A and B which are completely miscible with each other. On heating under constant pressure, say, under atmospheric pressure, it will start boiling when the total vapour pressure becomes equal to the atmospheric pressure. If p represents the atmospheric pressure, then the condition for boiling is

$$p = p_A + p_B \qquad \ldots (10.17)$$

where p_A and p_B are the partial pressures of the two components A and B. Since different compositions of a solution have different vapour pressures, the various solutions will not reach a total vapour pressure equal to the atmospheric pressure at he same temperature. Hence, the solutions of different compositions will boil at different temperatures. In general, solutions of low vapour pressure will boil at emperatures higher than those of solutions for which the vapour pressures are high. t is because solutions of high vapour pressure can have the total pressure equal to the tmospheric pressure at relatively lower temperatures as compared to solutions for which vapour pressures are low. Hence it is possible to draw temperature-composition iagrams which will correspond to the three general types of vapour pressure-omposition diagrams. First we shall study boiling point-composition curves of an eal solution.

Type I : Distillation of an Ideal Solution

Let us consider a binary mixture of liquids A and B obeying Raoult's law.



(a) (b)

Fig. 10.9 : a) Liquid and vapour composition plotted against vapour pressure at constant temperature for an ideal solution, b) liquid and vapour composition plotted against temperature at constant pressure for an ideal solution.

Let the vapour pressure of pure A be higher than that of pure B (Fig. 10.9 a). Consequently at constant pressure, the boiling point of A (T_A) will be lower than that of B (T_B). We can get an idea about the relative composition of the vapour phase over a solution using Konowaloff's rule. Although you have studied one of the forms of this rule in the last section, this rule can also be stated as follows :

In the distillation of a binary liquid mixture, vapours coming out will be richer in that component whose addition to the liquid mixture causes an increase in vapour pressure.

In other words, as compared to the liquid mixture, the vapour is richer in the more volatile component. In the liquid mixture that we have taken, A is more volatile than B. Hence, the vapour composition at any temperature must lie closer to A than the corresponding liquid composition. In other words, in the composition against temperature plot, the vapour composition curve must lie above the liquid composition curve as shown in Fig. 10.9 b. Note the difference in the relative positions of the liquid and vapour curves between Figs. 10.9 a and b.

Using Fig. 10.10 we can understand the various stages in the separation of the components of an ideal solution.

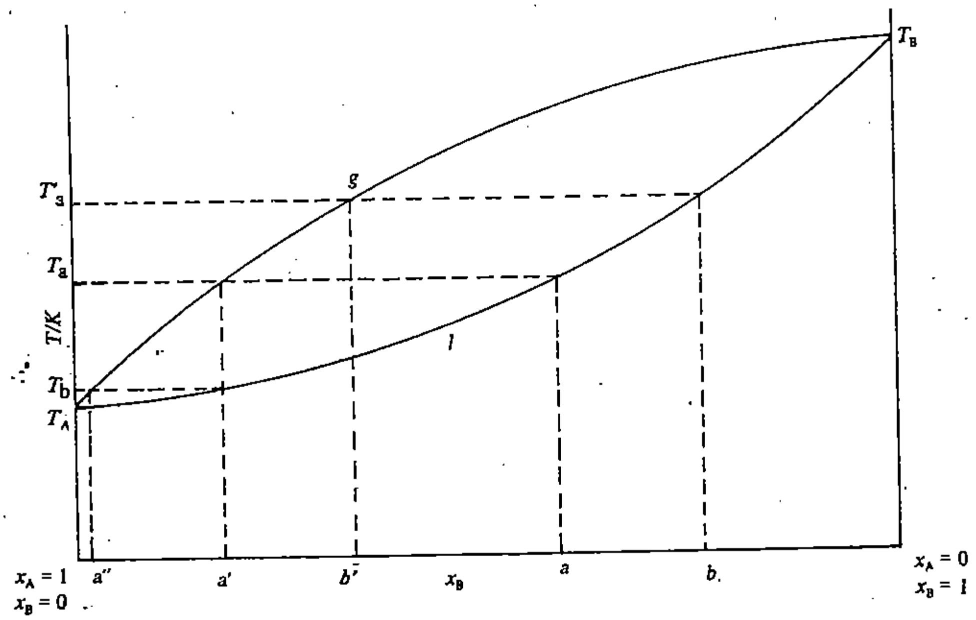


Fig. 10.10 : Separation of the components from an ideal solution at constant pressure.

Let us start with a solution of A and B having liquid composition, *a*. If this solution is heated, it boils at a temperature, T_a, when its vapour pressure is equal to the atmospheric pressure. At T_a, let the composition of the liquid and the vapour be *a* and *a'*, respectively. Since A is more volatile than B, vapours of composition *a'* will be richer in A than liquid of composition *a*. Assume that these vapours coming out of the liquid are collected and condensed to obtain the liquid. The liquid so obtained by cooling the vapours of composition *a'* also will have the same composition. As the vapours of composition *a'* (which are richer in A than the liquid of composition *a*) are removed, the composition of the residual liquid changes to *b*; note that the liquid of composition *b* is richer in B than the liquid of composition *a*. The boiling point of this residual liquid (T_a') is higher than T_a. At this temperature, vapours coming out of the boiling tube have composition *b'*. Again the vapours of composition *b'* are richer in A than the liquid of composition *b*. The vapours on condensation give liquid of composition *b'*. On the removal of vapours, the boiling point rises and the residual liquid becomes richer in *B*. So, if this process is continued, the boiling point of the residual solution will rise from initial boiling point T_a towards the boiling point of pure B, T_B. At the same time, the residue will become richer in B and if the process is repeated continuously, a final residue of pure B can be obtained.

Let us now consider the liquid *a'* obtained by cooling the vapours coming out at T_a. If this liquid is heated, it boils at T_b and the vapours coming out will have the composition *a''*, which on condensation give the liquid of same composition. It is obvious from Fig. 10.10 that liquid of composition *a''* is richer in A than that of composition *a'*. If the process of distillation and condensation is continued, we can obtain vapours of pure A. So, we can separate mixtures of type I into a residue of the less volatile component (B) and a distillate of more volatile component (A). The separation is practically more efficient using fractional distillation.

Fractional Distillation and Theoretical Plates

The several stages described for the separation of ideal solution into its pure components can be carried out in the continuous process which is called fractional distillation. In fractional distillation, the process of successive vaporization and condensation is carried out in a fractionating column. Let us understand it by taking benzene and toluene liquid mixture, having the composition *a* (Fig. 10.11).

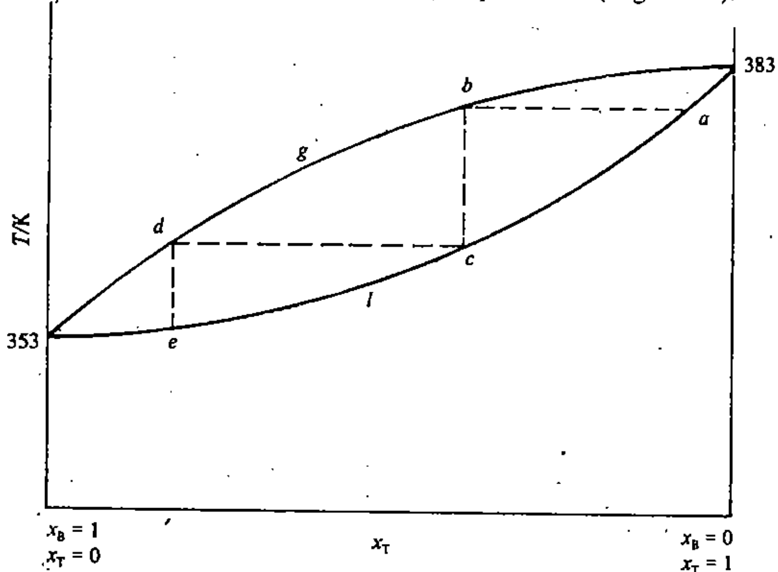


Fig. 10.11 : Liquid and vapour compositions of benzene and toluene; x_B and x_T refer to mole fractions of benzene and toluene.

The vapours in equilibrium are richer in the more volatile component, benzene, and will have the composition *b*. This vapour may be condensed by lowering the temperature along the line *bc*. If a small fraction of this condensate is vaporized, the vapours formed will have composition *d*. Finally, by repetition of vaporization and condensation, a vapour fraction rich in benzene can be obtained. Here, each vaporization and condensation represented by the path *abcde* corresponds to an idealized process in which only a small fraction of the vapour is condensed and only a small fraction of the condensate is revaporized. Practically, the fractionating column shown in Fig. 10.12 is more efficient.

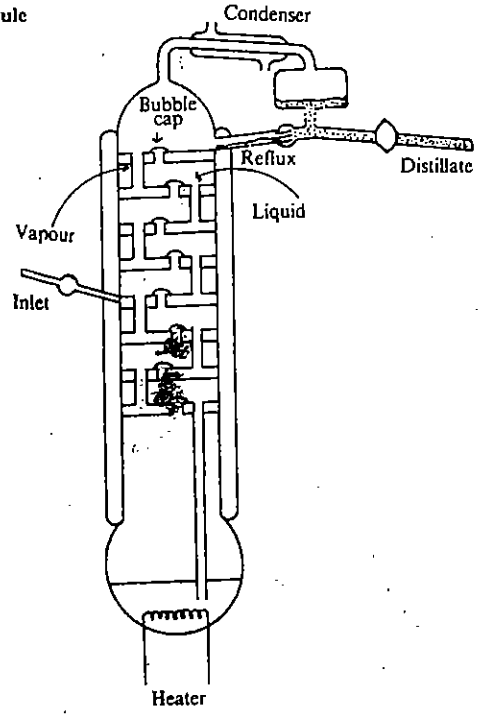


Fig. 10.12 : Fractionating column.

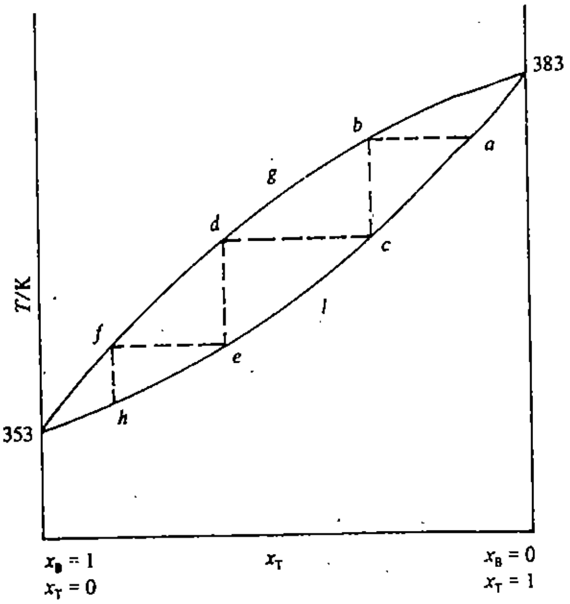


Fig. 10.13 : Fractionation of the components; x_B and x_T stand for mole fractions of benzene and toluene.

Each layer of the liquid on the plates of the column is equivalent to the boiling liquid in a distillation flask, and the liquid on the plate next above it is equivalent to the liquid condensed from the vapours. The vapour passes upwards through bubble caps, where it is partially condensed into the liquid and mixed with it. Part of the resulting solution is vaporized in the process and is condensed in the next higher layer, while part of the liquid overflows and runs down the tube to the next lower plate. The efficiency of a column is expressed in terms of the equivalent number of **theoretical plates.** The number of theoretical plates in a column is equal to the number of successive infinitesimal vaporizations required to give the separation to the desired extent. The number of theoretical plates in a distillation column under actual operation may be obtained by using Fig. 10.13 and counting the number of equilibrium vaporizations required to achieve the separation of the components to the required extent. Suppose that in distilling a solution of benzene and toluene of composition *a* with a certain distillation column, it is found that distillate of composition *h* is obtained (Fig. 10.13). Such a distillation is equivalent to three simple vaporizations and condensations as indicated by steps *abc*, *cde* and *efh*. Since the distilling pot itself corresponds to one theoretical plate, the column has two theoretical plates.

Type II : Distillation of a Solution Exhibiting Positive Deviation

Let us now take up the separation of a mixture of liquids showing positive deviation from Raoult's law. Fig. 10.14 represents the boiling point-composition diagram of such systems. Note that this system has a minimum point (C) where the liquid and vapour phases have the same composition.

Let us consider the distillation of a solution of composition, *a*, which is between A and C. The vapours coming off will have the composition *p* and will be richer in B than the liquid, *a*. Because of this, the composition of the residue will shift towards A. Hence, the residue will have to boil at a higher temperature than the original solution, *a*. If the distillation is continued (through the steps *abc*, *bcd* etc.), finally a residue of pure A, boiling at temperature T_A, will be obtained. Now, if the vapours of composition *p* coming out from the original solution, are condensed and redistilled repeatedly (through the steps *pqr*, *qrs*, etc.), vapours of composition C will eventually be obtained. Such vapours when condensed and redistilled will again yield the vapours of composition C i.e., vapours will have the same composition as that of the liquid solution. Hence, no further separation is possible by distillation. Because of this, the liquid of composition C is called the constant boiling mixture. Thus, any

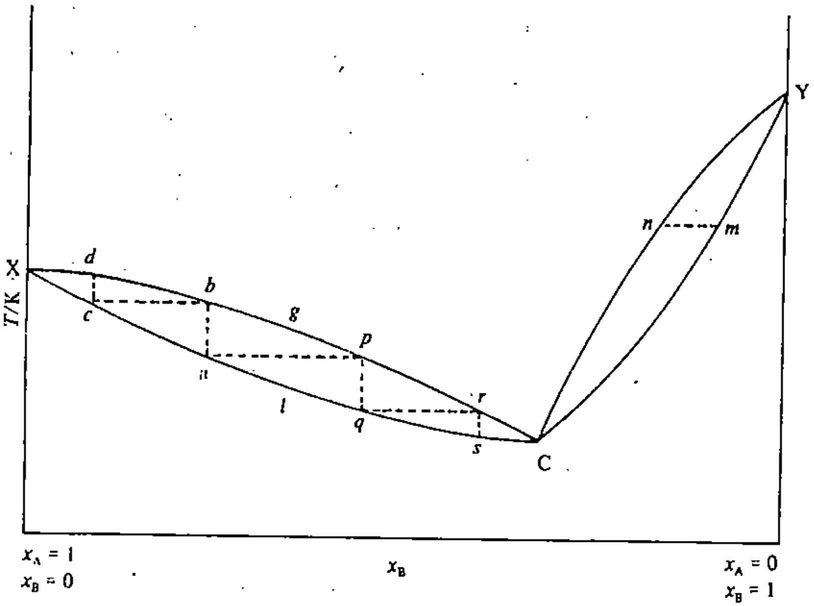


Fig. 10.14: Boiling point-composition digaram of a liquid-mixture showing positive deviation.

mixture having a composition between X and C can be separated by fractional distillation only into a residue of pure A and a final distillate of composition, C, but pure B cannot be recovered.

On the other hand, if a solution of composition *m* which is between C and Y is distilled, then the vapours of composition *n* which are coming out, will be richer in A than the original solution. Hence, on repeated distillation, the residue will tend towards pure B, while the distillate will tend towards C. Such solutions on complete distillation will yield, pure B in the residue and constant boiling mixture C in the distillate. Pure A cannot be recovered by the distillation of a liquid mixture of composition between C and Y.

Type III : Distillation of a Solution Exhibiting Negative Deviation

Now let us study the distillation behaviour of a mixture of liquids A and B showing negative deviation from Raoult's law. Fig. 10.15 represents the variation of liquid and vapour compositions of such a system at different temperatures.

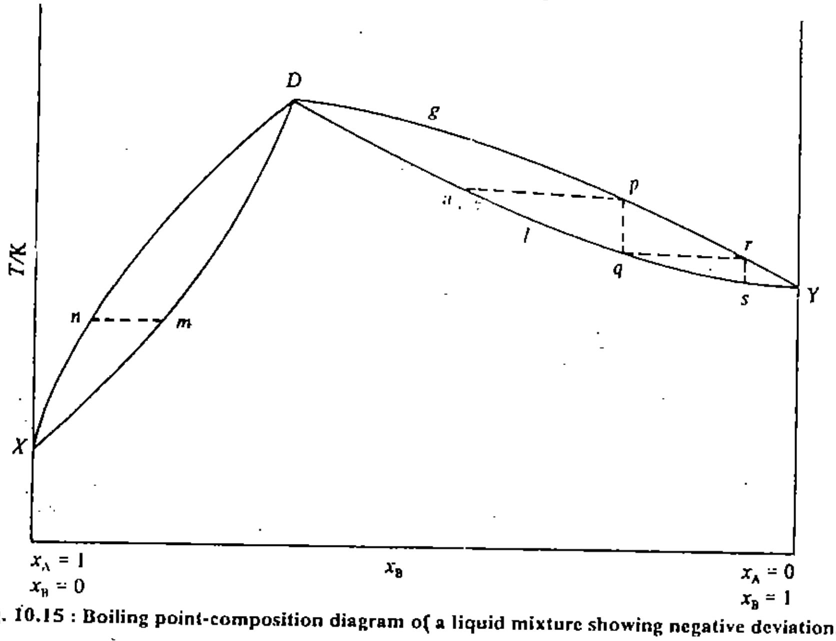


Fig. 10.15 : Boiling point-composition diagram of a liquid mixture showing negative deviation.

The behaviour of such a system on distillation is similar to the previous one. The difference is that the residues tend towards the maximum boiling mixture, while the distillates tend towards the pure constituents. If the starting mixture has a composition *a* which is between Y and D, then the vapours will have composition *p* richer in B than the solution *a*. Hence, the composition of the residue will shift towards D. Repeated distillation of the condensate will finally yield pure B in the vapour form. That is, repeated distillations and condensations of liquid *a* leads to a liquid residue of composition D and vapours of pure B.

A mixture of composition *m* between D and X will yield on distillation a vapour of composition *n* richer in A than the solution. Here again, the residue will shift towards D. By redistillation of the condensate, the vapours will tend towards pure A. Finally, we will have a residue of composition D and a distillate of pure A.

In general, we can separate a liquid mixture showing negative deviation into a residue of composition D, the constant maximum boiling mixture, and a distillate of either pure A or pure B, depending on whether the starting composition is between X and D or D and Y. But D cannot be separated further by distillation.

Azeotropes are called constant boiling mixtures, since these mixtures boil at constant temperature. The vapours coming out of the azeotropic mixture have the same composition as the liquid.

The constant boiling mixtures having composition C in type II solutions (Fig. 10.14) and composition D in type III solutions (Fig. 10.15) are called **azeotropes** (i.e., liquids boiling unchanged). They resemble pure compounds in their boiling behaviour. However, changes in pressure produce changes in the **composition** as well as the boiling point of the azeotropes (see Table 10.5). The azeotropes are not chemical compounds but are rather mixtures resulting from the interplay of intermolecular forces in solution. Table 10.6 lists some azeotropic mixtures along with their composition and boiling points. In Tables 10.5 and 10.6, T_B stands for the boiling point of a liquid.

Table 10.5 : Pressure Dependence of H_2O-HCl Azeotropes

Pressure/ 10^5 Pa	% HCl	T_B/ K
0.658	20.92	370.7
0.921	20.36	379.5
1.00	20.22	381.7
1.05	20.16	383.1

Table 10.6 : Azeotropes with Minimum Boiling Points (at 10^5 Pa)

Component-I	T_B of I	Component-II	T_B of II	Azeotrope	
	K		K	Mass % of I	T_B/K
H_2O	373.1	C_2H_5OH	351.4	4.50	351.3
H_2O	373.1	$CH_3COC_2H_5$	352.7	11.30	346.5
CCl_4	349.9	CH_3OH	337.8	79.44	328.8
CS_2	319.4	CH_3COCH_3	329.6	67.00	312.4
$CHCl_3$	334.3	CH_3OH	337.8	87.40	326.5

SAQ 6

Can azeotropes be separated into pure components by fractional distillation? Explain.

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SAQ 7

How many theoretical plates are there as per Fig. 10.12?

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10.10 SUMMARY

We have learnt in this unit about the solutions and their various properties. A solution is a homogeneous mixture of two or more substances. Solutions can be formed in all the three phases, namely, solid, liquid and gaseous. Solutions can be divided into nine types depending upon the physical state of the solute and the solvent. A solution which cannot dissolve more amount of a solute at a particular temperature is called a saturated solution. Pressure has only a small effect on the solubility of solids in liquids. The solubility of a gas varies with pressure.

Completely miscible liquid pairs may be ideal or non-ideal. Ideal solutions obey Raoult's law. Non-ideal solutions either show positive or negative deviation from Raoult's law. Ideal solution can be separated into pure components by fractional distillation. Non-ideal solution can be separated into two fractions by fractional distillation—one, a pure component and, another, a constant boiling azeotropic mixture.

10.11 TERMINAL QUESTIONS

1) Fill in the blanks in the following:
   i) The solubility of a solute .... with increase in temperature when the dissolution is accompanied by absorption of heat.
   ii) One molal solution contains a mole of a solute dissolved in .... of the solvent.
   iii) In an ideal solution, partial vapour pressure of a component of a solution = mole fraction × ....
   iv) The constituents of .... solution can be separated by fractional distillation into pure components.

2) Explain why we cannot prepare absolute alcohol by fractional distillation.

3) If 0.100 kg of an aqueous solution of potassium chloride contains 7.45×10^{-3} kg of the solute, then calculate the molality of the solution.

4) The vapour pressure of pure liquids A and B at 300 K are 2.6×10^4 Pa and 6.4×10^4 Pa, respectively. Calculate the mole fractions of A and B in vapour and liquid phases of a solution when the equilibrium total vapour pressure of the binary liquid solution is 4.5×10^4 Pa at 300 K. Assume that the liquid and the vapour are ideal.

5) The solubility of carbon dioxide in water at 298 K is 3.40×10^{-2} mol dm^{-3}. The partial pressure of carbon dioxide over the solution is 1.00×10^5 Pa. Assuming that one dm^3 of the solution contains 1.00 kg of water, calculate the Henry's lalw constant for carbon dioxide.

6) State whether the following statements are true or false:
   i) Azeotropes are compounds and not mixtures.
   ii) Molality is the number of moles of solute dissolved in one kilogram of the solvent.
   iii) Raoult's law for ideal solutions is applicable both to the liquid and the vapour phase compositions.
   iv) The solubilities of all substances, i.e., solids, liquids and gases, in liquids increase with rise in temperature.

7) State Konowaloff's rule.

8) Which of the following liquid pairs can be completely separated into its pure components?
   i) Ethanol — water
   ii) Ethylene chloride — ethylene bromide
   iii) Nitric acid — water
   iv) Acetone — carbon disulphide
   v) Carbon tetrachloride — silicon tetrachloride.

9) An azeotropic mixture of hydrochloric acid and water contains 20.2% hydrochloric acid. Calculate its molality.

10.12 ANSWERS

Self Assessment Questions

1) i) Solid in solid
   ii) Liquid in solid
   iii) Gas in liquid

2) The masses of ethanol and water are 0.100 kg each.

$$\text{No. of mol of ethanol} = \frac{0.100\ \text{kg}}{0.046\ \text{kg mol}^{-1}} = 2.17\ \text{mol}$$

$$\text{No. of mol of water} = \frac{0.100\ \text{kg}}{0.018\ \text{kg mol}^{-1}} = 5.56\ \text{mol}$$

Mole fraction of ethanol in the solution

$$= \frac{2.17\ \text{mol}}{(2.17\ \text{mol} + 5.56\ \text{mol})}$$

$$= \frac{2.17\ \text{mol}}{7.73\ \text{mol}} = 0.28$$

Mole fraction of water in the solution = (1−0.28) = 0.72.

3) The solubility of oxygen is less in warm water and hence the amount of oxygen is not enough for the fish to survive.

4) Mole fraction of acetone (x_A) = 0.500

Mole fraction of chloroform (x_C) = 0.500

Partial vapour pressure of acetone (p_A) = $0.500 \times 4.60 \times 10^4$ Pa
$= 2.30 \times 10^4$ Pa

Partial vapour pressure of choroform (p_C) = $0.500 \times 3.92 \times 10^4$ Pa
$= 1.96 \times 10^4$ Pa

If this solution were to behave ideally, the total vapour pressure should be (2.30×10^4 Pa) + (1.96×10^4 Pa) = 4.26×10^4 Pa. The observed value (3.47×10^4 Pa) is less than the value for an ideal solution. That is, acetone-chloroform mixture exhibits negative deviation from Raoult's law.

5) Not possible.

6) Azeotropes are constant boiling mixtures. They cannot be separated into pure components by fractional distillation.

7) 9 (8 + pot).

Terminal Questions

1) i) increases
   ii) 1 kg
   iii) vapour pressure of the pure component
   iv) an ideal.

2) When an aqueous solution of ethyl alcohol is fractionated, it forms a constant boiling mixture (containing 95.5% ethyl alcohol and 4.5% water).

3) Mass of the solute (KCl) = 7.45×10^{-3} kg

Mass of the solvent = $(100-7.45) \times 10^{-3}\ \text{kg} = 92.55 \times 10^{-3}$ kg

$$\text{No. of mol of the solute} = \frac{\text{Mass of the solute}}{\text{Molar mass of the solute}}$$

$$= \frac{7.45 \times 10^{-3}\ \text{kg}}{7.45 \times 10^{-2}\ \text{kg mol}^{-1}} = 0.1\ \text{mol}$$

$$\text{Molality of solution} = \frac{\text{Number of moles of the solute}}{\text{Mass of the solvent}}$$

$$= \frac{0.1 \text{ mol}}{92.55 \times 10^{-3} \text{ kg}} = 1.08 \text{ m}$$

4) From the given data $p_A^0 = 2.6 \times 10^4$ Pa and $p_B^0 = 6.4 \times 10^4$ Pa.
Let the mole fractions of A and B in the liquid phase be x_A and x_B, respectively.
Applying Raoult's law,

$$p_A = p_A^0 x_A \text{ and } p_B = p_B^\circ x_B$$

Total vapour pressure, $p = p_A + p_B = p_A^0 x_A + p_B^0 x_B$

or $4.5 \times 10^4 \text{ Pa} = (2.6 \times 10^4 \text{ Pa})\, x_A + (6.4 \times 10^4 \text{ Pa})\, x_B$

But $x_A + x_B = 1$ or $x_B = 1 - x_A$

$$4.5 \times 10^4 \text{ Pa} = (2.6 \times 10^4 \text{ Pa})\, x_A + (6.4 \times 10^4 \text{ Pa})\,(1 - x_A)$$

$$= 6.4 \times 10^4 \text{ Pa} - (3.8 \times 10^4 \text{ Pa}) x_A$$

$$\text{or } x_A = \frac{(6.4 \times 10^4 \text{ Pa}) - (4.5 \times 10^4 \text{ Pa})}{(3.8 \times 10^4 \text{ Pa})} = \frac{1.9 \times 10^4 \text{ Pa}}{3.8 \times 10^4 \text{ Pa}} = 0.5$$

$x_B = 1 - x_A = 1 - 0.5 = 0.5$

$p_A = p_A^0 x_A = 2.6 \times 10^4 \text{ Pa} \times 0.5 = 1.3 \times 10^4 \text{ Pa}$

$p_B = p_B^0 x_B = 6.4 \times 10^4 \text{ Pa} \times 0.5 = 3.2 \times 10^4 \text{ Pa}$

$$\text{Mole fraction of A in vapour phase} = \frac{p_A}{p} = \frac{1.3 \times 10^4 \text{ Pa}}{4.5 \times 10^4 \text{ Pa}} = 0.29$$

Mole fraction of B in vapour phase = 1−0.29 = 0.71.

5) According to Henry's law, Henry's constant, K, is given by

$$K = \frac{p}{x_{CO_2}}$$

Number of moles of carbon dioxide in 1 dm^3 of the solution
$= 3.40 \times 10^{-2}$ mol

Number of moles of water present in 1 dm^3 of the solution

$$= \frac{1.00 \text{ kg}}{0.018 \text{ kg mol}^{-1}} = 55.6 \text{ mol}$$

$$\text{Mole fraction of } CO_2\ (x_{CO_2}) = \frac{3.40 \times 10^{-2} \text{ mol}}{(3.40 \times 10^{-2} + 55.6) \text{ mol}} \simeq \frac{3.40 \times 10^{-2}}{55.6}$$

$$= 6.12 \times 10^{-4}$$

$$K = \frac{p}{x_{CO_2}} = \frac{1.00 \times 10^5 \text{ Pa}}{6.12 \times 10^{-4}} = 1.63 \times 10^8 \text{ Pa}$$

6) (i) False (ii) True (iii) False (iv) False.

7) See Secs. 10.8 and 10.9.

8) (ii) and (v).

9) Let us consider 0.100 kg of the azeotropic mixture.

Mass of water in 0.100 kg of the solution
$= (0.100 - 0.0202) \text{ kg} = 0.0798 \text{ kg}$

$$\text{No. of moles of HCl dissolved in 0.0798 kg } H_2O = \frac{\text{Mass of HCl}}{\text{Molar mass of HCl}}$$

$$= \frac{0.0202 \text{ kg}}{0.0365 \text{ kg mol}^{-1}} = 0.553 \text{ mol}$$

$$\text{Molality of the solution} = \frac{\text{No. of moles of HCl}}{\text{Mass of water}} = \frac{0.553 \text{ mol}}{0.0798 \text{ kg}}$$

$$= 6.93 \text{ m.}$$

UNIT 11 SOLUTIONS—II

Structure

11.1 INTRODUCTION

In Unit 10, we have discussed the completely miscible liquid systems. In this unit, we shall study the partially miscible and completely immiscible liquid systems. We shall explain Nernst distribution law and use it in calculating the amount of the substances left unextracted after a given number of extractions. This will help us in understanding the principle of extraction by the solvents. In the next unit, you shall study some of the aspects of dilute solutions.

Objectives

After studying this unit, you should be able to :

- describe the effect of temperature on the miscibility of partially miscible liquid pairs,
- define consolute temperature,
- describe the effect of impurities on the consolute temperature,
- explain the principle of steam distillation,
- explain distribution law, and
- explain the principle of solvent extraction.

11.2 PARTIALLY MISCIBLE LIQUID SYSTEMS

Some liquid pairs do not give homogeneous solutions at all compositions. Such liquid pairs are said to be partially miscible liquids. However due to increased solubility with increase or decrease of temperature, these may become completely miscible. We can explain such a system of liquids using phenol and water. When a very small amount of phenol is added to water at room temperature, it dissolves completely to give a single liquid phase. However, when the addition of phenol is continued, a point is reached when phenol does not dissolve anymore. At this point, two phases, i.e., two liquid layers are formed—one consisting of water saturated with phenol and the other containing phenol saturated with water. Further addition of phenol causes water to shift from water-rich layer to phenol-rich layer. If the addition of phenol is continued, a point is reached when phenol acts as a solvent for all the water present and the two phases merge with each other to form a single phase, i.e., solution of water in phenol. Thus, on shaking equal volumes of phenol and water, two layers are formed—one of phenol in water and the other of water in phenol.

It has been experimentally found that at constant temperature, the composition of the two layers, although different from each other, remains constant as long as the two phases are present. Such solutions of different compositions coexisting with each other are termed as conjugate solutions. The addition of small amounts of phenol or water changes the volume of the two layers and not their compositions. As the temperature is increased, the behaviour remains the same except that the mutual solubility of the two phases increases. When the temperature reaches 338.8 K, the composition of the two layers becomes identical and thereafter the two liquids are completely miscible; i.e., at and above 338.8 K, phenol and water dissolve in each other in all proportions and yield only a single liquid layer on mixing. The variation of mutual solubility of water and phenol with temperature is shown in Fig. 11.1

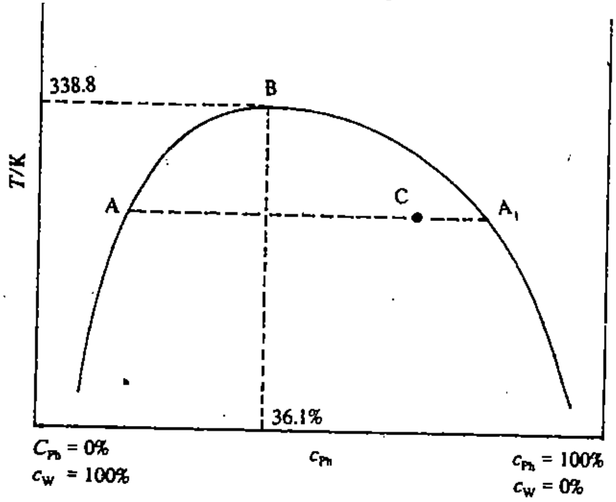

Fig. 11.1 : Phenol-water system; c_{Ph} stands for composition of phenol and c_w for composition of water.

At a particular temperature, say 325 K, point A represents the composition of water-rich layer and point A_1, represents the composition of phenol-rich layer in equilibrium with A. Between these compositions, all mixtures will yield two layers of compositions A and A_1. Outside these compositions, the two liquids are soluble mutually at 325 K. Similar behaviour is seen at other temperatures below 338.8 K. We can conclude that the dome-shaped area represents the range of existence of two liquid phases and the area outside the dome represents a single liquid phase. The temperature corresponding to the point B, i.e, the temperature at which the solubility becomes complete is called the **critical solution temperature** or the **consolute temperature.** Since the mutual solubility of phenol and water increases with rise in temperature, the critical solution temperature (CST) lies well above the room temperature. Hence, such liquid systems are said to possess an upper critical solution temperature or upper consolute temperature. Thus, the critical solution temperature, for phenol-water system is 338.8 K. At and above 338.8 K, phenol and water are completely miscible with each other in all proportions. At this temperature, the composition of the solution is 36.1% phenol and 63.9% water. At any point C, the relative weights of the two separate layers is given by the relationship,

$$\frac{\text{Mass of the first layer}}{\text{Mass of the second layer}} = \frac{A_1C}{AC} \qquad \text{... (11.1)}$$

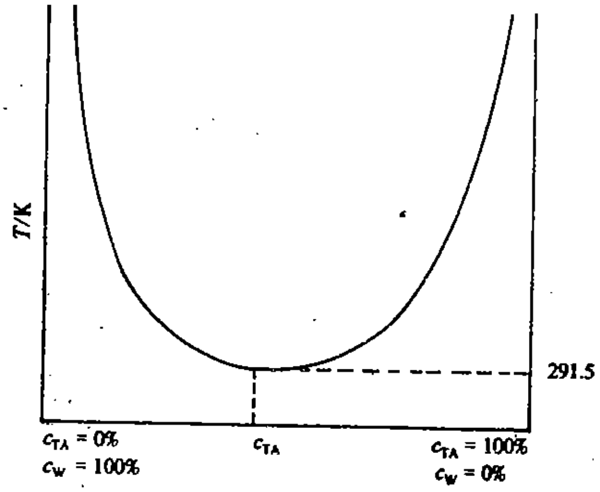

Fig. 11.2: Triethylamine-water system; c_{TA} stands for the composition of triethylamine.

There are some liquid pairs (e.g., triethylamine-water) for which mutual solubilities decrease with rise in temperature. As the temperature is decreased, the mutual solubilities increase and below the consolute temperature, the two liquids become miscible in all proportions. Such systems possess lower consolute temperatures. The variation of mutual solubility of triethylamine and water with temperature is shown in Fig. 11.2. Above 291.5 K, on shaking triethylamine and water, two layers are formed; but below 291.5 K, triethylamine and water are completely miscible with each other in all proportions.

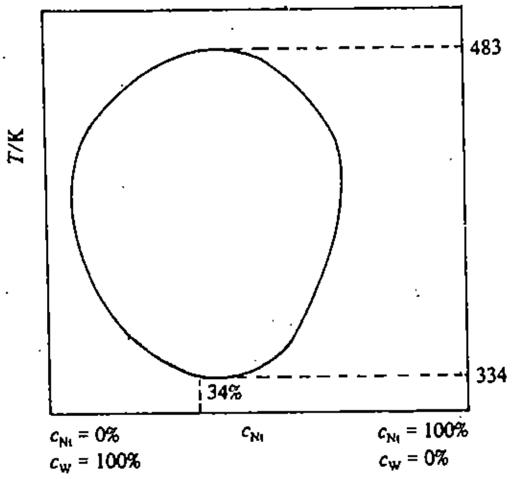

Fig. 11.3 : Nicotine-water system; c_{Nt} stands for the composition of nicotine.

Some liquid pairs, e.g., nicotine and water, show both the upper and lower consolute temperatures. These liquid pairs are completely miscible above a certain temperature (upper consolute temperature) and below a certain temperature (lower consolute temperature). The variation of mutual solubilities of nicotine and water with temperature is shown in Fig. 11.3. Within the enclosed area, the liquids are only partially miscible, while outside the enclosed area, they are completely miscible. The composition corresponding to both the upper and the lower consolute temperatures is the same, i.e., 34% nicotine. Table 11.1 lists the consolute temperatures of some liquid pairs. The two components are denoted as A and B.

Table 11.1 : Consolute Temperatures of Some Liquid Pairs

Components		Consolute temperature K	
A	B	Upper	Lower
Water	Phenol	338.8	—
Aniline	Hexane	333.6	—
Methanol	Carbon disulphide	323.5	—
Water	Diethylamine	—	316
Water	Triethylamine	—	291.5
Water	Nicotine	483	334
Glycerol	m-Toluidine	393	280

Effect of impurities on CST values

The presence of an impurity, dissolved in one or both of the phases, changes the CST values as well as the liquid phase composition at CST. Substances soluble in only one of the liquids raises the upper CST and lowers the lower CST. For example, one per cent solution of sodium chloride raises the upper CST of phenol-water system by 12° About 0.12 molar solution of naphthalene (insoluble in water) in phenol raises the upper CST of phenol-water system by about 30°. Substances which are soluble in both the liquids tend to lower the upper CST and raise the lower CST. For example, sodium oleate is soluble in both water and phenol. Addition of 1% solution of sodium oleate to phenol-water system lowers the CST value by 45°.

As seen above, the presence of small amounts of impurities produces a very large change in the CST values. The changes in CST values is usually a linear function of concentration of impurities. Traces of water present in alcohol are estimated by measuring their CST values with cyclohexane.

As mentioned above, a very small amount of sodium oleate lowers the CST value of phenol-water system considerably. Thus, by making phenol completely miscible with water (by adding appropriate amounts of sodium oleate), lysol-like disinfectants are made.

SAQ 1

Give one example each for liquid pairs with,

a) lower critical solution temperature

b) upper critical solution temperature

c) both upper and lower critical solution temperatures.

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SAQ 2

What is the effect of adding 0.1 molar KCl on the CST of phenol-water system?

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SAQ 3

What would happen when potassium carbonate is added to a solution of water and alcohol ?

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11.3 IMMISCIBLE LIQUID PAIRS

In Sec. 11.2, we studied the partially miscible liquid pairs. In this section, we discuss the characteristics of the completely immiscible liquid pairs. We should, however, understand that there is always some solubility of a substance into the other. But this is so low that we can call it insoluble or completely immiscible.

According to Raoult's law, the vapour pressure of a liquid is lowered on the addition of another liquid, if the latter is soluble in the former. Otherwise, the vapour pressure of each component remains unaffected and each liquid exerts its own vapour pressure independent of the other. Thus, when two completely immiscible liquids A and B are mixed, the total vapour pressure (p) above the mixture will be the sum of the vapour pressures of the pure liquids at that temperature, i.e.,

$$p = p_A^0 + p_B^0 \qquad \ldots (11.2)$$

where p_A^0 and p_B^0 are respectively, the vapour pressures of pure A and B. It is known that a system starts boiling when its total vapour pressure becomes equal to the atmospheric pressure. The mixture of immiscible liquids A and B will thus start boiling at a temperature (T) at which,

$$p_A^0 + p_B^0 = \text{atmospheric pressure} \qquad \ldots (11.3)$$

This temperature will be lower than the normal boiling point of A or B. The mixed vapours thus obtained and condensed will have a composition dependent on the partial pressures of A and B at temperature *T*. Since the number of moles of each component present in the vapour phase is proportional to its vapour pressure, the mole ratio of A to B (n_A/n_B) in the condensate is given by

$$\frac{n_A}{n_B} = \frac{p_A^\circ}{p_B^\circ} \qquad \ldots (11.4)$$

Condensate or distillate is the liquid obtained by condensing the vapours.

If w_A and w_B are the masses of A and B in the condensate, and M_A and M_B their respective molar masses, then

$$\frac{n_A}{n_B} = \frac{w_A/M_A}{w_B/M_B} = \frac{w_A M_B}{w_B M_A} = \frac{p_A^\circ}{p_B^\circ} \qquad \ldots (11.5)$$

$$\text{or } \frac{w_A}{w_B} = \frac{p_A^\circ M_A}{p_B^\circ M_B} \qquad \ldots (11.6)$$

The fact, that a system of immiscible liquids starts boiling at temperatures less than the normal boiling points of both the liquids, is made use of in steam distillation. The steam distillation is a process of purifying organic liquids which have high boiling points and are immiscible with water. For purification by steam distillation, an impure compound

i) must be immiscible in water

ii) should not decompose at the temperature of steam

iii) should have a fairly high vapour pressure at 373 K

iv) should have non-volatile impurities.

For example, chlorobenzene has a boiling point of 405 K. A mixture of water and chlorobenzene distils at a constant temperature of 363.3 K, when the external pressure is 9.8×10^4 Pa, by passing steam through it. Let us explain the procedure for purifying an organic liquid using steam distillation. The apparatus used for steam distillation is as shown in Fig. 11.4

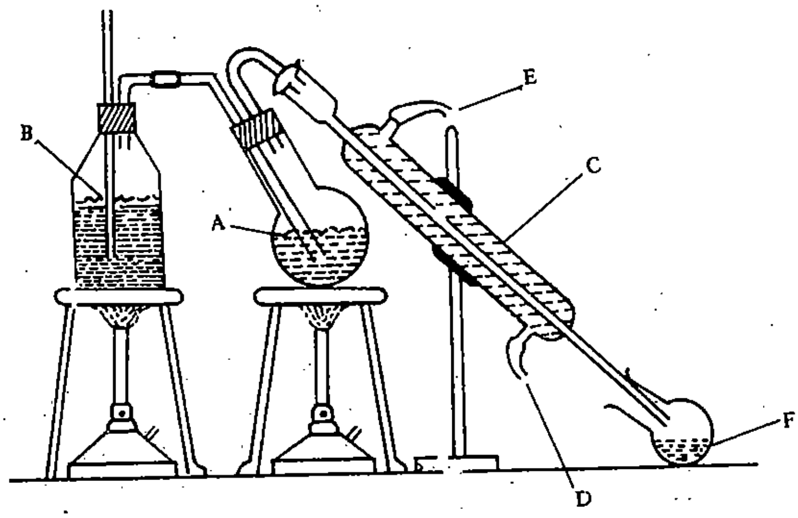

Fig. 11.4: Steam distillation.

A water condenser has a water inlet (D) and an outlet (E). This condenser is used for cooling the vapours (below 373 K) to get the liquid.

The impure organic compound is taken in a round-bottomed flask (A) and a small quantity of water is added. The flask must be kept in a slanting position to prevent the impure liquid from splashing up into the condenser. The flask A is then heated gently on a sand bath. Now steam from flask B is bubbled through the contents in the flask. The vapours of the organic compound mix with steam and escape into the water condenser C. The condensate thus obtained in the flask F is a mixture of water and the organic compound. This mixture can be separated by means of a separating funnel.

Let us illustrate the application of Eq. 11.6.

Example 1

A mixture of water and an organic liquid A, which is immiscible in water, distils at 368 K when the external pressure is 1.00×10^5 Pa. The vapour pressure of water at 368 K is 8.35×10^4 Pa. Calculate the relative molecular mass of A if the distillate contains 40% by weight of water.

Solution

Let us represent the vapour pressures of pure water and the organic liquid A at 368 K as $p^\circ_{H_2O}$ and p°_A, respectively. At a total pressure of 1.00×10^5 Pa, the liquid mixture boils, i.e.,

$$p^\circ_{H_2O} + p^\circ_A = 1.00 \times 10^5 \text{ Pa}$$

At the distillation temperature, $p^\circ_{H_2O} = 8.35 \times 10^4$ Pa

Hence $p^\circ_A = (1.00 \times 10^5 \text{ Pa} - 8.35 \times 10^4 \text{ Pa}) = 1.65 \times 10^4$ Pa

Using Eq. 11.6,

$$\frac{w_{H_2O}}{w_A} = \frac{p^\circ_{H_2O} \times M_{H_2O}}{p^\circ_A \times M_A}$$

But water is 40% by weight; hence we can write

$$\frac{40}{60} = \frac{8.35 \times 10^4 \text{ Pa}}{1.65 \times 10^4 \text{ Pa}} \times \frac{0.018 \text{ kg mol}^{-1}}{M_A}$$

$$\text{or} \quad M_A = \frac{8.35 \times 10^4 \text{ Pa}}{1.65 \times 10^4 \text{ Pa}} \times 0.018 \text{ kg mol}^{-1} \times \frac{60}{40}$$

$$= 0.137 \text{ kg mol}^{-1}$$

The relative molecular mass of A = 137.

SAQ 4

Why does a mixture of two immiscible liquids boil at a temperature which is lower than the boiling point of any of the pure liquids?

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11.4 DISTRIBUTION LAW

In this section, we discuss the effect of the addition of a solute to a pair of immiscible liquids. Water and carbon tetrachloride, for example, are practically immiscible with each other but iodine dissolves both in water and carbon tetrachloride. When iodine is added to a mixture of water and carbon tetrachloride at a certain temperature, iodine distributes itself between the two immiscible layers — water and carbon tetrachloride. Let the concentration of iodine in water and carbon tetrachloride be c_I and c_{II}, respectively, at a particular temperature. Then we have,

$$\frac{c_I}{c_{II}} = K \qquad \text{...(11.7)}$$

where K is a constant at a constant temperature.

If more of iodine is added to this system, it again distributes itself between the two layers. Now the concentration of iodine in both the layers will be more than that in the previous case. Let the concentrations be c_I' and c_{II}' in water and CCl_4 layers, respectively. Though $c_I' > c_I$ and $c_{II}' > c_{II}$, the ratio c_I'/c_{II}' is again equal to the constant, K, i.e.,

$$\frac{c_I}{c_{II}} = \frac{c'_I}{c'_{II}} = K \qquad \text{. . . (11.8)}$$

It is evident that, in each case, I_2 distributes itself between the two immiscible layers in such a way that the ratio of its concentration in the two layers is a constant at a certain temperature. It was pointed out by Nernst that the ratio, c_I/c_{II}, is constant only when the solute exists in the same molecular form, i.e., the relative molecular mass of the solute is the same in two layers. The Nernst distribution law may be stated as follows:

At a fixed temperature, a substance X distributes itself between the two immisible solvents A and B in equilibrium with each other in such a way that the ratio of the concentrations of X in the two solvents is constant, provided that the solute X is in the same molecular state in both the solvents.

Mathematically,

$$K = \frac{\text{Concentration of X in solvent A}}{\text{Concentration of X in solvent B}} \qquad \text{. . . (11.9)}$$

The constant K is called the distribution or partition coefficient of the solute between the two solvents. You can see from the data given in Table 11.2 that the value of K is fairly constant in dilute solutions. As the concentration increases, there is a deviation.

Table 11.2: Distribution of I_2 between H_2O and CCl_4

$\frac{10^4 \times c_{H_2O}}{\text{Mol dm}^{-3}}$	$\frac{10^2 \times c_{CCl_4}}{\text{Mol dm}^{-3}}$	$K = \frac{c_{H_2O}}{c_{CCl_4}}$
3.22	2.745	1.17×10^{-2}
5.03	4.29	1.17×10^{-2}
7.63	6.54	1.17×10^{-2}
11.5	10.1	1.14×10^{-2}
13.4	11.96	1.12×10^{-2}

K depends upon

- nature of the solute
- nature of the solvent and
- temperature

The distribution law can be derived taking into account thermodynamic considerations.

Thermodynamic Derivation of Distribution Law

In Unit 9, Eqs. 9.83, 9.84 and 9.85 were derived by relating the chemical potential of an ideal gas to its partial pressure, concentration and mole fraction in a mixture of gases. We are going to use the modified from of Eq. 9.85 to denote the chemical potentials a solute (such as iodine) in the two immiscible liquids. Instead of mole fraction used in Eq. 9.85, we are going to use activity (a) which is an 'effective' mole fraction. In the case of an infinitely dilute solution, activity becomes equal to mole fraction. Hence using Eq. 9.85, the chemical potentials of iodine, μ_1 and μ_2 in water and carbon tetrachloride are given by equations.

$$\mu_1 = \mu_1^0 + RT \ln a_1 \qquad \text{... (11.10)}$$

$$\mu_2 = \mu_2^0 + RT \ln a_2 \qquad \text{... (11.11)}$$

Where μ_1^0 and μ_2^0 are standard chemical potentials of iodine in water and carbon tetra chloride at unit activity; also a_1 and a_2 are the activities of iodine in water and carbon tetrachloride, respectively.

At equilibrium, $\mu_1 = \mu_2$

Hence $\mu_1^0 + RT \ln a_1 = \mu_2^0 + RT \ln a_2$

$$\text{or} \quad \mu_2^0 - \mu_1^0 = RT \ln a_1 - RT \ln a_2$$
$$= RT \ln a_1/a_2$$

At constant temperature, μ_1^0 and μ_2^0 are constants.

Also R is constant. It follows that

$$a_1/a_2 = \text{constant} \qquad \ldots(11.12)$$

This is another form of the distribution law. At low concentrations, activities can be replaced by concentrations, and we get

$$\frac{a_1}{a_2} = \frac{c_1}{c_2}$$

Nernst first gave attention to the fact that the above statement of the distribution law is valid only when the solute undergoes no change such as dissociation or association in either of the solvents. If a solute dissociates into simple molecules or ions or if it associates to form complex molecules, then the distribution law does not apply to the total concentration of the solute in each of the two phases. It is applicable to the concentration of a particular species common to both the layers. Let us look at this in some detail taking the following cases.

Dissociation of a Solute in one of the Solvents

Let us take a solute X which remains undissociated in phase I. We assume that its concentration in phase I is c_1. In phase II, let it undergo dissociation into A and B. If c_2 is the total concentration in phase II before dissociation, and α is the degree of dissociation, then we can write

Eqs. 11.13 to 11.21 are written following the principles of chemical equilibrium which we will study in detail in Unit 14 of this course.

$$\underset{c_2(1-\alpha)}{X} \rightleftharpoons \underset{c_2\alpha}{A} + \underset{c_2\alpha}{B} \qquad \ldots(11.13)$$

Evidently, the concentration of the undissociated molecules of X in phase II is $c_2(1-\alpha)$. So as per distribution law, the distribution coefficient is given by

$$K = \frac{\text{concentration of X in phase I}}{\text{concentration of undissociated X in phase II}}$$

$$\text{or } K = c_1/c_2\,(1-\alpha) \qquad \ldots(11.14)$$

Example 2

An organic acid A, distributes between 1.0 dm³ each of an organic solvent, S, and water. The concentration of the acid in aqueous layer is 1.20×10^{-2} kg dm^{-3} and in the organic layer, it is 1.44×10^{-3} kg dm^{-3}. If the distribution coefficient of the acid between the organic solvent and water is 0.16, calculate the degree of dissociation of the organic acid in water. Assume that the acid does not undergo any change in its molecular state in the organic solvent, S.

Solution

Let the concentration of the acid in the organic and water layer be c_1 and c_2, respectively. Hence

$$c_1 = 1.44 \times 10^{-3}\ \text{kg dm}^{-3}$$
$$\text{and}\quad c_2 = 1.20 \times 10^{-2}\ \text{kg dm}^{-3}$$

Using Eq. 11.14, we have

$$0.16 = \frac{1.44 \times 10^{-3}\ \text{kg dm}^{-3}}{1.20 \times 10^{-2}\ \text{kg dm}^{-3}\,(1-\alpha)} = \frac{0.12}{(1-\alpha)}$$

$$\text{or}\quad (1-\alpha) = \frac{0.12}{0.16} = 0.75$$

$$\therefore \alpha = 1 - 0.75 = 0.25$$

The percentage dissociation of the acid in water is 25%.

Association of the Solute in one of the Solvents

Let X be a solute that does not undergo dissociation or association in phase I. Let its concentration be c_1 in phase I. Let it associate in phase II as given in Eq. 11.15 to give the molecules, X_n.

Let us assume that c_2 is the concentration of the solute in phase II, if there is no association. Let α be the fraction of the molecules that is associated in phase II to give the molecules X_n.

$$\begin{array}{ccc} nX & \rightleftharpoons & X_n \\ c_2(1-\alpha) & & c_2\alpha/n \end{array} \qquad \text{... (11.15)}$$

Then the concentration of the associated molecules can be calculated as follows:

The concentration of the unassociated X = $c_2(1-\alpha)$

$$\left.\begin{array}{r}\text{The concentration of X used for forming} \\ \text{associated molecules}\end{array}\right\} = c_2\alpha$$

Since n moles of X give one mole of the associated species, X_n

$$\left.\begin{array}{l}\text{concentration of the} \\ \text{associated species, } X_n\end{array}\right\} = c_2\,\frac{\alpha}{n} \qquad \text{... (11.16)}$$

$$\text{Then, } K = \frac{\text{Concentration of X in phase I}}{\text{Concentration of the unassociated species in phase II}}$$

$$\text{or} \quad K = \frac{c_1}{c_2\,(1-\alpha)} \qquad \text{... (11.17)}$$

Also it is possible to calculate the equilibrium constant, K_{eq}, for equilibrium represented by Eq. 11.15, if α is known.

$$K_{eq} = \frac{c_2\,\frac{\alpha}{n}}{[c_2\,(1-\alpha)]^n} \qquad \text{... (11.18)}$$

$$\text{or } [c_2\,(1-\alpha)]^n = \frac{c_2\,\frac{\alpha}{n}}{K_{eq}} \qquad \text{... (11.19)}$$

$$c_2\,(1-\alpha) = \left[\frac{c_2\,\alpha/n}{K_{eq}}\right]^{1/n}$$

$$c_2\,(1-\alpha) = \left[\frac{c_2\,\alpha}{nK_{eq}}\right]^{1/n} \qquad \text{... (11.20)}$$

Substituting Eq. 11.20 in Eq. 11.17,

$$K = \frac{c_1}{\left[\frac{c_2\,\alpha}{nK_{eq}}\right]^{1/n}} = \frac{c_1}{c_2^{1/n}}\left[\frac{nK_{eq}}{\alpha}\right]^{1/n}$$

At constant temperature, n, K_{eq} and α are constants.

$$K = \frac{c_1}{c_2^{1/n}}\ .\ \text{constant}$$

$$K' = \frac{K}{\text{constant}} = \frac{c_1}{c_2^{1/n}} \qquad \text{...(11.21)}$$

Hence if c_1, c_2 and n are known, K' could be found out. The value of n could help us in finding out whether the solute remains as a dimer, trimer etc. in a particular solvent.

With the help of Eq. 11.21, it is possible to determine approximate values of n. Two important methods are illustrated below:

1) **Method of Trial and Error**

In Eq. 11.21, integer values starting with 1 and above are given to n. The value for which Eq. 11.21 gives a constant value for K' is adopted.

n is called the order of association.

2) **Graphical Method**

Eq. 11.21 can be written as,

$$c_1 = K' (c_2)^{1/n}$$

Taking logarithms on both sides, we get

$$\log c_1 = \log K' + \frac{1}{n} \log c_2$$

or $$\log c_1 = \frac{1}{n} \log c_2 + \log K' \qquad \text{...(11.22)}$$

Eq. 11.22 is of the type $y = mx + c$ which is an equation for a straight line. If a graph is plotted between $\log c_1$ and $\log c_2$, a straight line is obtained as shown in Fig. 11.5. The slope of the line gives the value of $1/n$ from which n can be calculated. The intercept on the Y-axis gives the value of $\log K'$ and hence K' can be calculated.

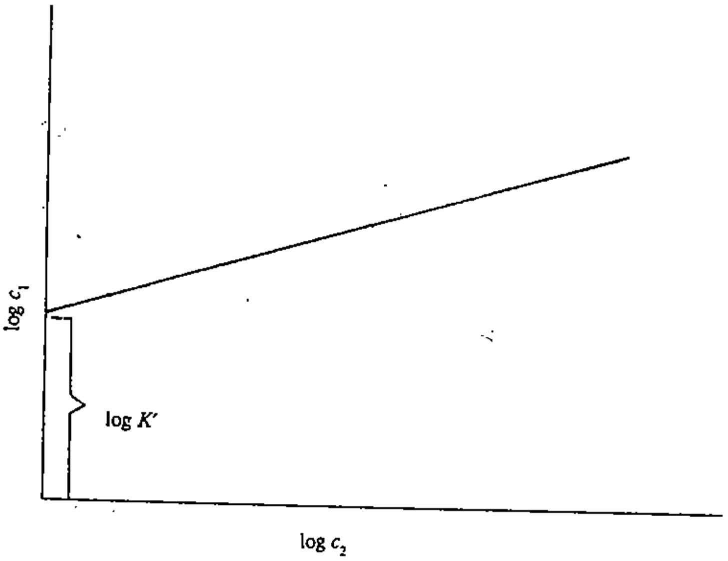

Fig. 11.5: log c_1 plotted against log c_2.

Example 3: The following results were obtained for the distribution of benzoic acid between water and benzene at 298 K:

Concentration in H_2O $(c_1)/(\text{mol dm}^{-3})$	0.0033	0.0058	0.0075
Concentration in C_6H_6 $(c_2)/(\text{mol dm}^{-3})$	0.0156	0.0495	0.0835

What conclusion can be drawn from these results concerning the molecular form of benzoic acid in benzene? Assume that c_1 represents the concentration of the undissociated benzoic acid in water.

Solution

It is known that benzoic acid is dissociated in water into its ions. The concentration c_1 of the undissociated benzoic acid is given above. If benzoic acid remains as normal molecules in benzene, then $\frac{c_1}{c_2}$ must be constant. Let us see whether it is so.

$$\frac{c_1}{c_2} = \frac{0.0033 \text{ mol dm}^{-3}}{0.0156 \text{ mol dm}^{-3}} = 0.211$$

$$\frac{c_1}{c_2} = \frac{0.0058 \text{ mol dm}^{-3}}{0.0495 \text{ mol dm}^{-3}} = 0.117$$

$$\frac{c_1}{c_2} = \frac{0.0075 \text{ mol dm}^{-3}}{0.0835 \text{ mol dm}^{-3}} = 0.090$$

As $\frac{c_1}{c_2}$ varies considerably, benzoic acid in benzene is not present as normal molecules. We can find the value of n using trial and error method. Substituting $n = 2$ in Eq. 11.21, let us try whether we get a constant value for $\frac{c_1}{c_2^{1/2}}$.

$$\frac{c_1}{c_2^{1/2}} = \frac{0.0033 \text{ mol dm}^{-3}}{(0.0156 \text{ mol dm}^{-3})^{1/2}} = 0.0264\ (\text{mol dm}^{-3})^{1/2}$$

$$\frac{c_1}{c_2^{1/2}} = \frac{0.0058 \text{ mol dm}^{-3}}{(0.0495 \text{ mol dm}^{-3})^{1/2}} = 0.0260\ (\text{mol dm}^{-3})^{1/2}$$

$$\frac{c_1}{c_2^{1/2}} = \frac{0.0075 \text{ mol dm}^{-3}}{(0.0835 \text{ mol dm}^{-3})^{1/2}} = 0.0260\ (\text{mol dm}^{-3})^{1/2}$$

It is clear from the above calculations that the values of $\frac{c_1}{c_2^{1/2}}$ are fairly constant.

Hence, benzoic acid in benzene exists as a dimer, $(C_6H_5COOH)_2$.

To understand the application of distribution law, when the solute undergoes association in one solvent and dissociation in another, let us consider the distribution of benzoic acid between water and chloroform as given in Table 11.3.

In Table 11.3, c_{w1} is the concentration of undissociated benzoic acid in aqueous layer and c_{c1} is the concentration of unassociated benzoic acid in chloroform layer.

Table 11.3.: Distribution of Benzoic Acid between Water and Chloroform at 313 K

$\frac{10^3 \times c_w}{\text{mol dm}^{-3}}$	$\frac{10^3 \times c_c}{\text{mol dm}^{-3}}$	$\frac{c_w}{c_c}$	$\frac{10^3 \times c_{w1}}{\text{mol dm}^{-3}}$	$\frac{10^3 \times c_{c1}}{\text{mol dm}^{-3}}$	$K = \frac{c_{w1}}{c_{c1}}$
2.11	7.21	0.293	1.78	4.04	0.441
2.68	10.8	0.248	2.31	5.23	0.442
3.53	16.8	0.210	3.10	7.01	0.442
7.25	57.0	0.127	6.62	15.0	0.441
12.7	167.0	0.076	11.8	26.9	0.439

In Example 3, the concentrations of undissociated benzoic acid in aqueous layer (c_1) have been given. But in Table 11.3, c_w gives the total concentration of benzoic acid in the aqueous layer and it includes the dissociated and undissociated forms. Also, c_c is the total concentration of benzoic acid in chloroform layer. You see that c_w/c_c is not constant. The observed results can be explained on the basis that the acid is partially dissociated in water into hydrogen ion and benzoate ion and partially associated in chloroform into dimers.

Since the distribution law can be applied to the common species present in both the phases (i.e., undissociated or unassociated benzoic acid), correction must be applied for association and dissociation. After applying these corrections, you see that $\frac{c_{w1}}{c_{c1}}$ is constant as given in the last column.

Applications of the Distribution Law

The study of the distribution of a solute between two immiscible solvents is quite useful in a number of ways. A few of these applications are given below:

1) By studying the distribution of acetic acid and benzoic acid between water and benzene, it is possible to show that acetic acid and benzoic acid exist as dimers in benzene.

2) If a solute dissociates in one of the solvents, then knowing the distribution coefficient, the degree of dissociation of the solute can be calculated at a particular temperature.

3) The distribution law has been used in study of many problems, e.g., solvent extraction, analysis and determination of equilibrium constants. Extraction is used both at laboratory and industrial scale in various processes. An organic compound can often be extracted economically from an aqueous solution or a suspension by,

- adding an organic solvent,
- shaking and separating the two layers, and
- finally distilling off the organic solvent to recover the purified compound.

If the distribution coefficient of a solute between ether and water is 3 in favour of ether, it means that the solute is 3 times more soluble in ether as compared to that in water.

In the process of extraction, we make use of the fact that the distribution coefficient of most of the organic compounds is very large in favour of organic solvents. It can be shown that with a given volume of an extracting liquid, the organic compound extracted is more if the extracting liquid is used in a number of instalments than if the whole of it is used in one lot. Let us derive a general formula which enables the calculation of the amount that is left unextracted after a given number of extractions.

Let us consider an aqueous solution of volume V. Let the mass of an organic compound dissolved in it be w. Let us use volume v of the organic liquid for each extraction and let the mass of the organic compound that remained unextracted in water after one extraction be w_1.

After the First Extraction

Concentration of the organic compound in the aqueous layer = $\frac{w_1}{V}$

Mass of the organic compound in the organic layer = $(w - w_1)$

Concentration of the organic compound in the organic layer = $\frac{(w - w_1)}{v}$

Distribution coefficient, K, is given by the following expression:

$$K = \frac{\text{Concentration of the compound in the aqueous layer}}{\text{Concentration of the compound in the organic layer}}$$

$$\text{or} \quad K = \frac{\frac{w_1}{V}}{\frac{(w-w_1)}{v}} = \frac{w_1 v}{(w-w_1)\,V}$$

$$\text{or} \quad K(w-w_1)V = w_1 v$$

$$\text{or} \quad KwV = w_1 v + K w_1 V = w_1 (v + KV)$$

$$\text{or} \quad w_1 = \frac{KwV}{(v + KV)} = w \frac{KV}{v + KV}$$

After the Second Extraction

Similarly, after the second extraction, the mass of the organic compound that remains unextracted is,

$$w_2 = w_1 \frac{KV}{v+KV} = w \left(\frac{KV}{v+KV}\right)^2$$

After n Extractions

In general, the mass of the organic compound that remains unextracted after n extractions is given by,

$$w_n = w \left(\frac{KV}{v+KV}\right)^n \qquad \text{... (11.23)}$$

Often we have to recover the organic compounds from an aqueous solution using extraction method.

Desilverisation of Argentiferrous Lead

Desilverisation means removal of silver. Argentiferrous galena is an ore of lead containing silver.

Argentiferrous galena contains small quantities of silver which could be extracted quite economically by Parke's process. In this process, zinc is used for extracting silver from argentiferrous lead. The distribution coefficient of silver between molten Zn and molten Pb is 300 at 1073 K. Therefore, when molten zinc is added to molten argentiferrous lead, practically the whole of silver present passes into the molten zinc layer. As molten zinc and lead are immiscible, the two layers can be separated easily. Moreover, Zn-Ag alloy solidifies easily. As zinc is volatile, it can be separated from silver by distillation.

11.5 SUMMARY

When two liquids are mixed, they may be completely miscible, partially miscible or nearly completely immiscible. The miscibility of partially miscible liquid pairs varies with temperature. The miscibility of some partially miscible liquid pairs, e.g., phenol — water increases with rise in temperature. The temperature at which a pair of partially miscible liquids becomes completely miscible is called critical solution temperature. Thus phenol-water system possesses an upper CST. Some liquid pairs possess lower CST, i.e., their mutual solubility decreases with rise in temperature. Below a certain temperature, such liquid pairs are completely miscible. Some liquid pairs possess both lower and upper CST. The presence of an impurity in one or both the phases changes the CST values. Substances soluble in one of the liquids raise the upper CST and lower the lower CST. Substances soluble in both the liquids tend to lower the upper CST and raise the lower CST.

A pair of immiscible liquids boil at a temperature lower than the boiling points of any of the liquids. This fact is made use of in steam distillation. When a solute is added to a pair of immiscible liquids, it distributes itself between the two liquids in such a way that the ratio of the concentration of the solute in the two phases remains constant. This is called the distribution law. The distribution law can be used to study the state of association or dissociation of the solute in one or both the phases. It also helps in determining the degree of dissociation of a solute.

11.5 TERMINAL QUESTIONS

1) Two liquids A and B are completely immiscible with each other. Their normal boiling points are T_A and T_B respectively, and T_A is less than T_B. The two liquids taken together will boil at.

   a) T_A
   b) T_B
   c) $\frac{T_A + T_B}{2}$
   d) a temperature less than T_A
   e) none of these temperatures.

2) An immiscible mixture of an organic liquid, A and water on steam distillation boils at 372 K at pressure of 1.00×10^5 Pa. At this temperature the vapour pressure of water is 9.60×10^4 Pa. The ratio of the mass of water to the mass of A in the distillate is 4:1. Calculate the relative molecular mass of liquid A.

3) Explain the behaviour of partially miscible liquid systems with respect to change of temperature.

4) Derive distribution law thermodynamically.

5) When 1.00 dm^3 of an aqueous solution containing 5.00×10^{-3} kg of a solute is shaken with 5.00×10^{-2} dm^3 ether, it is found that 8.50×10^{-4} kg of the solute passes into ether. How much of the solute will be left unextracted, if the same aqueous solution is shaken with a second instalment of 5.00×10^{-2} dm^3 ether? The solute exists in the same molecular state in both water and ether.

6) Succinic acid is associated in benzene. Find the order of association (n) from the following data on the distribution of succinic acid between water and benzene. Assume that c_1 is the concentration of undissociated succinic acid in water and c_2 is the total concentration of succinic acid in benzene.

$10^3 \times c_1$ in water/(kg dm^{-3})	1.10	1.95	2.90
$10^3 \times c_2$ in benzene/(kg dm^{-3})	14.2	41.2	96.5

11.7 ANSWERS

Self Assessment Questions

1) See Table 11.1.

2) Raises the critical solution temperature of phenol-water system.

3) Since potassium carbonate is highly soluble in water but not in ethanol, the solubility of ethanol in water decreases and two layers and formed.

4) The sum of the vapour pressures of the two liquids becomes equal to the atmospheric pressure at a lower temperature.

Terminal Questions

1) d.

2) Given that,

$$\frac{\text{Mass of water}}{\text{Mass of A}} = \frac{4}{1}$$

Vapour pressure of water ($p^{\circ}_{H_2O}$) = 9.60×10^4 Pa

Vapour pressure of liquid A (p°_{A}) = 1.00×10^5 Pa $- 9.60 \times 10^4$ Pa
$= 4.00 \times 10^3$ Pa

Using Eq. 11.6,

$$\frac{w_{H_2O}}{w_A} = \frac{p^{\circ}_{H_2O} \times M_{H_2O}}{p^{\circ}_{A} \times M_A}$$

$$\text{or } M_A = \frac{p^{\circ}_{H_2O} \times M_{H_2O}}{p^{\circ}_{A}} \times \frac{w_A}{w_{H_2O}}$$

$$= \frac{9.60 \times 10^4 \text{ Pa} \times 0.018 \text{ kg mol}^{-1}}{4.0 \times 10^3 \text{ Pa}} \times \frac{1}{4}$$

$$= 0.108 \text{ kg mol}^{-1}$$

Hence, the relative molecular mass of A = 108

3) See Sec. 11.2.

4) See Sec. 11.4.

5) Concentration of the solute in aqueous layer
(c_1) = $(5.00 - 0.850) \times 10^{-3}$ kg/1.00 dm^3
$= 4.15 \times 10^{-3}$ kg dm^{-3}

Concentration of the solute in ether layer

$$(c_2) = \frac{8.50 \times 10^{-4}\ \text{kg}}{5.00 \times 10^{-2}\ \text{dm}^3} = 1.70 \times 10^{-2}\ \text{kg dm}^{-3}$$

Distribution coefficient between water and ether

$$K = \frac{c_1}{c_2} = \frac{4.15 \times 10^{-3}\ \text{kg dm}^{-3}}{1.70 \times 10^{-2}\ \text{kg dm}^{-3}} = 0.244$$

Using Eq. 11.23, the amount of the solute left after the second extraction is

$$w_2 = w\left(\frac{KV}{v + KV}\right)^2$$

$$= 5.00 \times 10^{-3}\ \text{kg}\left[\frac{0.244 \times 1.00\ \text{dm}^3}{5.00 \times 10^{-2}\ \text{dm}^3 + (0.244 \times 1.00\ \text{dm}^3)}\right]^2$$

$$= 3.44 \times 10^{-3}\ \text{kg}$$

6) By trial and error method, let us try whether $\frac{c_1}{c_2}$ is constant keeping $n = 1$ in Eq. 11.21.

$$\frac{c_1}{c_2} = \frac{1.10 \times 10^{-3}\ \text{kg dm}^{-3}}{14.2 \times 10^{-3}\ \text{kg dm}^{-3}} = 0.077$$

$$= \frac{1.95 \times 10^{-3}\ \text{kg dm}^{-3}}{41.2 \times 10^{-3}\ \text{kg dm}^{-3}} = 0.047$$

$$= \frac{2.90 \times 10^{-3}\ \text{kg dm}^{-3}}{96.5 \times 10^{-3}\ \text{kg dm}^{-3}} = 0.030$$

As the value of $\frac{c_1}{c_2}$ is not constant, $n \neq 1$.

Let us now try for $n = 2$.

$$K = \frac{c_1}{\sqrt{c_2}} = \frac{1.10 \times 10^{-3}\ \text{kg dm}^{-3}}{\sqrt{14.2 \times 10^{-3}\ \text{kg dm}^{-3}}} = 9.23 \times 10^{-3}\ (\text{kg dm}^{-3})^{\frac{1}{2}}$$

$$= \frac{1.95 \times 10^{-3}\ \text{kg dm}^{-3}}{\sqrt{41.2 \times 10^{-3}\ \text{kg dm}^{-3}}} = 9.61 \times 10^{-3}\ (\text{kg dm}^{-3})^{\frac{1}{2}}$$

$$= \frac{2.90 \times 10^{-3}\ \text{kg dm}^{-3}}{\sqrt{96.5 \times 10^{-3}\ \text{kg dm}^{-3}}} = 9.34 \times 10^{-3}\ (\text{kg dm}^{-3})^{\frac{1}{2}}$$

As the value of $\frac{c_1}{c_2^{1/2}}$ is constant, the order of association is 2. Hence, succinic acid exists as a dimer in benzene.

UNIT 12 COLLIGATIVE PROPERTIES

Structure

12.1 INTRODUCTION

In Unit 10, we discussed the completely miscible liquid systems. In Unit 11, we discussed the partially miscible and nearly immiscible liquid systems. In this unit, we shall study colligative properties of the solutions containing non-volatile solutes. The colligative properties depend only upon the number of particles of the solute in the solution. They do not depend upon the nature of the solute. These properties help us in determining the relative molecular mass of a non-volatile solute. The colligative properties are :

- relative lowering of vapour pressure,
- elevation of boiling point,
- depression of freezing point, and
- osmotic pressure.

We shall study these properties in this unit.

Objectives

After studying this unit, you should be able to :

- explain what is meant by colligative property,
- state Raoult's law of relative lowering of vapour pressure,
- derive an expression relating the elevation of boiling point of a solution to its molality,
- define molal elevation constant,
- derive an expression relating the depression of freezing point of a solution to its molality,
- define molal depression constant,
- define osmotic pressure,
- suggest a method for determining the relative molecular mass of a non-volatile solute using osmotic pressure measurement,
- state van't Hoff laws of osmotic pressure, and
- explain van't Hoff factor.

12.2 RELATIVE LOWERING OF VAPOUR PRESSURE

If a pure liquid is placed in a closed container that is initially evacuated, the liquid evaporates to fill up the space above the liquid. At any given temperature when equilibrium is established, the pressure exerted by the vapours of a liquid is called the vapour pressure of the pure liquid (p_1^0). If a non-volatile solute is added to this liquid, the equilibrium vapour pressure (p_1) over the solution is found to be less than that of the pure liquid. According to Raoult's law, the vapour pressure (p_1) of the solvent of an ideal solution is given by $p_1 = p_1^0 x_1$ . . . (12.1)

The vapour pressure of a solution containing a non-volatile solute is less than the vapour pressure of the pure solvent.

where x_1 is the mole fraction of the solvent in the solution and p_1^0 is the vapour pressure of the pure solvent. Since the solute is non-volatile, its contribution towards the vapour pressure of the solution is negligible. Hence, the vapour pressure of solution containing a non-volatile solute is only due to the solvent. Since the mole fraction (x_1) of the solvent is less than one, it is clear from Eq. 12.1 that p_1 will also be less than p_1^0. The lowering of vapour pressure when a non-volatile solute is added to a solvent is given by ($p_1^0 - p_1$).

Substituting for p₁ from Eq. 12.1, we get

$$p_1^\circ - p_1 = p_1^\circ - p_1^\circ x_1 = p_1^\circ (1 - x_1) \quad \text{. . . (12.2)}$$

Since $x_1 + x_2 = 1$,

$$p_1^0 - p_1 = p_1^0 x_2 \quad \text{. . .(12.3)}$$

where x_2 is the mole fraction of the solute.

According to Eq. 12.3, the lowering of vapour pressure of the solvent depends both on the vapour pressure of the pure solvent and on the mole fraction of the solute in the solution. In other words, it depends on the nature of the solvent and on the concentration of the solute and not on the nature of the solute. Eq. 12.3 can be written as

$$\frac{p_1^0 - p_1}{p_1^0} = x_2 \quad \text{. . .(12.4)}$$

The expression on the left-hand side of Eq. 12.4 is called the **relative lowering of vapour pressure.** Eq. 12.4 also may be stated as:

It is the relative lowering of vapour pressure which is a colligative property and not the lowering of vapour pressure.

> "The relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute."

The above statement is also called Raoult's law of relative lowering of vapour pressure.

Determination of Relative Molecular Mass from the Lowering of Vapour Pressure

It is possible to measure the relative molecular mass of a non-volatile solute, if the vapour pressure of a dilute solution containing the non-volatile solute is known. Thus if w_2 kg of the solute having molar mass M_2 kg mol^{-1} is dissolved in w_1 kg of the solvent having molar mass M_1 kg mol^{-1}, then from Eq. 12.4, we have

$$\frac{p_1^\circ - p_1}{p_1^\circ} = x_2 = \frac{n_2}{n_1 + n_2} \quad \text{. . . (12.5)}$$

$$\text{or} \quad \frac{p_1^\circ - p_1}{p_1^\circ} = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2} \quad \text{. . . (12.6)}$$

For a dilute solution, the number of moles of the solute (n_2) is negligible in comparison to the number of moles of solvent (n_1). Thus Eq. 12.6 reduces to

$$\frac{p_1^\circ - p_1}{p_1^\circ} \simeq \frac{w_2/M_2}{w_1/M_1} = \frac{w_2 M_1}{w_1 M_2} \quad \text{. . . (12.7)}$$

Thus knowing the mass of the solvent, its relative molecular mass, mass of the solute, the vapour pressure of the solution and of the pure solvent, the relative molecular mass of the solute can be calculated from Eq. 12.7.

Measurement of Vapour Pressure Lowering

The lowering of vapour pressure of a solvent when a non-volatile solute is dissolved in it can be measured by the following methods:

i) Static Method

In this method, the difference between the vapour pressures of the solvent and the solution is determined with the help of a differential manometer. The apparatus is as shown in Fig. 12.1. It consists of two bulbs which are connected to a manometer. One arm of the manometer is connected with the bulb, A, containing the solvent and the other arm with the bulb, B, containing the solution. The manometric liquid is an inert, non-volatile, low density liquid such as β-bromonaphthalene, n-butylphthalate, etc. From the difference in the levels of the liquid in the two arms, the difference in vapour pressure between the solvent and the solution can be read directly.

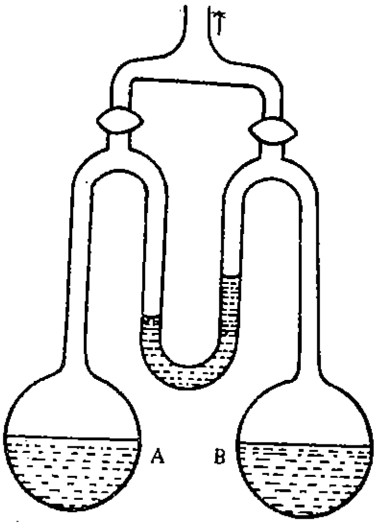

Fig. 12.1: Static method for determining the lowering of vapour pressure.

ii) Dynamic Method

This method is due to Ostwald and Walker. In this method (Fig. 12.2), a stream of dry and purified air is first passed through a pre-weighed set of bulbs containing the solution. The air coming out of the bulbs takes up an amount of vapour which is proportional to the vapour pressure of the solution. Evidently the loss in mass suffered by the bulbs containing the solution is proportional to the vapour pressure of the solution. If w_A is the loss in mass suffered by the solution-bulbs and p_1 is the vapour pressure of the solution, then we have

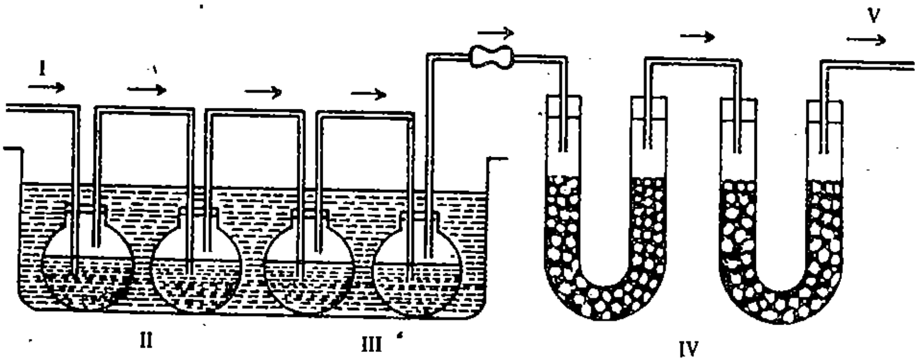

Fig. 12.2: Ostwald and Walker's apparatus for measuring the vapour pressure lowering:
I) air;
II) solution bulbs;
III) solvent bulbs; IV) weighed $CaCl_2$ tubes;
V) dry air.

$$w_A \propto p_1 \qquad \ldots (12.8)$$

The air coming out of the solution bulbs is then passed through pre-weighed set of bulbs containing the solvent. As the air containing vapours of the solvent passes through the solvent, it takes up a further amount of vapour which is proportional to the difference in vapour pressures of the pure solvent and the solution. Evidently the loss in mass suffered by the solvent bulbs is proportional to the difference in vapour pressures of the pure solvent and the solution. If w_B is the loss in mass suffered by the solvent-bulbs and p_1° is the vapour pressure of the solvent, then we have

$$w_B \propto p_1^\circ - p_1 \qquad \ldots (12.9)$$

From Eqs. 12.8 and 12.9 we have

$$(w_A + w_B) \propto p_1 + p_1^\circ - p_1$$

$$\text{or} \quad (w_A + w_B) \propto p_1^\circ \qquad \ldots (12.10)$$

From Eqs. 12.9 and 12.10 we have,

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{w_B}{w_A + w_B} \qquad \ldots (12.11)$$

Thus knowing w_A and w_B, the relative lowering of vapour pressure can be calculated using Eq. 12.11.

Fused calcium chloride is hygroscopic in nature and absorbs moisture from moist air.

If the solvent is water, the moist air coming out of the solvent bulbs may be passed through a weighed tube containing fused calcium chloride which absorbs moisture from moist air. The mass of calcium chloride tube will increase and the increase in mass will be equal to $(w_A + w_B)$.

Example 1

The vapour pressure of a solution containing 0.012 kg of a solute dissolved in 0.100 kg of water at 300 K is 3.50×10^3 Pa. Calculate the molar mass of the solute, if the vapour pressure of water at 300 K is 3.70×10^3 Pa.

Solution

$w_1 = 0.100$ kg; $\quad w_2 = 0.012$ kg

$M_1 = 0.018$ kg mol^{-1}; $\quad M_2 = ?$

$p_1^\circ = 3.70 \times 10^3$ Pa; $\quad p_1 = 3.50 \times 10^3$ Pa

Using Eq. 12.7, we have

$$\frac{(3.70 \times 10^3\ \text{Pa} - 3.50 \times 10^3\ \text{Pa})}{3.70 \times 10^3\ \text{Pa}} = \frac{(0.012\ \text{kg})\ (0.018\ \text{kg mol}^{-1})}{(0.100\ \text{kg})\ (M_2)}$$

$$\text{or } M_2 = \frac{(0.012\ \text{kg})\ (0.018\ \text{kg mol}^{-1})}{0.100\ \text{kg}} \times \frac{3.70 \times 10^3\ \text{Pa}}{0.20 \times 10^3\ \text{Pa}}$$

$$= 0.040\ \text{kg mol}^{-1}$$

In this section, we discussed the correlation between the relative lowering of vapour pressure and the mole fraction of a non-volatile solute in a solution. In the next section, we shall study how the boiling point of a solvent is affected when a non-volatile solute is added to it.

SAQ 1

State whether the following statements are true or false:

i) Lowering of vapour pressure is not a colligative property.

ii) Relative lowering of vapour pressure is equal to the mole fraction of the solvent.
iii) Relative lowering of vapour pressure depends upon the number of particles of the solute and the solvent.

....

....

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12.3 ELEVATION OF BOILING POINT

The temperature, at which the vapour pressure of the liquid becomes equal to the atmospheric pressure, is called the boiling point of the liquid. Since, according to Raoult's law, the vapour pressure of a solution containing a non-volatile solute is less than that of its pure solvent, the boiling point of such a solution will be higher than the boiling point of the pure solvent. This is because when a non-volatile solute is added to a solvent at a particular temperature, the vapour pressure of the solvent decreases. Thus the solution has to be heated further to make its vapour pressure equal the atmospheric pressure. This can be understood from the vapour pressure curves plotted in Fig. 12.3.

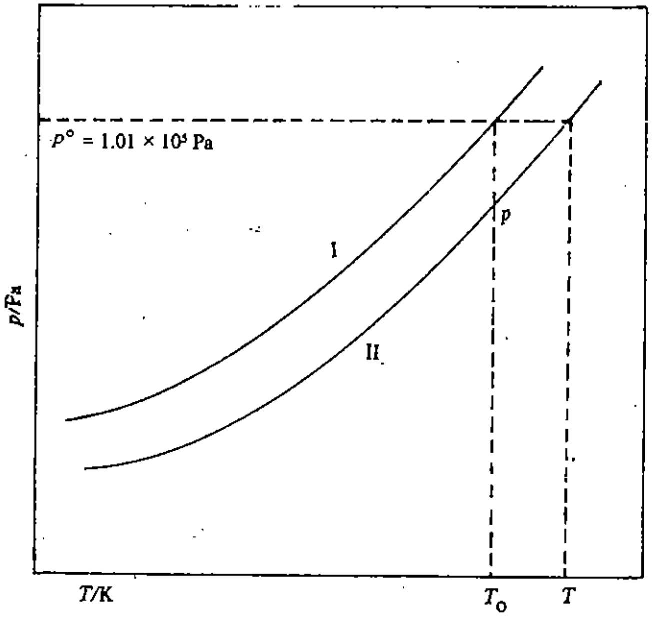

Fig. 12.3: Elevation of boiling point.

The curve I represents the variation of vapour pressure of the pure solvent with temperature. The curve II represents the variation of vapour pressure of a dilute solution of known concentration with temperature. The boiling point of the solvent is T_0 and that of the solution is T so that the elevation in boiling point is $T - T_0 = \Delta T_b$. At temperature T_0, the lowering of vapour pressure of a solvent, when a non-volatile solute is added to it, is $p^\circ - p$. From the vapour pressure curve of the solution, it is clear that the vapour pressure of the solution is p at T_0 and p° at T. Applying the integrated form of the Clausius-Clapeyron equation (Eq. 9.59), we have,

$$\ln \frac{p^\circ}{p} = \frac{\Delta H_{vap}}{R} \left[\frac{T - T_0}{T T_0} \right] \quad \ldots (12.12)$$

where ΔH_{vap} represents the molar enthalpy of vaporization of the solvent at its normal boiling point T_0. Since, the solution is dilute, T_0 and T are not much different from each other. Eq. 12.12 may be written as

$$\ln \frac{p^\circ}{p} = \frac{\Delta H_{vap}}{R} \; \frac{\Delta T_b}{T_0^2} \quad \ldots (12.13)$$

where, ΔT_b = Elevation in boiling point = $T - T_0$ and $T \simeq T_0$ so that $TT_0 \simeq T_0^2$. But

$$\ln \frac{p^o}{p} = -\ln \frac{p}{p^o} = -\ln\left(1 - \frac{p^o - p}{p^o}\right)$$

$= -\ln(1 - x_2)$ (using Eq. 12.4 where x_2 is the mole fraction of the solute).

In the case of a dilute solution, x_2 is very small as compared to 1. In such cases, we can apply the approximation, $\ln(1 - x_2) = -x_2$

Hence, $\ln \dfrac{p^o}{p} = x_2$ .... (12.14)

From Eqs. 12.13 and 12.14, we have

$$x_2 = \frac{\Delta H_{vap}}{R} \quad \frac{\Delta T_b}{T_0^2} \qquad \text{... (12.15)}$$

But $$x_2 = \frac{n_2}{n_1 + n_2} \qquad \text{... (12.16)}$$

where n_1 and n_2 are the number of moles of the solvent and the solute, respectively.

When the solution is dilute, the number of moles of the solute is negligible in comparison with the number of moles of the solvent. Eq. 12.16 may be written as,

$$x_2 = \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1} \qquad \text{... (12.17)}$$

From Eqs. 12.15 and 12.17, we have

$$\frac{\Delta H_{vap}}{R} \quad \frac{\Delta T_b}{T_0^2} = \frac{w_2/M_2}{w_1/M_1} \qquad \text{... (12.18)}$$

or $$\Delta T_b = \frac{RT_0^2}{\Delta H_{vap}} \frac{w_2/M_2}{w_1/M_1} = \frac{RT_0^2 M_1}{\Delta H_{vap}} \times \frac{w_2}{w_1 M_2} \qquad \text{... (12.19)}$$

When one mole of a solute ($w_2 = M_2$) is dissolved in 1 kg of the solvent ($w_1 = 1$ kg), Eq. 12.19 reduces to

$$\Delta T_b = \frac{RT_0^2 M_1}{\Delta H_{vap}} \qquad \text{... (12.20)}$$

The right hand side of Eq. 12.20 consists of constants R, T_0, M_1 and ΔH_{vap}. Its value is a constant for a particular solvent and it is called the molal elevation constant for a particular solvent. It is denoted by K_b.

$$K_b = \frac{RT_0^2 M_1}{\Delta H_{vap}} \qquad \text{... (12.21)}$$

Using Eqs. 12.19 and 12.21, we can write

$$\Delta T_b = K_b \frac{w_2}{w_1 M_2} \qquad \text{... (12.22)}$$

or $$\Delta T_b = K_b \frac{n_2}{w_1} \qquad \text{... (12.23)}$$

$$\Delta T_b = K_b m \qquad \text{.. (12.24)}$$

where n_2 is the number of moles of the solute and m is the molality of the solution.

Molality is the number of moles of the solute dissolved in 1 kg of the solvent. If n_2 moles of a solute are dissolved in w_1 kg of the solvent, its molality is given by.

$$m = \frac{n_2}{w_1}$$

Determination of Relative Molecular Mass from Elevation of Boiling Point

A known mass of a non-volatile solute, for which the relative molecular mass is to be determined, is dissolved in a known mass of the solvent. By measuring the elevation in boiling point, it is possible to calculate the relative molecular mass of the solute from Eq. 12.25 which is a rearranged from Eq. 12.22.

$$M_2 = \frac{K_b}{\Delta T_b} \cdot \frac{w_2}{w_1} \qquad \text{... (12.25)}$$

The molal elevation constants (K_b) for some liquids are given in Table 12.1.

Table 12.1: Molal Elevation Constants

Solvent	K_b K kg mol^{-1}	Solvent	K_b K kg mol^{-1}
Water	0.51	Ethyl alcohol	1.23
Acetone	1.71	Benzene	2.53
Carbon tetrachloride	4.95	Chloroform	3.90
Methyl alcohol	0.86	Cyclohexane	2.79

Determination of Boiling Point Elevation

For measuring the elevation of boiling point, a number of methods are available. In all these methods, care is taken to avoid superheating of the liquid. The most commonly used methods are given below:

Superheating means that the temperature of the liquid may rise above the boiling point of liquid and the liquid may not boil.

1) The Landsberger Method

In this method, the solvent or the solution is heated to its boiling point by passing the vapours of the solvent through them. As the vapours condense, they give up their latent heat to heat the solvent or the solution. Superheating is nearly impossible in this way because, when the boiling point is reached, the vapours will be in equilibrium with the liquid at atmospheric pressure and no more vapours will condense. The apparatus is shown in Fig. 12.4a. It consists of flask A which contains the solvent.

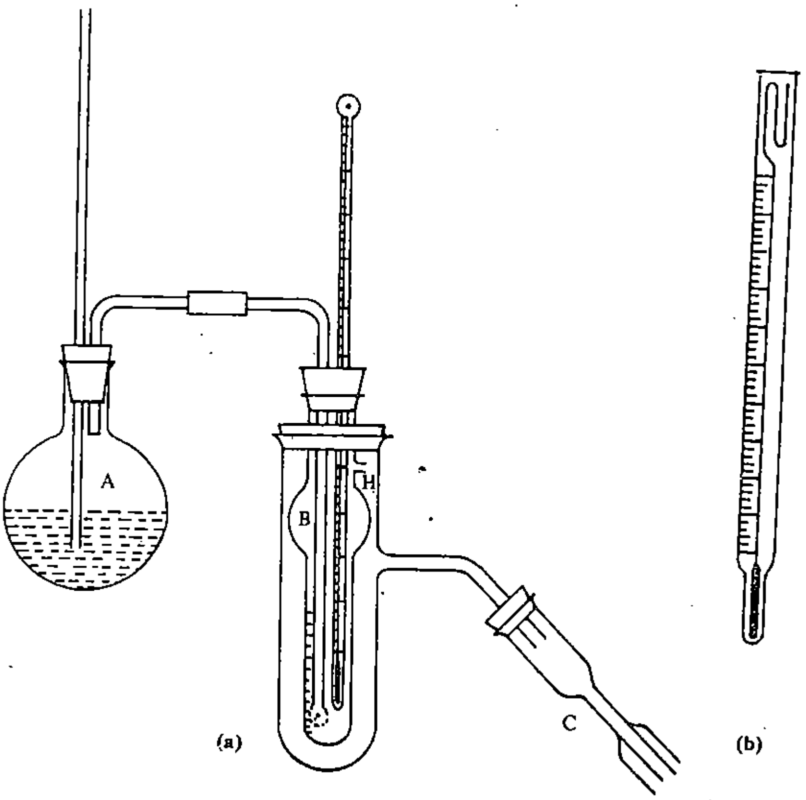

Fig. 12.4 : a) Apparatus for Landsberger method; b) Beckmann thermometer.

The flask is connected to a graduated tube B which also contains the solvent. Solvent in flask A is boiled so that the vapours pass into the solvent in B, where these vapours emerge in small bubbles through a number of holes at the end of the tube. The temperature of the solvent rises and when it becomes constant, it is noted. Any excess vapours pass from the right hand top portion (H) of the graduated tube (B) into the condenser (C). A known mass of the non-volatile solute is then added to the solvent in

Beckmann thermometer contains a mercury reservoir at the top. The amount of mercury in the bulb can be varied. The thermometer can be used to measure temperatures from 234 K to 523 K. This thermometer does not give actual temperature. For measuring rise of boiling point, or depression in freezing point, only difference in temperature is required. This can be used with an accuracy of 0.001.

B. The solution is then again heated by passing the vapours of the solvent through it. When the temperature reaches a constant value, it is noted. The passage of vapours is stopped and the volume of the solution is noted as shown on the graduated tube. A thermometer, which is graduated in tenths of a degree and is capable of reading upto 0.01°, is generally used. One such thermometer is the Beckmann thermometer (Fig. 12.4b). Knowing the density of the solvent, the mass of the solvent in the solution can be calculated. The volume of the solute is supposed to be negligible. The difference between the two boiling points gives the elevation in boiling point.

2) Cottrell's Method

The apparatus is as shown in Fig. 12.5. It consists of a graduated tube A which contains the liquid-solvent or the solution. An inverted funnel is placed in the tube A through which the bubbles rise. When the liquid starts boiling, a steam of liquid and the vapours is poured over the bulb of a Beckmann thermometer so that the bulb of the thermometer is covered with a thin layer of the boiling liquid. After determining the boiling point of the pure solvent, a known mass of the solute is added and the boiling point of the solution is again determined. The difference between the two readings gives the elevation in boiling point.

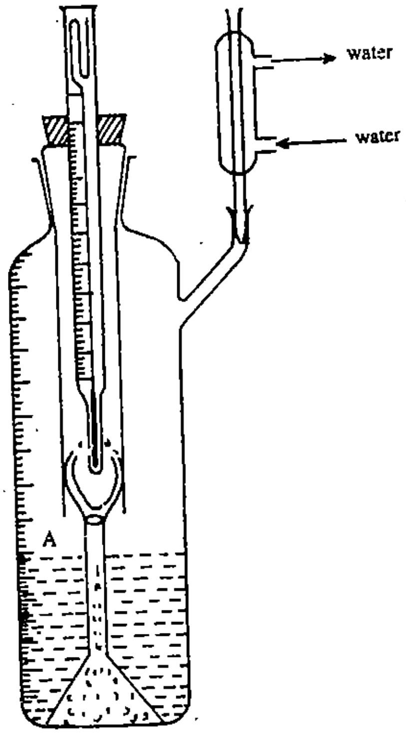

Fig. 12.5: Apparatus for Cottrell's method.

Example 2

The boiling point of chloroform was raised by 0.320 K when 5.15×10^{-4} kg of an organic compound was dissolved in 3.50×10^{-2} kg of chloroform. Calculate the molar mass of the organic compound. Molal elevation constant for chloroform is 3.90 K kg mol^{-1}

Solution

$$\Delta T_b = 0.320\ \text{K};\ w_2 = 5.15 \times 10^{-4}\ \text{kg}$$
$$w_1 = 3.50 \times 10^{-2}\ \text{kg};\ K_b = 3.90\ \text{K kg mol}^{-1}$$

Using Eq. 12.25, we have

$$M_2 = \frac{3.90\ \text{K kg mol}^{-1} \times 5.15 \times 10^{-4}\ \text{kg}}{0.320\ \text{K} \times 3.50 \times 10^{-2}\ \text{kg}}$$

$$= 0.179\ \text{kg mol}^{-1}$$

In the next section, we shall study the effect of addition of a non-volatile solute on the freezing point of a solvent.

SAQ 2

Explain why the boiling point of a solution is higher than that of a pure solvent.

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12.4 DEPRESSION OF FREEZING POINT

Freezing point of a liquid is the temperature at which the liquid and the corresponding solid form have the same vapour pressure. Since, the addition of a non-volatile solute decreases the vapour pressure of the solvent, the vapour pressure-temperature curve of a solution (II) lies below that of pure solvent (I) as shown in Fig. 12.6. When the solution reaches the freezing point, the solid phase separating out is the pure solvent. Assuming that vapours obey ideal gas laws and that the volumes of the solid and the liquid are negligible in comparison with the volume of vapours, the equilibrium between solid solvent (ice) and vapour at constant external pressure is given by Clausius-Clapeyron equation,

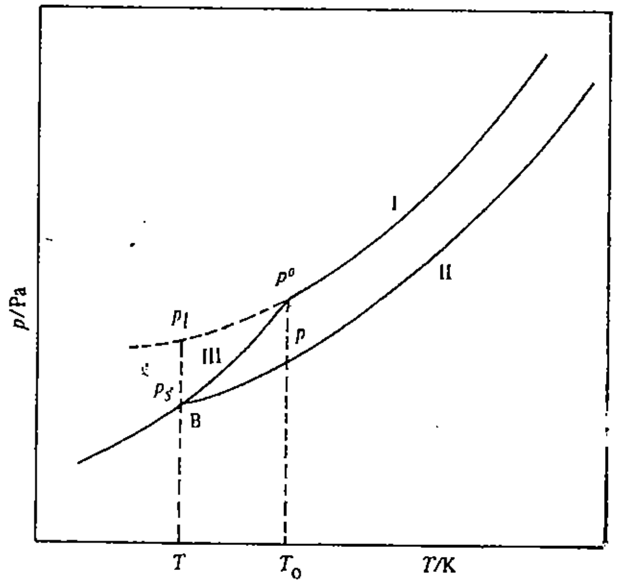

Fig. 12.6 : Depression of freezing point: I) solvent curve; II) solution curve; III) curve for ice.

$$\frac{\mathrm{d}\ln p_s}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{sub}}}{RT^2} \qquad \ldots (12.26)$$

where ΔH_{sub} is the molar enthalpy of sublimation. Similarly, for the equilibrium between liquid and vapour, the Clausius-Clapeyron equation gives,

$$\frac{\mathrm{d}\ln p_l}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{vap}}}{RT^2} \qquad \ldots (12.27)$$

where ΔH_{vap} is the molar enthalpy of evaporation of the liquid. If this equation is to hold good for the supercooled liquid, then Eqs. 12.26 and 12.27 will be applicable at the same temperature, i.e., T in Fig. 12.6.

Subtracting Eq. 12.27 from Eq. 12.26, we have,

$$\frac{\mathrm{d}\ln p_s}{\mathrm{d}T} - \frac{\mathrm{d}\ln p_l}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{sub}}}{RT^2} - \frac{\Delta H_{\mathrm{vap}}}{RT^2} \qquad \ldots (12.28)$$

or

$$\frac{\mathrm{d}\ln (p_s/p_l)}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{sub}} - \Delta H_{\mathrm{vap}}}{RT^2} \qquad \ldots (12.29)$$

$$\text{or}\quad \frac{d\ln(p_s/p_l)}{dT} = \frac{\Delta H_{fus}}{RT^2} \qquad \dots(12.30)$$

where ΔH_{fus} is the molar enthalpy of fusion and is equal to $(\Delta H_{sub} - \Delta H_{vap})$. At the freezing point of the solution, the vapour pressure of the solid (ice) must be equal to that of the solution (p_1) with which it is in equilibrium, i.e., at the point B in Fig. 12.6, $p_s = p_1$. Hence at the freezing point of the solution,

$$\frac{d\ln(p_1/p_l)}{dT} = \frac{\Delta H_{fus}}{RT^2} \qquad \dots(12.31)$$

where p_1 is the vapour pressure of the solution and p_l that of the supercooled solvent at the same temperature. According to Raoult's law (Eq. 12.1),

$$\frac{p_1}{p_l} = x_1 \qquad \dots(12.32)$$

Using this in Eq. 12.31,

$$\frac{d\ln x_1}{dT} = \frac{\Delta H_{fus}}{RT^2} \qquad \dots(12.33)$$

For the pure solvent ($x_1 = 1$), the freezing point is T_0 and for the solution ($x_1 = x_1$), the freezing point is T. On integration of Eq. 12.33 between T_0 and T as also between 1 and x_1, we get

$$\int_1^{x_1} d\ln x_1 = \frac{\Delta H_{fus}}{R}\int_{T_0}^{T}\frac{dT}{T^2}$$

$$\ln x_1 = -\frac{\Delta H_{fus}}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]$$

$$\text{or}\quad \ln x_1 = -\frac{\Delta H_{fus}}{R}\left[\frac{T_0 - T}{TT_0}\right] \qquad \dots(12.34)$$

If the solution is very dilute, T and T_0 are not much different and $TT_0 \simeq T_0^2$.

Also $T_0 - T = \Delta T_f =$ Depression in freezing point.

Eq. 12.34 thus reduces to

$$\ln x_1 = -\frac{\Delta H_{fus}}{R}\cdot\frac{\Delta T_f}{T_0^2} \qquad \dots(12.35)$$

Since $x_1 + x_2 = 1$

$$\ln x_1 = \ln(1 - x_2)$$

and since x_2 is very small, $\ln(1 - x_2) = -x_2$

Eq. 12.35 thus reduces to

$$-x_2 = -\frac{\Delta H_{fus}}{R}\cdot\frac{\Delta T_f}{T_0^2}$$

$$\text{or}\quad \Delta T_f = \frac{RT_0^2}{\Delta H_{fus}}\,x_2 \qquad \dots(12.36)$$

But $x_2 = \dfrac{w_2 M_1}{w_1 M_2}$ in the case of a dilute solution as per Eq. 12.17.

Hence Eq. 12.36 can be writen as

$$\Delta T_f = \frac{RT_0^2 M_1}{\Delta H_{fus}}\cdot\frac{w_2}{w_1 M_2} = \frac{K_f w_2}{w_1 M_2} \qquad \dots(12.37)$$

$$\text{where } K_f = \frac{RT_0^2 M_1}{\Delta H_{fus}} \qquad \dots(12.38)$$

K_f is the molal depression constant.

Eq. 12.37 can also we written as

$$\Delta T_f = \frac{K_f w_2 / M_2}{w_1} = K_f \frac{n_2}{w_1}$$

i.e., $\Delta T_f = K_f m$ . . . (12.39)

where m is the molality of the solution.

The molal depression constants (K_f) for a few solvents are given in Table 12.2.

Table 12.2: Molal Depression Constants

Solvent	K_f K kg mol^{-1}	Solvent	K_f K kg mol^{-1}
Water	1.85	Cyclohexane	20.20
Benzene	5.12	Camphor	40.00
Nitrobenzene	6.90	Acetic acid	3.90

Determination of Relative Molecular Mass

Eq. 12.37 is used for determining the relative molecular mass of a non-volatile soulte. Note that the solution should be dilute and, on cooling, the solid solvent alone must separate. The following methods are used for measuring the depression of freezing points.

1) The Beckmann Method

The type of apparatus used is shown in Fig. 12.7.

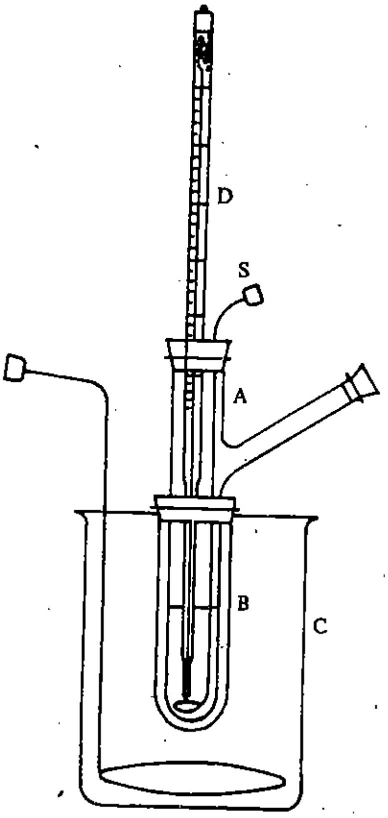

Fig. 12.7 : Determination of freezing point—Beckmann method.

A known mass (w_1) of the pure solvent is taken in the tube A fitted with a Beckmann thermometer D and a stirrer(S). The tube A is fitted inside another tube B leaving an air space between the outer wall of the tube A and the inner wall of the tube B. The whole arrangement described above is immersed in a freezing mixture contained in the vessel C. The temperature of the freezing mixture should be about 5° below the freezing point of the pure solvent. The temperature of the solvent in the tube A is allowed to fall until it is 0.5° below its normal freezing point, i.e., the liquid is allowed to be supercooled without the solid being separated. The liquid is then stirred.

vigorously. It causes the crystallization to commence and the temperature of the solvent rises to its freezing point which is recorded. The tube A is then removed, the solvent is allowed to melt and a weighed amount of the solute (w_2) is dissolved. The freezing point of the solution is determined by the same method as for the solvent. The difference between the two readings gives the depression of the freezing point.

2) Rast Method

This method can be used for determining the relative molecular masses of those non-volatile solutes which are soluble in molten camphor. It can be seen from Table 12.2 that the molal depression constant of camphor is very high, i.e., 40.00 K kg mol^{-1}. It means that when one mole of a solute is dissolved in one kilogram of camphor, the depression in freezing point is 40°, which can be read using ordinary thermometers.

For a substance, the melting po. of the solid phase and the freezing point of the liquid phase are the same.

A small amount of camphor is thoroughly powdered and then introduced into a capillary tube. Its melting point is then determined. A known mass of the solute is then mixed with 10 to 15 times its mass of camphor and, the whole mixture is melted. After cooling, the solid mixture is thoroughly powdered and, its melting point determined as described for camphor. The difference between the two readings gives the depression of freezing point.

Example 3

An aqueous solution containing 5.00×10^{-4} kg of a solute in 4.00×10^{-2} kg of water was found to freeze at 272.72 K. Calculate the molar mass of the solute. Molar enthalpy of fusion of ice at its melting point (273.15 K) is 6021 J mol^{-1}.

Solution

Using Eq. 12.38, we have

$$K_f = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})^2 \times (0.018 \text{ kg mol}^{-1})}{6021 \text{ J mol}^{-1}}$$

$$= 1.85 \text{ K kg mol}^{-1}$$

$$\Delta T_f = (273.15 - 272.72) \text{ K} = 0.43 \text{ K}$$

(Since 273.15 K is the freezing point of water)

Using Eq. 12.37.

$$M_2 = \frac{K_f\, w_2}{\Delta T_f\, w_1} = \frac{1.85\text{K kg mol}^{-1}}{0.43 \text{ K}} \times \frac{5.00 \times 10^{-4} \text{ kg}}{4.00 \times 10^{-2} \text{ kg}}$$

$$= 0.0538 \text{ kg mol}^{-1}$$

Molar mass of the solute = 0.0538 kg mol^{-1}

SAQ 3

When a non-volatile solute is added to a solvent, the depression in freezing point is more than the elevation of boiling point. Explain.

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12.5 OSMOTIC PRESSURE

When a solution is separated from the pure solvent by a semipermeable membrane, it is observed that the solvent tends to pass through the membrane into the solution and dilutes it. This phenomenon, called **osmosis**, was first reported by Noket in 1748 for low molecular mass solutes in water. The best semipermeable membrane known is a film of copper ferrocyanide, $Cu_2[Fe(CN)_6]$. For high molecular mass solutes in organic solvents, the membranes used are thin films of either cellulose acetate or cellulose nitrate.

Let us now understand the term, osmotic pressure (π). Consider Fig. 12.8 in which A is a chamber open at one end and, fitted with a movable piston B, at the other. The chamber is divided by means of a semipermeable membrane C into two sections; one is filled with a pure solvent and the other with the solution of a non-volatile solute in the same solvent. Because of osmosis, the solvent will tend to pass through the membrane into the solution and displace the piston upward. The motion of the piston and, osmosis of the solvent, can be prevented by the application of a pressure over the piston. The mechanical pressure which must be applied on a solution to prevent osmosis of the solvent into the solution through a semipermeable membrane is called the **osmotic pressure** of the solution. This pressure for a given solution depends on many factors but not on the nature of the membrane.

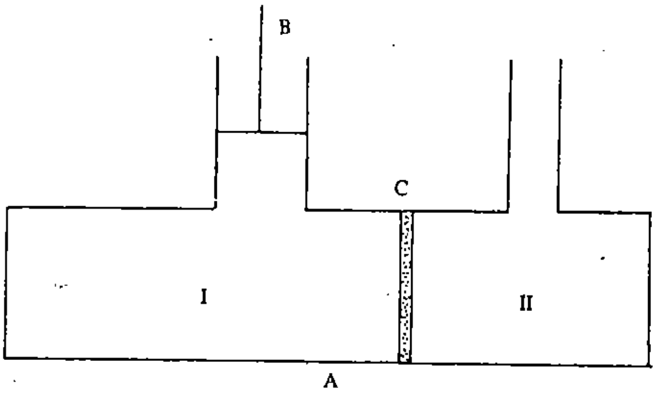

Fig. 12.8 : Osmotic pressure measurement; I-section containing the solution; II-section containing the solvent.

A semipermeable membrane allows the passage of only the solvent particles through it. It does not allow the passage of solute particles through it. Various substances which may serve as semipermeable membranes are plant cells, cells in animal body, etc. These membranes are, however, very weak and are not perfectly semipermeable. In the laboratory, a semipermeable membrane of copper ferrocyanide is generally used. To withstand high pressure, copper ferrocyanide is deposited on the walls of a porous pot electrolytically.

An alternative definition for osmotic pressure can be given as follows:

The chemical potential of a solvent is smaller in a solution than in pure state. Osmotic pressure is also defined as the pressure applied to the solution so that the chemical potential of the solvent in the solution becomes equal to that of pure solvent.

Isotonic solutions are those solutions which have the same osmotic pressure.

Osmosis takes place in living cells also. If a cell is immersed in a solution having a higher osmotic pressure than the cell sap, water will pass out of the cell through the selectively permeable membrane. The cytoplasm will then shrink and detach from the cell wall. This phenomenon is called **'Plasmolysis'**. By taking a number of solutions of a given substance at different concentrations and observing the change in the cell, it is possible to find out the solution which just fails to bring about plasmolysis. So this solution will have the same osmotic pressure as that of the cell sap and is said to be **isotonic** with it. It has been observed that red blood corpuscles are isotonic with a 0.91 per cent solution of sodium chloride.

Measurement of Osmotic Pressure

The most commonly used method for measuring osmotic pressure of solutions is that discovered by Berkeley and Hartley.

Berkeley and Hartley's Method

The apparatus is as shown in Fig. 12.9. It consists of a porous tube A with a semipermeable membrane of copper ferrocyanide deposited in its walls. The porous tube is fitted with a solvent reservoir on one side and a capillary indicator (B) on the other side. The porous tube containing the semipermeable membrane is filled with the pure solvent and is surrounded by another tube (C) made of gun metal, containing the solution whose osmotic pressure is to be measured. Due to osmosis, the solvent from the porous tube passes through the semipermeable membrane into the solution. This movement of solvent particles is indicated by a fall in level in the capillary indicator.

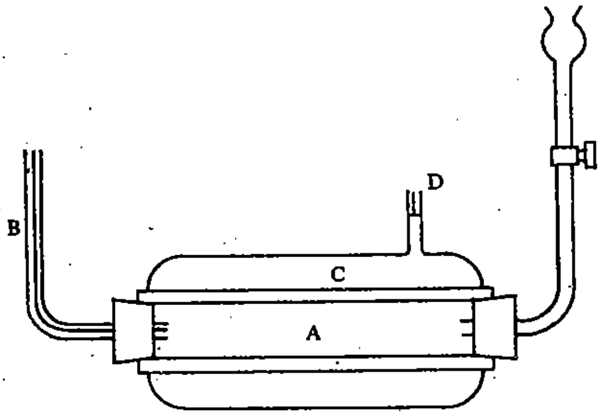

Fig. 12.9: Berkeley and Hartley's apparatus.

A hydrostatic pressure is applied to the solution through the tube D. The pressure at which the movement of the solvent is reversed is the osmotic pressure of the solution.

The osmotic pressure values of aqueous solutions of sucrose at 287 K are given in Table 12.3.

Table 12.3: Osmotic Pressure Values of Aqueous Solutions of Sucrose at 287 K.

c/mol dm^{-3}	$10^{-5} \times \pi$/Pa	
	Observed	Calculated
5.88×10^{-2}	1.34	1.39
8.09×10^{-2}	2.00	1.91
1.19×10^{-1}	2.75	2.80
1.80×10^{-1}	4.04	4.23

The experimental values of osmotic pressure of solutions as shown in Table 12.3 indicate that in dilute solutions, the osmotic pressure is proportional to the concentration of the solution at constant temperature. Based on such observations, van't Hoff deduced the laws of osmotic pressure and an equation (Eq. 12.48) relating concentration of a solution to its osmotic pressure. Using Eq. 12.48, it is possible to calculate osmotic pressure of a solution. Some calculated osmotic pressure values are entered in Table 12.3. Let us now study the laws of osmotic pressure and, deduce Eq. 12.48.

Laws of Osmotic Pressure

van't Hoff deduced the laws of osmotic pressure from the results of various investigations on osmotic pressure. These are given below:

i) Osmotic pressure at constant temperature is directly proportional to the concentration of the solution. Mathematically.

$$\pi \propto c \qquad \ldots (12.40)$$

Since the concentration of a solution (in mol dm^{-3}) is inversely proportional to its volume (in dm^3 mol^{-1}), it follows that for a solution.

$$\pi \propto \frac{1}{V} \qquad \ldots (12.41)$$

or $\pi V = \text{constant}$ ... (12.42)

Eq. 12.42 is the analogue of Boyle's law for ideal gases.

ii) Osmotic pressure of a solution of given concentration is directly proportional to the temperature (in kelvin scale)

$$\pi \propto T \qquad \ldots (12.43)$$

iii) At constant temperature, equimolar solutions of different solutes have the same osmotic pressure. In other words, osmotic pressure of a solution is directly proportional to the number of moles of the solute.

$$\pi \propto n_2 \qquad \ldots (12.44)$$

From Eqs. 12.41, 12.43 and 12.44, we have,

$$\pi \propto \frac{n_2 T}{V} \qquad \ldots (12.45)$$

or $$\pi V = n_2 RT \qquad \ldots (12.46)$$

where R is a constant

or $$\pi = \frac{n_2}{V} RT \qquad \ldots (12.47)$$

But $\frac{n_2}{V}$ = concentration of the solution = c

i.e., $\pi = cRT$ ... (12.48)

Eq. 12.47 can also be written as,

$$\pi = \frac{w_2 RT}{M_2 V} \qquad \ldots (12.49)$$

By comparing the osmotic pressure of a cane sugar solution with the pressure exerted by hydrogen gas at the same temperature and concentration, van't Hoff showed that the value of R is the same as the gas constant. Thus, R may be taken to be equal to gas constant.

Using Eq. 12.49, we can calculate the osmotic pressure of a solution, if we know the mass and molar mass of the solute as well as the temperature and volume of the solution.

Example 4

Calculate the osmotic pressure of an aqueous solution containing 50.0 kg of sucrose ($C_{12}H_{22}O_{11}$) in 1.00 m^3 of a solution at 300 K.

Solution

Mass of solute = 50.0 kg

Molar mass of solute = 0.342 kg mol^{-1}

Volume of solution = 1.00 m^3

Temperature = 300 K

Using Eq. 12.49,

$$\pi = \frac{50.0 \text{ kg}}{0.342 \text{ kg mol}^{-1}} \times \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{1.00 \text{ m}^3}$$

$$= 3.65 \times 10^5 \text{ Pa}$$

12.6 VAN'T HOFF FACTOR

The colligative properties depend on the number of particles of the solute. In cases where the solute associates or dissociates in solution, abnormal results are obtained.

In case of association, the number of effective molecules decreases and consequently, the observed values of the colligative properties are less in magnitude than those calculated for unassociated molecules. Also due to association, each molecular cluster will have more than one molecule, and hence, the experimentally obtained relative molecular masses will be higher than the actual relative molecular masses.

In case of dissociation, the number of effective particles will increase and hence, the colligative properties will be higher in magnitude than those calculated for

Theoretical value refers to the value calculated assuming no association or dissociation. Apparent or observed value refers to the value calculated based on experimental results.

undissociated molecules. The experimentally observed relative molecular mass value will be less than that of the actual value.

vant't Hoff introduced a factor *i*, now known as van't Hoff factor, to indicate such deviations from normal behaviour.

$$i = \frac{\text{Observed value of the colligative property}}{\text{Theoretical value of the colligative property}} \qquad \dots (12.50)$$

Since these properties vary inversely to the relative molecular masses of the solutes, we can write Eq. 12.50 as,

$$i = \frac{\text{Theoretical molar mass}}{\text{Observed molar mass}} \qquad \dots (12.51)$$

We will now explain how this van't Hoff factor is used in calculating the degree of association or dissociation.

Calculation of Degree of Association

Degree of association is defined as the fraction of the total number of molecules which combine to form bigger molecules. Consider one mole of A dissolved in a given volume of a solvent. We can write for association of *n* molecules,

$$nA \rightleftharpoons A_n \qquad \dots (12.52)$$

If x is the degree of association, then the number of moles of unassociated A = $(1-x)$ and the number of moles of $A_n = \frac{x}{n}$

Hence, the total number of effective moles of A

$$= (1-x) + \frac{x}{n}$$

Since the observed colligative property is proportional to number of effective moles of A, observed colligative property is proportional to $(1-x+\frac{x}{n})$. But if we were to get the theoretical value for the colligative property, the number of mole of A must be one only.

Then from Eq. 12.51, we have,

$$i = \frac{\text{Theoretical molar mass}}{\text{Observed molar mass}} = \frac{\text{Observed colligative property}}{\text{Theoretical colligative property}}$$

$$i = \frac{(1-x+x/n)}{1} = (1-x+x/n) \qquad \dots (12.53)$$

Thus, knowing n and i, x can be calculated.

Example 5

1.65×10^{-3} kg of acetic acid, when dissolved in 0.100 kg of benzene, increased the boiling point by 0.36 K. Calculate the van't Hoff factor and the degree of association of acetic acid in benzene assuming that acetic acid exists as a dimer in benzene. K_b for benzene is 2.53 K kg mol^{-1}.

Solution

Theoretical molar mass of acetic acid = 0.060 kg mol^{-1}

Using Eq. 12.25, observed molar mass of acetic acid

$$= \frac{(2.53 \text{ K kg mol}^{-1})}{0.36 \text{ K}} \times \frac{1.65 \times 10^{-3} \text{ kg}}{0.100 \text{ kg}} = 0.116 \text{ kg mol}^{-1}$$

Using Eq. 12.51, van't Hoff factor,

$$i = \frac{0.060 \text{ kg mol}^{-1}}{0.116 \text{ kg mol}^{-1}} = 0.517$$

Since acetic acid exists as a dimer in benzene, we can write the following expression:

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

Let x be the degree of association and the number of moles of CH_3COOH before association be 1.

Hence, number of moles of unassociated $CH_3COOH = 1-x$ and number of moles of associated $CH_3COOH = \frac{x}{2}$

Total no. of effective moles $= 1-x+\frac{x}{2} = 1-\frac{x}{2}$

Using Eq. 12.53,

$$0.517 = \frac{1-\frac{x}{2}}{1}$$

or $x = 0.966$

Thus, acetic acid is 96.6% associated.

Calculation of Degree of Dissociation

The degree of dissociation denotes the fraction of the total number of molecules which dissociates to give smaller species. Let us consider the dissociation of MA to give M^+ and A^- ions. Let x be the degree of dissociation.

$$\begin{array}{ccc} MA & \rightleftharpoons & M^+ + A^- \\ 1-x & & x \quad x \end{array}$$

Total number of moles after dissociation $= 1-x+x+x = 1+x$. Then,

$$i = \frac{\text{Theoretical molar mass}}{\text{Observed molar mass}} = \frac{\text{Observed colligative property}}{\text{Theoretical colligative property}}$$

Hence $i = \frac{1+x}{1}$ ...(12.54)

Hence, x can be calculated, if i is known.

Example 6

4.60×10^{-3} kg of sodium chloride was dissolved in 0.130 kg of water at 280 K. The osmotic pressure of the solution was found to be 2.66×10^6 Pa. Calculate the van't Hoff factor and the degree of dissociation. Density of the solution is 1.02×10^3 kg m .

Solution

$$\text{Volume of the solution} = \frac{\text{Mass of the solution}}{\text{Density of the solution}}$$

$$= \frac{(4.60 \times 10^{-3} \text{ kg} + 0.130 \text{ kg})}{1.02 \times 10^3 \text{ kg m}^{-3}}$$

$$= 1.32 \times 10^{-4} \text{ m}^3$$

Using Eq. 12.49, the theoretical value of the osmotic pressure can be calculated as follows:

$$\pi = \frac{4.60 \times 10^{-3} \text{ kg} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 280 \text{ K}}{5.85 \times 10^{-2} \text{ kg mol}^{-1} \times 1.32 \times 10^{-4} \text{ m}^3}$$

$$= 1.39 \times 10^6 \text{ Pa}$$

Using Eq. 12.50,

$$i = \frac{2.66 \times 10^6 \text{ Pa}}{1.39 \times 10^6 \text{ Pa}} = 1.91$$

Using Eq. 12.54,

$$1.91 = \frac{1 + x}{1} = 1 + x$$

$$x = 0.91$$

SAQ 4

State whether the following statements are true or false:

i) Two solutions having same concentration and at the same temperature are isotonic.

ii) van't Hoff factor, $i = \frac{\pi_{\text{observed}}}{\pi_{\text{calculated}}}$

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SAQ 5

Which of the following solutions will exert greater osmotic pressure:

0.1 M sodium chloride or 0.1 M sucrose? What is the reason?

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12.7 SUMMARY

The colligative properties of a solution depend upon the number of particles of a solute present in the solution. These properties are independent of the nature of the solute. The colligative properties are relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. According to Raoult's law, relative lowering of vapour pressure is equal to the mole fraction of the solute. Since the addition of a non-volatile solute to a solvent decreases the vapour pressure of the solvent, the boiling point of the solution containing a non-volatile solute is higher than that of the pure solvent. On the other hand, the freezing point of a solvent is lowered by the addition of a non-volatile solute to it.

When two solutions of different concentrations are separated by means of a semipermeable membrane, the flow of solvent occurs from a solution of lower solute concentration to that of higher concentration. This is called osmosis. van't Hoff showed that the osmotic pressure bears the same relationship to the concentration and temperature of the solution as the pressure of a gas to its concentration and temperature. When two solutions have the same osmotic pressure, they are called isotonic solutions. When a solute associates or dissociates in the solution, abnormal results are obtained. To account for all abnormal cases, van't Hoff introduced a factor *i*, now called van't Hoff factor.

12.8 TERMINAL QUESTIONS

1) Define colligative property. Name four of them.

2) How is molal elevation constant related to the enthalpy of vaporization? What are its units?

3) Derive the formula, $\Delta T_f = K_f m$.

4) The molal depression constant for water is 3.6 times its value for molal elevation constant. If the boiling point of an aqueous solution of urea is 373.25 K, what will be its freezing point? Assume that water boils at 373 K and freezes at 273 K.

5) Calculate the molal depression constant of water at 273 K. The enthalpy of fusion of ice at 273 K is 6.03 kJ mol^{-1}

6) A current of dry air was passed through a solution containing 5.0×10^{-3} kg of a non-volatile solute in 0.10 kg of water and then through pure water. The loss in mass of the solution was found to be 8.00×10^{-4} kg and the loss in mass of pure water 2.00×10^{-5} kg. Find the molar mass of the solute.

7) The molar enthalpy of vaporization of water at 373 K is 40.6 kJ. At what temperature will a solution containing 5.60×10^{-3} kg of glucose in 1.00 kg of water boil? Assume the boiling point of water to be 373 K.

8) A solution containing 4.0×10^{-3} kg of a non-volatile organic solute in 1.00×10^{-3} m^3 of the solution exerts an osmotic pressure of 6.66×10^4 Pa at 300 K. Calculate the molar mass of the solute.

9) An aqueous solution prepared by dissolving 0.5 kg of potassium chloride in 100 kg of water was found to freeze at 272.76 K. Calculate the van't Hoff factor and degree of dissociation of solute at this concentration. K_f for H_2O is 1.85 K kg mol^{-1} and the freezing point of water is 273 K.

12.9 ANSWERS

Self Assessment Questions

1) i) True ii) False iii) False,

2) See Sec. 12.3.

3) We know that $\Delta T_f = K_f m$ and $\Delta T_b = K_b m$. It is clear from the above expressions that since the molal depression constant for a solvent is more than the molal elevation constant, $\Delta T_f > \Delta T_b$.

4) i) True ii) True.

5) 0.1 M NaCl solution will exert greater osmotic pressure due to dissociation.

Terminal Questions

1) Colligative properties of solutions are those properties which depend only upon the number of particles of solute present in the solution and are independent of the nature of the solute. These are relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure.

2) $K_b = \dfrac{R T_0^2 M_1}{\Delta H_{vap}}$

The units of K_b are K kg mol^{-1}.

3) See Sec. 12.4.

4) If molal elevation constant is K_b, then molal depression constant is 3.6 K_b.

Boiling point of water = 373 K.

Elevation in boiling point = ΔT_b = (373.25 K − 373 K) = 0.25 K

Using Eq. 12.24,

$$\Delta T_b = 0.25\ \text{K} = K_b m \qquad (1)$$

and using Eq. 12.39,

$$\Delta T_f = K_f m = 3.6\ K_b m \qquad (2)$$

Dividing Eq. (2) by (1) we get

$$\frac{\Delta T_f}{0.25\ \text{K}} = \frac{3.6\ K_b m}{K_b m} = 3.6$$

$$\Delta T_f = 3.6 \times 0.25\ \text{K} = 0.9\ \text{K}$$

Freezing point of solution = 273 K − 0.9 K
= 272.1 K.

5) Using Eq. 12.38,

$$K_f = \frac{8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times (273\ \text{K})^2 \times 1.8 \times 10^{-2}\ \text{kg mol}^{-1}}{6.03 \times 10^3\ \text{J mol}^{-1}}$$

$$= 1.85\ \text{K kg mol}^{-1}.$$

6) Mass of solute (w_2) = 5.0×10^{-3} kg

Mass of solvent (w_1) = 0.10 kg

Molar mass of solvent (M_1) = 1.80×10^{-2} kg mol^{-1}

Loss in mass of solution (w_A) = 8.00×10^{-4} kg

Loss in mass of water (w_B) = 2.00×10^{-5} kg

Using Eqs. 12.7 and 12.11,

$$\frac{w_2 M_1}{w_1 M_2} = \frac{w_B}{w_A + w_B}$$

$$M_2 = \frac{w_2 M_1}{w_1} \cdot \frac{w_A + w_B}{w_B} = \frac{5.0 \times 10^{-3}\ \text{kg} \times 1.8 \times 10^{-2}\ \text{kg mol}^{-1} \times 8.20 \times 10^{-4}\ \text{kg}}{0.10\ \text{kg} \times 2.00 \times 10^{-5}\ \text{kg}}$$

$$M_2 = 0.0370\ \text{kg mol}^{-1}$$

7) Molar enthalpy of vaporisation of water at 373 K
= 40.6 kJ mol^{-1}
= 4.06×10^4 J mol^{-1}

Using Eq. 12.21,

$$K_b = \frac{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times (373\ \text{K})^2 \times 1.8 \times 10^{-2}\ \text{kg mol}^{-1}}{4.06 \times 10^4\ \text{J mol}^{-1}}$$

$$= 0.513\ \text{K kg mol}^{-1}$$

$$\text{No. of moles of Glucose} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{5.60 \times 10^{-3}\ \text{kg}}{1.80 \times 10^{-1}\ \text{kg mol}^{-1}}$$

$$= 3.11 \times 10^{-2}\ \text{mol}$$

$$\text{Molality of the solution } (m) = \frac{\text{No. of moles of solute}}{\text{Mass of solvent (kg)}}$$

$$= \frac{3.11 \times 10^{-2}\ \text{mol}}{1.00\ \text{kg}} = 3.11 \times 10^{-2}\ \text{mol kg}^{-1}$$

Using Eq. 12.24,

$$\Delta T_b = K_b m = 0.513\ \text{K kg mol}^{-1} \times 3.11 \times 10^{-2}\ \text{mol kg}^{-1}$$

$$= 0.016\ \text{K}$$

Boiling point of solution = 373 K + 0.016 K = 373.016 K

8) Using Eq. 12.49, we have

$$6.66 \times 10^4 \text{ Pa} \times 1.00 \times 10^{-3} \text{ m}^3 = \frac{4.0 \times 10^{-3} \text{ kg}}{M_2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}$$

$$\text{or } M_2 = \frac{(4.0 \times 10^{-3} \text{ kg})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{6.66 \times 10^4 \text{ Pa} \times 1.00 \times 10^{-3} \text{ m}^3}$$

$$= 0.150 \text{ kg mol}^{-1}.$$

9) Normal molar mass of KCl = 7.45×10^{-2} kg mol^{-1}
Using Eq. 12.37, observed molar mass of KCl

$$= \frac{(1.85 \text{ K kg mol}^{-1}) \times (0.5 \text{ kg})}{(100 \text{ kg})(0.24 \text{ K})}$$

$$= 3.85 \times 10^{-2} \text{ kg mol}^{-1}$$

Using Eq. 12.51, van't Hoff factor,

$$i = \frac{\text{Theoretical molar mass of KCl}}{\text{Observed molar mass of KCl}}$$

$$i = \frac{7.45 \times 10^{-2} \text{ kg mol}^{-1}}{3.85 \times 10^{-2} \text{ kg mol}^{-1}} \quad \text{... (1)}$$

Let x be the degree of dissociation of KCl. Then

$$\begin{array}{ccc} KCl & \rightleftharpoons & K^+ + Cl^- \\ 1-x & & x \quad\quad x \end{array}$$

Total number of moles at equilibrium after dissociation
$= 1-x+x+x = 1+x$

$$\text{van't Hoff factor, } i = \frac{\text{Theoretical molar mass}}{\text{Observed molar mass}} = \frac{1+x}{1} \quad \text{... (2)}$$

From (1) and (2) we have $1 + x = 1.94$

Hence, degree of dissociation, $x = 0.94$.

UNIT 13 PHASE EQUILIBRIA

Structure

13.1 INTRODUCTION

The study of the effect of various parameters such as pressure, temperature or composition on the physical state of chemical substances is the subject matter of phase equilibria. In Unit 9, you have studied the criteria for equilibrium. In unit 14, we shall consider the various aspects of chemical equilibria. In this unit, we shall discuss physical equilibria. This means :

- focussing our attention on the equilibria regarding physical state and
- relating physical equilibria to various parameters such as pressure, temperature and composition using phase rule.

We shall define the terms such as phase, component, degrees of freedom and phase transition. We will deduce phase rule. One component system will be studied in the light of phase rule. Among the two component systems, only solid-liquid and solid-gas systems will be discussed. We have discussed liquid-liquid systems in Units 10 and 11 of this block. Applications of phase equilibria study will also be included in our discussion.

Objectives

After studying this unit, you should be able to:

- define the terms, phase, component and degree of freedom,
- calculate the number of phases, components and degrees of freedom in a system,
- state and deduce the phase rule,
- comment on the stability of the phases of subliming and non-subliming substances,
- explain the two types of phase transitions, and
- apply the phase rule to the study of one component and two component systems.

13.2 DEFINITION OF THE TERMS

In 1876, Gibbs deduced a simple relationship among the number of phases in equilibrium, the number of components and the number of intensive variables known as degrees of freedom. Let us first define the terms phase, component and degrees of freedom.

Phase

Phase (P) is defined as a physically distinct and homogeneous part of the system that is mechanically separable from other parts of the system. The definition as suggested by Gibbs is that a phase is a state of matter that is uniform throughout, not only in chemical composition but also in physical state.

Let us discuss some examples for counting the number of phases in a system.

- A gas or a gaseous mixture is a single phase since there cannot be an interface between one gas and another. Air, for example, is one phase system, although it is a mixture of many gases.

- A system of totally miscible liquids will exist in one phase only as far as the liquid phase is concerned. But since each liquid has its vapour above, the total number of phases in a system of miscible liquids is two, one for the liquid and the other for vapour. These two phases are separated by the surface of the solution in the liquid phase.

- A system of two immiscible liquids has a total of three phases, two for the substances in the liquid state and another for the vapour phase containing vapours of both the liquids.

- A crystal is a single phase. Different solids having different crystal structures constitute different phases, irrespective of the fact whether they have same chemical composition or not. A mixture of graphite and diamond constitutes two phases although both are only allotropic modifications of carbon.

Next we take up the definition of the word, component.

Components

The number of components (C) in a system is the smallest number of substances in terms of which the composition of all the phases in the system can be described separately. The number of components may be smaller than the number of chemical substances that are present in the system.

The definition is easy to apply when the species do not react, for then we simply count their number. For example, phase equilibria containing ice, water and its vapour is a one component system since the composition of each phase can be expressed in terms of the component, H_2O, only. A mixture of ethanol and water is a two component system.

If the species react chemically and are at equilibrium, we have to take into account the significance of the phrase' all the phases' in the above definition. Dissociation of calcium carbonate in a closed vessel is a two component system although at first it may appear to be a three component system, namely, $CaCO_3$, CaO and CO_2.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

You can see that the composition of any one species is related to the other two and the dissociation of calcium carbonate is, therefore, a two component system.

In the case of solid ammonium chloride being heated in a closed vessel, there is an equilibrium between the solid ammonium chloride and its vapour (which consists of ammonia and hydrogen chloride molecules). Since both the phases have the formal composition 'NH_4Cl', it is a one component system. However, if ammonia or hydrogen chloride is added to the system, the system has two components because now the relative amounts of hydrogen chloride and ammonia are not the same.

If there are 'S' substances (may be chemical compounds or ionic species) and 'R' relations (which include equations representing chemical equilibria or charge neutrality) among them, then the number of components (C) can be calculated using the equation,

$$C = S - R \qquad \ldots (13.1)$$

To illustrate this, we can consider two examples. If you consider a solution of glucose in water, there are two substances and hence $S = 2$. But there is no relation between them and so $R = 0$; therefore, $C = 2$ and this is a two component system.

Let us reexamine the equilibrium of solid ammonium chloride with its vapour. Here $S = 3$ since there are three substances, NH_4Cl, NH_3 and HCl. But $R = 2$ since these are two relations as shown below :

(1) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl\ (g)$

(2) Concentration of NH_3 = Concentration of HCl (and both of them are in gaseous phase).

Therefore $C = S - R = 3 - 2 = 1$. This is a one component system. If extra $HCl\ (g)$ is added, then the second relation given above no more holds. That is, $R = 1$ although $S = 3$. This is therefore a two component system, as $C = S - R = 3 - 1 = 2$.

Degrees of Freedom

The number of degrees of freedom (F) or variance of a system is the smallest number of intensive variables such as pressure, temperature and composition which are to be specified to describe the state of the system completely.

- If $F = 0$, the system is invariant and this means none of the intensive variables can be changed.
- In case $F = 1$, the system is univariant and one of the intensive variables can be changed.
- For a bivariant system, F is equal to 2, and two of the intensive variables can be changed.

The phase rule relates the degrees of freedom to the number of phases and the components. Before studying phase rule, let us recapitulate the criteria for equilibrium.

SAQ 1

Calculate the number of phases in the following cases :

a) A closed beaker partially filled with toluene and water;

b) A closed beaker partially filled with acetone and water.

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SAQ 2

Calculate the number of components in the following cases :

a) Dissociation of ammonia in a closed vessel;

b) Dissociation of ammonia in a closed vessel containing nitrogen.

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13.3 CRITERIA FOR EQUILIBRIUM

In unit 9, we have discussed the conditions for equilibrium; the changes in Helmholtz free energy function (at constant volume and temperature) and Gibbs free energy function (at constant pressure and temperature) are zero for a system under equilibrium.

That is, $dA = 0$ and $dG = 0$ . . . (13.2)

Apart from this, the chemical potential of a component must be the same in all the phases at equilibrium. If there are three phases α, β and γ for the component i, then we can write

$$\mu_{i\alpha} = \mu_{i\beta} = \mu_{i\gamma} \qquad \ldots (13.3)$$

The conclusion given in Eq. 13.3 comes from the fact that a substance will tend to pass spontaneously from the phase where it has higher chemical potential to the phase of lower chemical potential. The phase change of a substance would continue till the chemical potentials become equal in all the phases (in which case the resulting system is said to have attained equilibrium). For example, if at any temperature and pressure, ice, water and its vapour are in equilibrium then,

$$\mu_{\text{ice}} = \mu_{\text{water}} = \mu_{\text{vapour}}$$

Normally, a system can attain equilibrium conditions from either direction. For example, the equilibrium between ice and water at 273.15 K and 1.013×10^5 Pa (1 atm) pressure can be attained either by partial melting of ice or partial freezing of water. This is a stable equilibrium. But yet another variety, called metastable equilibrium, also exists which certainly does not represent a condition of stability. To illustrate this, you can consider the case of cooling water slowly and carefully to a temperature of 272 K (or even lower) without the appearance of ice. But starting from ice at a lower temperature, and heating it, it is not possible to have water at 272 K. Thus a metastable equilibrium can be attained from one way only and not by both the ways. A system under metastable equilibrium reverts to stable equilibrium if disturbed even slightly by stirring or by the addition of a phase which is stable under the experimental conditions. Thus water at 272 K on slight stirring or on the addition of a small quantity of ice, begins to solidify and, as temperature rises to 273 K, the conditions of stable equilibrium are established.

13.4 PHASE RULE

In a heterogeneous equilibrium, not influenced by gravitational or electrical or magnetic forces, the number of degrees of freedom (F) of the system is defined by the number of components (C) and the number of phases (P) according to the equation,

$$F = C - P + 2 \qquad \ldots (13.4)$$

Once the values of C and P are known, F can be calculated.

Let us take up some examples to understand Eq. 13.4. In the vaporization equilibrium of water ($C = 1$), there are two phases (liquid and vapour) and hence, $F = C - P + 2 = 1 - 2 + 2 = 1$. That is, specifying pressure or temperature fixes the other. This is all the more understandable from the general statement that at a particular temperature, vapour pressure of a liquid is constant. If all the three phases, ice, water and its vapour, are to be in equilibrium, then $F = 1 - 3 + 2 = 0$; that is, the system is invariant. This means all the three phases of water are in equilibrium only at a fixed temperature and pressure. Any effort to change pressure or temperature results in the disappearance of one of the phases.

Deduction of Phase Rule

Having stated the phase rule, we shall now deduce the same. Consider a system of C components existing in P phases. We want to calculate the number of independent variables or degrees of freedom 'F' in order to define the state of the system completely. The value of F can be given by the following equation also:

$$F = \text{(Total number of variables)} - \text{(number of relations)} \qquad \ldots (13.5)$$

First let us calculate the total number of variables. To define the composition of each phase, it is necessary to define the concentration of $(C-1)$ constituents of that phase. For P phases, the total number of concentration variables is $P(C-1)$ and these, along with two variables, pressure and temperature, constitute the total number of variables.

$$\text{Total number of variables} = P(C-1) + 2 \qquad \ldots (13.6)$$

Regarding the number of relations, we know that for one component existing in three phases α, β and γ, there are two relations,

$$\mu_\alpha = \mu_\beta \text{ and } \mu_\beta = \mu_\gamma$$

The relation $\mu_\alpha = \mu_\gamma$ need not be specified but is understood. As two relations are required for three phases of a component, $(P-1)$ relations are there for P phases of a **component.** Hence, a total number of $C(P-1)$ relations exist for P phases of C components.

$$\text{Number of relations} = C(P-1) \qquad \ldots (13.7)$$

Using Eqs. 13.6 and 13.7 in Eq. 13.5,

$$F = P(C-1) + 2 - C(P-1)$$

$$= PC - P + 2 - PC + C$$

$$\text{i.e., } F = C - P + 2 \qquad \ldots (13.8)$$

Having derived phase rule, we will apply it to various systems. Its application can be seen in the study of phase diagrams. A phase diagram speaks about the stability of various phases at various temperatures, pressures and compositions.

SAQ 3

The four phases of sulphur are rhombic, monoclinic, liquid and vapour. Can all these four phases exist in equilibrium at a particular temperature and pressure?

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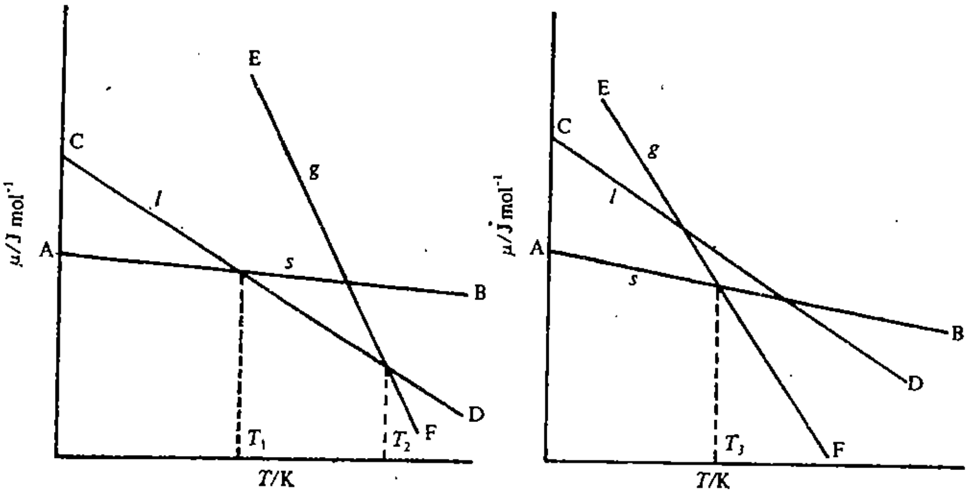
13.5 STABILITY OF THE PHASES OF A PURE SUBSTANCE

The golden rule with reference to phase study is that the phase with the lowest chemical potential is the stable phase. This rule can be used in making inferences from the curves obtained by plotting chemical potential of a pure substance against temperature for each phase. For most of the substances, μ against T plots for solid, liquid and vapour phases are of the type shown in Fig. 13.1 (a).

At the melting point (T_1), the solid curve (AB) and the liquid curve (CD) meet. Similarly, at the boiling point (T_2), the liquid curve (CD) and the vapour curve (EF) meet.

Applying the golden rule given at the beginning of this section, we can infer that for substances exhibiting behaviour of the type represented in Fig. 13.1 (a), solid phase is the stable phase below the melting point. Between melting and boiling points, liquid phase is stable and above boiling point, vapour phase is stable. Evidently this is applicable for non-subliming substances.



(a) (b)

Fig.13.1: μ against T plots at constant pressure: (a) for non-subliming substances; (b) for subliming substances; in both the plots, g, l and s refer to vapour, liquid and solid phase curves.

In the case of subliming substances, μ against T curves are of the type shown in Fig. 13.1 (b). The sublimation temperature (T_3), is the point of intersection between the solid (AB) and the vapour (EF) curves. Hence, below T_3, solid phase is stable and above T_3, the vapour phase is stable.

As per Clapeyron equation studied earlier, we are aware that a decrease in pressure affects melting and boiling points to different extent. If the pressure is reduced sufficiently, the boiling point of a liquid may even fall below the melting point of a solid whereby the substance is said to sublime. Hence the type of μ Vs T curves and the type of stable phases would be decided by the experimental conditions of pressure as well. This explains the fact that above 5.2×10^5 Pa pressure, solid carbon dioxide melts to give a liquid and, below 5.2×10^5 Pa pressure, solid carbon dioxide sublimes.

Clapeyron equation (Eq. 9.49 of Unit 9) gives a quantitative account of the variation of equilibrium temperature with pressure,

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \qquad \text{... (9.49)}$$

This equation could be used for any phase equilibria.

SAQ 4

Fig. 13.1a or b gives μ against T plot of a pure substance at constant pressure. For a substance in a closed system,

$$d\mu = \bar{V}dp - \bar{S}dT.$$

What thermodynamic property of a substance is given by the slope of Fig. 13.1a or b?

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13.6 PHASE TRANSITIONS AND HEAT CAPACITY ANOMALIES

The transition from one phase to another on the change of temperature or pressure or both is generally referred to as phase transition. The phase transitions are of two types. Those phase transitions requiring latent heat for the transition are called first order phase transitions. Typical examples of this category are the conversion of ice to water or water to steam or rhombic sulphur to monoclinic sulphur. During each of these transitions, heat is absorbed but without any observable temperature change. This means that in a first order phase transition, heat capacity, which is the ratio of heat absorbed to temperature change, is infinitely large.

The other variety, second order phase transition, does not require any latent heat. As a result, during the transition, heat capacity also changes through a finite amount only. Typical examples for second order phase transitions are in the conducting — superconducting transformations. During this transition, material loses electrical resistance. Lead, indium and titanium etc undergo transition of this type. In the following sections, we discuss the application of the phase rule to one and two component systems which are instances of first order phase transition.

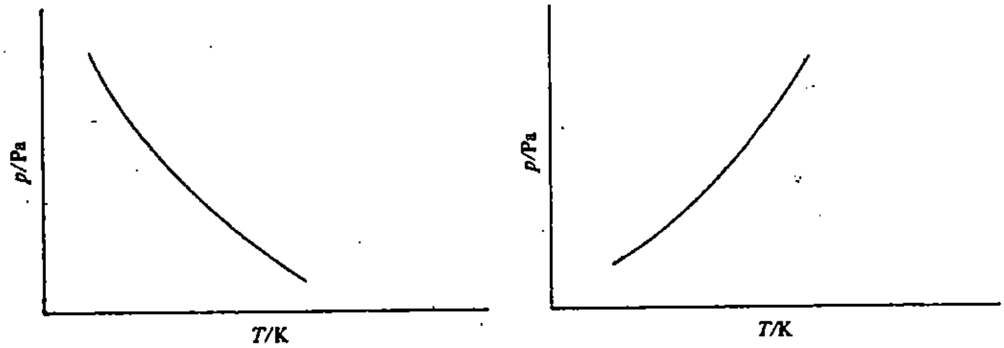
13.7 APPLICATION OF PHASE RULE TO ONE COMPONENT SYSTEMS

Application of phase rule (Eq. 13.8) to one component system leads to the general expression,

$$F = 1 - P + 2 = 3 - P \qquad \ldots (13.9)$$

Hence, a maximum of three phases can be present at a point in this case. It is called a triple point and the system is invariant ($F = 0$).

For one component system, p against T plot is quite convenient. Then, $\mathrm{d}p/\mathrm{d}T$ gives the slope of the plot. For each equilibrium, this is defined by Clapeyron equation (Eq. 9.49). If $\mathrm{d}p/\mathrm{d}T$ is negative, you can expect that as temperature increases ($\mathrm{d}T$ = positive), pressure would decrease ($\mathrm{d}p$ = negative) and the curve is of the type shown in Fig. 13.2(a). But if $\frac{\mathrm{d}p}{\mathrm{d}T}$ is positive, then an increase in temperature ($\mathrm{d}T$ = positive) causes an increase in pressure also ($\mathrm{d}p$ = positive), as shown in Fig. 13.2(b).



(a) (b)

Fig. 13.2: Types of p against T plots: (a) $\frac{\mathrm{d}p}{\mathrm{d}T}$ is negative; b) $\frac{\mathrm{d}p}{\mathrm{d}T}$ is positive.

You can calculate $\mathrm{d}p/\mathrm{d}T$ using Clapeyron equation once ΔH and ΔV are known. Normally to calculate the change in molar volume of a substance between two phases α, and β, densities of the phases (d_α and d_β) and the molar mass (M) of the substance are used.

$$\Delta V = V_\beta - V_\alpha = \left(\frac{M}{d_\beta} - \frac{M}{d_\alpha}\right) = M\left(\frac{1}{d_\beta} - \frac{1}{d_\alpha}\right) \qquad \ldots (13.10)$$

The p against T plots for various phases are made by measuring the equilibrium temperatures corresponding to various pressures. Let us now study the phase diagram of water.

Phase Diagram of Water

The phase diagram for water is given in Fig. 13.3. It would be interesting to apply Clapeyron equation (Eq. 9.49) and phase rule (Eq. 13.8) to this phase equilibria.

Let us first apply Clapeyron equation to the following three equilibria:

i) Fusion (ice ⟶ water)

ii) Vaporization (water ⟶ vapour)

iii) Sublimation (ice ⟶ vapour)

For all the above transitions, ΔH is positive. Ice floats on water and this means, density of water is more than that of ice and the molar volume of ice is more than that of water. Again, when a small quantity of water is heated, steam comes out in large volume. Thus the molar volume of steam is more than that of liquid water. Similarly, molar volume of steam is larger than that of ice. We use V to represent the molar volume of a particular phase.

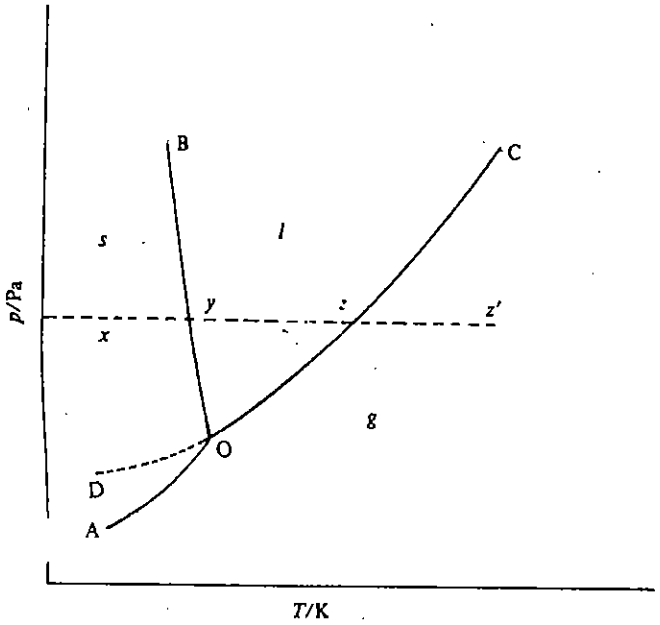


Fig. 13.3: Phase diagram of water; s, l and g stand for solid, liquid and vapour phases.

Using the above ideas, $\frac{dp}{dT}$ values for the three equilibria can be calculated. Note that the temperatures are all positive.

$$\text{Fusion: } \frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{(+ve)}{(+ve)\,(-ve)} = (-ve) \qquad \ldots (13.11)$$

$$\text{Vaporization: } \frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{(+ve)}{(+ve)\,(+ve)} = (+ve) \qquad \ldots (13.12)$$

$$\text{Sublimation: } \frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{(+ve)}{(+ve)\,(+ve)} = (+ve) \qquad \ldots (13.13)$$

Eq. 13.11 shows a negative slope for the p against T plot for fusion, and the curve OB, the fusion curve of ice, illustrates this. Eqs. 13.12 and 13.13 indicate positive slopes. The vaporization curve of water (OC) and the sublimation curve of ice (AO) bear testimony to this. In short, the increase of pressure depresses the melting point of ice, whereas the boiling point of water and sublimation temperature of ice are increased. Also the sublimation curve (AO) has a steeper slope than the vaporization curve (OC) since near the point O,

$$\Delta H_{\text{sublimation}} = \Delta H_{\text{vaporization}} + \Delta H_{\text{fusion}}.$$

Although ice exists in various crystalline modifications at high pressures, they have not been shown in Fig. 13.3 for simplicity.

$\Delta V_{\text{fusion}} = V_{\text{water}} - V_{\text{ice}} =$ negative
$\Delta V_{\text{vaporization}} = V_{\text{vapour}} - V_{\text{water}} =$ positive
$\Delta V_{\text{sublimation}} = V_{\text{vapour}} - V_{\text{ice}} =$ positive

The decrease of melting point of ice with increase of pressure has an interesting application in winter sports. In ice-skating, for example, there is a bladelike metal frame attached to the shoes of the skater. This arrangement ensures minimum area of contact between the skater and ice surface. Because of this, there is a high pressure exerted on the ice surface on which the skater stands and moves. At this increased pressure, the melting point of ice is much low. Hence ice melts and provides a lubricating layer of water which speeds up the skater's movement.

Application of Phase Rule to Curves

Let us now apply phase rule, $F = 3 - P$ to these three curves. Since along each curve, there are two phases in equilibrium, $P = 2$ and $F = 3 - 2 = 1$. That is, the mention of temperature or pressure automatically fixes the value of the other parameter when two phases are in equilibrium. The curve OD is the vapour pressure curve of metastable water. You may be interested to know that water, if cooled very carefully, may exist in the liquid state even below freezing temperature. Water is then said to be supercooled. It is in a metastable equilibrium with its vapour under these conditions. The p against T relationship of this metastable equilibrium is given by the dotted curve OD. The curve OD is above OA signifying that the metastable system has a higher vapour pressure than the stable one at the same temperature. Slight stirring or addition of ice to water in metastable equilibrium results in the commencement of solidification of water and return to stable equilibrium. The curve OC terminates at C, the critical temperature, above which a substance exists only as a gas.

Application of Phase Rule to Areas in the Diagram

Inside the area AOB, ice is the stable phase, whereas in the regions BOC and AOC, the stable phases are water and vapour, respectively. Application of phase rule requires ($F = 3 - 1 = 2$) two degrees of freedom, namely, precise specification of both temperature and pressure to specify a point.

Triple Point

The point O is called the triple point and all the three phases coexist at this pressure and temperature (273.16 K and 610 Pa). This is an invariant point, since $F = 3 - 3 = 0$ and the change of temperature or pressure causes the disappearance of one of the phases.

Let us utilise the phase diagram in understanding the changes taking place when ice at atmospheric pressure (approximately 10^5 Pa) and below 273.15 K, as represented by the point x, is heated. At 273.15 K, ice begins to melt and this is indicated by the point y. The temperature remains constant till fusion is complete. Again the temperature increases and at a point z (373.15 K), there is equilibrium between water and vapour. Once again temperature remains constant till vaporization is complete. After this, again the temperature increases, and at a point z', it is in the form of steam completely. So far, we studied the phase diagram of water. Let us now study the phase diagram of sulphur.

The Phase Diagram of Sulphur

The phase diagram of sulphur (Fig. 13.4) is interesting due to the phase transition curves of the two allotropic modifications, and the presence of a metastable triple point.

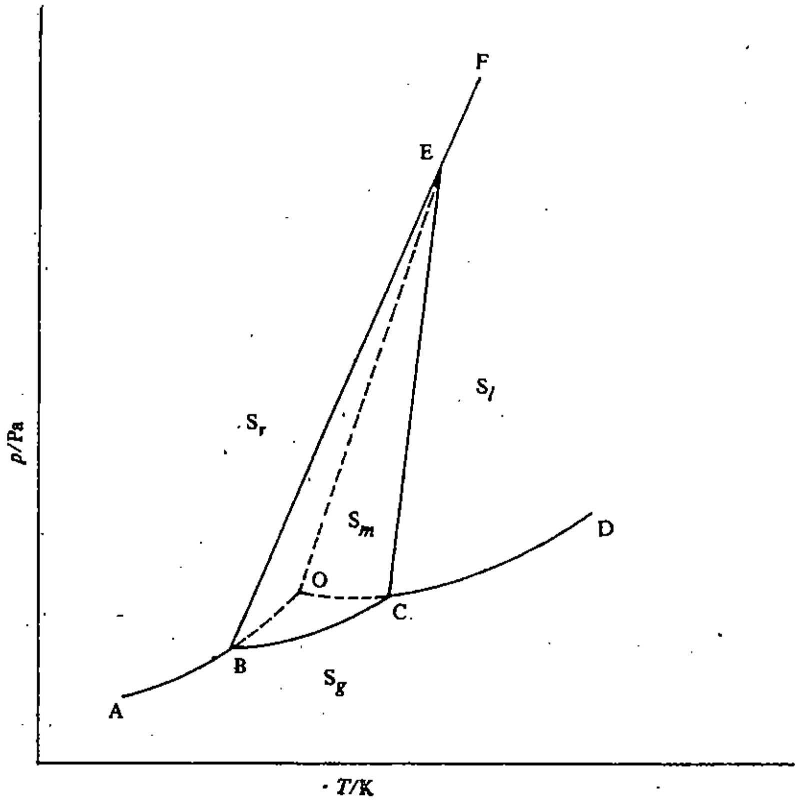


Fig. 13.4: Phase diagram of sulphur; S_r, S_m, S_l and S_g refer to rhombic, monoclinic, liquid and vapour phases of sulphur.

The stable form of sulphur at ordinary temperatures and under one atmosphere pressure is rhombic sulphur. If rhombic sulphur is heated, it slowly transforms to solid monoclinic sulphur at 368.6 K. Above 368.6 K, monoclinic sulphur is stable and it melts at 392.2 K to give liquid sulphur which is stable upto its boiling point (717.8 K). The transformation of one crystalline modification to another is often very slow and, if rhombic sulphur is heated quickly to 387.2 K, it melts. The curve BO represents the metastable equilibrium, between rhombic sulphur and sulphur vapour. Likewise, if liquid sulphur is allowed to cool quickly, monoclinic sulphur may not separate out at C, and CO represents metastable equilibrium between liquid and vapour forms of sulphur. The curve OE is the fusion curve of rhombic sulphur and it again represents metastable equilibrium.

The curves AB and BC are the sublimation curves of rhombic and monoclinic forms. BE represents the transition from rhombic to monoclinic form. CE and EF are the fusion curves of monoclinic and rhombic forms. CD is the vapour pressure curve of liquid sulphur.

Application of Clapeyron equation to various equilibria mentioned above indicates that for all these changes (from left to right in every case in Fig. 13.4), the change in enthalpy and molar volume are positive although the magnitudes are different. Hence the slopes $\frac{\mathrm{d}p}{\mathrm{d}T}$ (as given by $\frac{\Delta H}{T\Delta V}$) are positive for all the curves. This indicates that for all the transitions (from left to right in Fig. 13.4), the equilibrium temperatures increase with pressure. Application of phase rule to these curves gives $F = 3 - P = 3 - 2 = 1$, which means that specification of temperature or pressure is sufficient to define the equilibrium along each of the curves.

In the regions ABE, BEC, ECD and below ABCD, only one phase is stable and hence $F = 3 - 1 = 2$. That is, within the above regions, both pressure and temperature are to be specified to define any point.

There are four triple points corresponding to three stable equilibria and one metastable equilibria. The phases under equilibrium in each of these triple points is given in Table 13.1. In this table, B, C, E and O stand for the points specified in Fig. 13.4. Also S_r, S_m, S_l and S_g stand for rhombic, monoclinic, liquid and vapour forms of sulphur.

Table 13.1: Triple points in the Phase Diagram of Sulphur

At	Phases under equilibrium
B	S_r, S_m and S_g
C	S_m, S_l and S_g
E	S_r, S_m and S_l
O	S_r, S_l and S_g (metastable)

The application of phase rule to these triple points indicates that the system is invariant ($P = 3$ and $F = 3 - 3 = 0$). In this section, we applied the phase rule to one component systems. In the next section, we shall take up the study of two component systems.

SAQ 5

The phase diagram of carbon dioxide is given in Fig. 13.5.

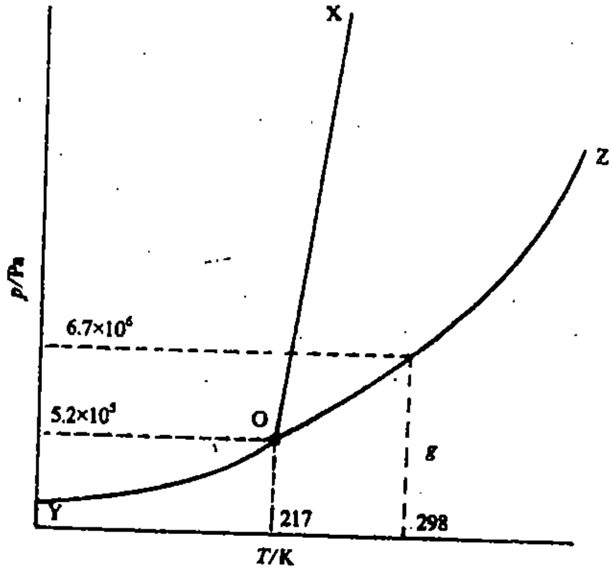


Fig. 13.5: Phase diagram of carbon dioxide; *s*, *l* and *g* stand for solid, liquid and vapour phases.

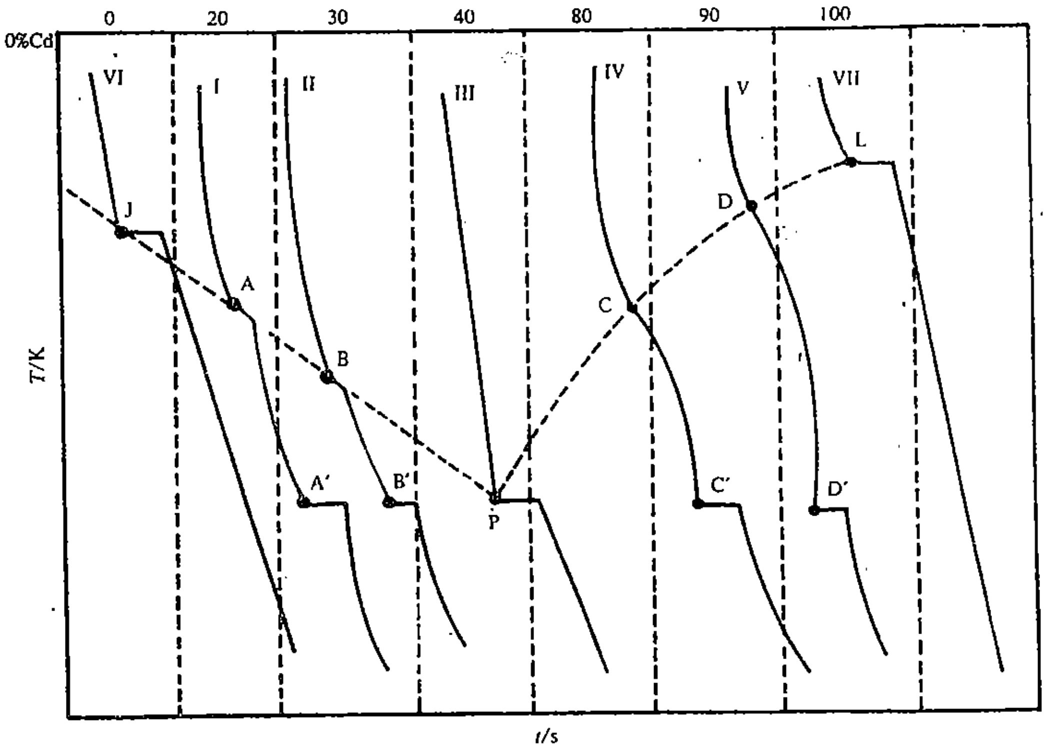


Fig. 13.8: Cooling curves for Bi—Cd system.

mixture of Bi and Cd. The word 'eutectic' in Greek means easily melted. At temperatures below 413.2 K, the system is completely a solid. Although eutectic mixture contains both metals in a definite ratio, it is not a compound, as under a microscope, the presence of two different crystals can be seen.

The significance of the phase digaram can be understood by considering the cooling curve pattern of several mixtures of Bi and Cd (Fig. 13.8). On cooling a 20% solution of Cd (curve I) in Bi, the temperature drops gradually and on reaching the point A. solid Bi begins to separate. During crystallisation, heat equivalent to the enthalpy of fusion of bismuth, is released. Because of this, there is a break in the curve at the point A. Along AA′, more and more solid Bi separates and the remaining liquid melt becomes richer in Cd. At A′, the eutectic mixture separates, and due to the presence of three phases, temperature remains constant. This corresponds to the horizontal portion of the curve. Once the liquid is completely solidified into the eutectic mixture, cooling proceeds smoothly again. The curve II represents a cooling of 30% Cd melt. The only difference between I and II is that solid Bi appears at a still lower temperature B. Again, at B′, there is a halt signifying the separation of the eutectic mixture. If a melt containing 40% Cd is cooled (curve III), there is no break in the curve; but a halt is seen at 413.2 K indicating the crystallisation of the eutectic mixture. Curve IV represents cooling of 80% Cd solution and the cooling curve experiences a break at C representing the separation of solid Cd, while the remaining melt approaches the eutectic composition. At C′, the eutectic mixture solidifies which is again marked by a halt in the cooling curve. Curve V is a cooling curve for 90% Cd solution, having a break at D and a halt at D′. The curves VI and VII represent the cooling curves of pure bismuth and cadmium liquids, respectively. Both the curves VI and VII correspond to one component systems and hence there is a halt in these curves where solid bismuth (at J) or solid cadmium (at L) begin to separate. From the cooling curves I to VII, the temperatures at J, A, B, P, L, D and C, corresponding to the different compositions of bismuth and cadmium, are noted and used in the plot of temperature against composition given in Fig. 13.7.

Apart from Bi—Cd system, there are many other examples such as Al—Sn, Sn—Pb, Ag—Pb, etc., which form eutectic mixtures. Eutectic systems have many practical applications.

- Solder which is used for joining electrical components is an eutectic mixture consisting of 67% by weight tin and 33% by weight lead.
- Pattinson's process of extracting silver from a lead—silver alloy containing even a

low percentage of silver also makes use of the eutectic formation principle. A solid lead—silver alloy containing a low percentage (say, 1%) of silver is heated above its melting point and slowly cooled. When the temperature reaches 600 K lead separates out as solid which can be removed from the melt. The melt continuously becomes richer in silver. At 576 K, eutectic mixture containing 2.6% silver solidifies from which silver can be extracted.

- The eutectics formed by salt—water system are used as freezing mixtures. We shall shortly study this in detail.

It is worth pointing out that the formation of compounds and of solid solutions are also known in the solid—liquid equilibria of two component systems. But the studies are quite similar to eutectic systems, although individual phase diagrams differ considerably.

Salt—Water System

Salt-water system can belong to one of the following types:
i) Eutectic type (Example: $KI—H_2O$)
ii) Compound formation (Example: $Na_2SO_4—H_2O$)

As an illustration of salt—water system, we discuss $KI—H_2O$ system for which the phase diagram is given in Fig. 13.9. The curve AB is the fusion curve of ice. The addition of KI to ice depresses the melting point of ice. BC is the solubility curve of KI. You can see that the curve BC does not extent upto the melting point of pure KI since it is quite above the critical temperature of water. Both the curves meet at B, the eutectic point (250.2 K) of this system. It is the lowest temperature that can be attained by the addition of KI to ice.

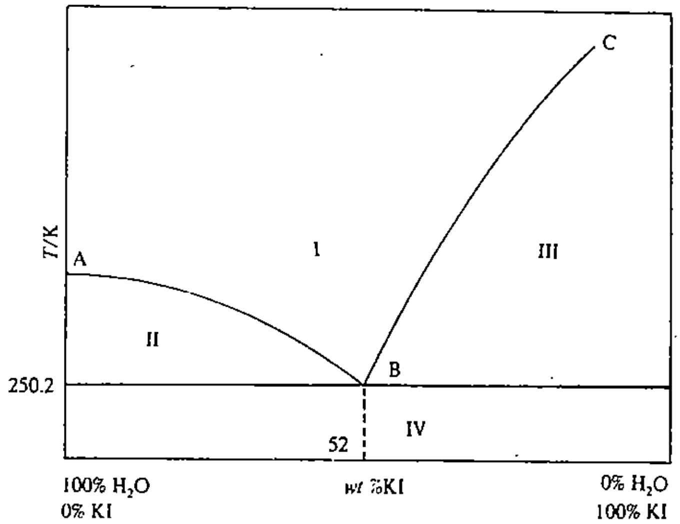


Fig. 13.9 : $KI—H_2O$ system:
I) Solution;
II) Solution + ice;
III) Solution + KI;
IV) KI + ice.

One of the applications of salt-water system is in the preparation of freezing mixtures. When salt is added to ice under adiabatic conditions (i.e., to ice in vacuum flask), ice melts. In doing so, it absorbs heat from the rest of the mixture. The temperature falls and, if enough salt is added, cooling continues down to the eutectic temperature.

In Table 13.2, eutectic temperature and eutectic composition of various ice—salt systems are given.

Table 13.2: Eutectic temperature of Freezing Mixtures

Name of the system	% Salt in the eutectic	(Eutectic temperature)/K
NH_4NO_3—ice	43.0	255.2
NH_4Cl—ice	19.7	257.8
$NaNO_3$—ice	33.3	255.1
KI—ice	52.0	250.2
$NaCl.2H_2O$—ice	23.0	252.1

Another application of salt-ice equilibrium is in the clearance of ice blocked roads in the cold countries. If for example, the temperature in that region is above 252 K, the spreading of a large quantity of common salt (more than corresponding to eutectic composition) on the road covered with ice helps melting the ice. The heat for melting the ice is readily available from the surrounding atmosphere of the ice-covered road. Hence, melting takes place without a decrease in temperature.

SAQ 6

Silver and lead form an eutectic with 2.6% by weight silver. The eutectic temperature is 576 K. The melting points of lead and silver are 600 K and 1243 K. Draw the phase diagram of Pb—Ag system on a rough scale and mark the stable phases in various regions. Explain the changes that would occur if melt containing 60% silver is cooled.

....

....

....

13.9 APPLICATION OF PHASE RULE TO SOLID-GAS EQUILIBRIA

A simple example of gas-solid equilibrium which involves compound formation is the reaction between solid calcium oxide and gaseous carbon dioxide yielding calcium carbonate.

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$$

The application of phase rule to this equilibrium gives $F = 2 - 3 + 2 = 1$; this means, fixation of temperature fixes equilibrium pressure of carbon dioxide. In Unit 14 of Block IV of this course, we will arrive at the conclusion that at constant temperature, the equilibrium pressure of carbon dioxide, also known as dissociation pressure, is constant for the above system.

It is interesting to study using Fig. 13.10 as to what happens when carbon dioxide is steadily admitted into a closed space containing calcium oxide at constant temperature. No reaction will occur until the pressure of the gas has risen to the dissociation pressure value at that temperature. At this pressure, the combination takes place and the pressure remains constant until all the calcium oxide has been converted to calcium carbonate. After this, pressure will rise again.

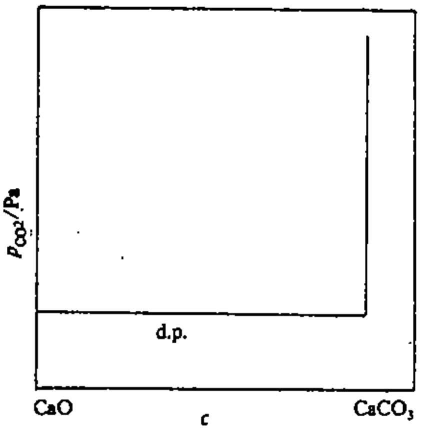


Fig. 13.10: $CaCO_3$—CaO—CO_2 system; d.p. stands for dissociation pressure; p_{CO_2} stands for the pressure of CO_2 c the composition.

Similarly, starting from calcium carbonate kept in presence of carbon dioxide at a high pressure, let us decrease the pressure gradually. No dissociation takes place till the pressure reaches its dissociation pressure value at the temperature. Once this value is reached, the dissociation of calcium carbonate starts and the pressure remains constant. After complete dissociation of calcium carbonate to calcium oxide, pressure of carbon dioxide can be decreased again.

13.10 SUMMARY

In this unit, we have explained the terms phase, component and degree of freedom and derived the phase rule. The phase rule has then been applied to phase equilibria of one and two component systems. This unit helps us in understanding the influence of parameters like pressure, temperature and composition on the phase equilibria of substances. Some of the practical applications of such studies have also been explained.

13.11 TERMINAL QUESTIONS

1) Examine the following statements and write 'true' for the correct ones and 'false' for the wrong ones :
   a) The number of phases of a mixture of three gases enclosed in a container is 3.
   b) The number of phases of a mixture of ethyl alcohol and water is 2.
   c) The equilibrium point among ice, water and vapour is called eutectic point.
   d) The number of phases present in a vessel half filled with water is 1.
   e) The melting point of ice decreases with increasing pressure.
2) Fill in the blanks :
   a) The equilibrium between liquid water and vapour below 273 K is an example for a ..
   ....
   b) In a one component system, maximum number of phases that can coexist in a true equilibrium is ....
   c) Boiling point of water .... with increase in pressure.
   d) A phase transition requiring latent heat is called .... phase transition.
   e) A melt of eutectic composition when cooled shows only a .... in the cooling curve.
3) Suggest some applications of eutectic system studies.
4) Rice, dal and vegetables are cooked faster inside a pressure cooker than in an open vessel. Explain the reason.
5) If solid ammonium chloride is allowed to dissociate in a vessel already containing some ammonia, calculate the value of F.
6) Using Fig. 13.9, identify the solids that will come out in sequence if, the following solutions are cooled from 298 K to 250.2 K :
   a) 20% KI solution
   b) 60% KI solution
   c) 52% KI solution.
7) Calculate the slope $\frac{dp}{dT}$ of the fusion curve of ice near its melting point, if the enthalpy of fusion ice is 6.003×10^3 J mol^{-1}, the densities of water and ice are 999.8 and 916.8 kg m^{-3} and the normal melting point of ice is 273.15 K.
8) Calculate the number of components in the following system :
   a) Sugar in water
   b) Potassium chloride in water.

13.12 ANSWERS

Self-Assessment Questions

1) a) 3 (two due to toluene and water liquids which are immiscible and, one due to their vapours)

   b) 2 (since acetone and water are miscible).

2) a) $C = 1$ as per Eq. 13.1, since $S = 3$ and $R = 2$.
   b) $C = 2$, since $S = 3$ and $R = 1$.

3) The four phases of sulphur cannot coexist since then $F = -1$.

4) $\left(\frac{\partial \mu}{\partial T}\right)_p = -\bar{S}$ for a closed system, hence the slope of Fig. 13.1a or b gives the partial molar entropy of a substance with the sign inverted.

5) a) Sublimation curve
   b) The point O corresponding to pressure 5.2×10^5 Pa and temperature 217 K.
   c) Liquid and vapour.

6)

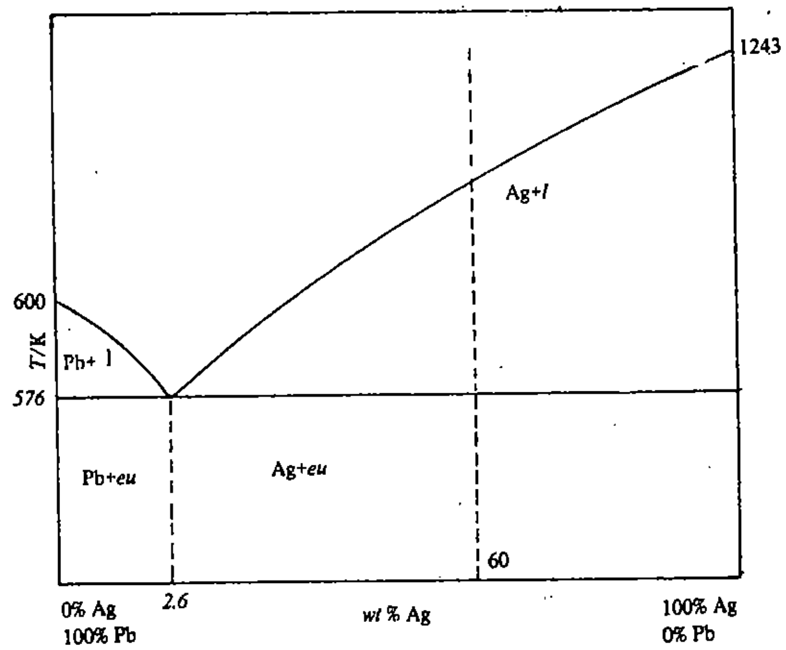


Fig. 13.11 : Ag-Pb System; *l* stands for melt and *eu* stands for eutectic.

When a melt containing 60% Ag is cooled, first the temperature decreases gradually. Then solid Ag starts forming and there is a break in the cooling rate. Once the remaining melt reaches 2.6% Ag composition, the whole mass begins to solidify and the temperature is constant till the solidification is complete. After that, the temperature decreases again.

Terminal Questions

1) a) False b) True
   c) False d) False
   e) True.

2) a) metastable equilibrium
   b) 3
   c) increases
   d) first order
   e) halt.

3) See Sec. 13.8.

4) Increase of pressure inside the closed cooker causes an increase in the boiling point of water. Due to higher temperature thus obtained, the cooking is faster inside the pressure cooker. In an open vessel, the boiling point of water is 373 K and the temperature is not enough for fast cooking.

5) $C = 2$, $P = 2$ and $F = 2$.

6) a) First ice separates and finally a mixture of ice and KI solidifies
   b) First KI separates and finally a mixture of ice and KI solidifies
   c) A mixture of KI and ice separates together at 250.2 K.

7) Using Eq. 13.10 and Eq. 9.49 we get.

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{TM\left(\frac{1}{d_{\text{water}}} - \frac{1}{d_{\text{ice}}}\right)}$$

Where $\Delta H = 6.003 \times 10^3$ J mol^{-1}
$T = 273.15$ K
$M = 0.018$ kg mol^{-1}
$d_{water} = 999.8$ kg m^{-3}
$d_{ice} = 916.8$ kg m^{-3}
Slope $dp/dT = -1.34 \times 10^7$ Pa K^{-1}

8) a) Using Eq. 13.1, $C = 2$, since $S = 2$ and $R = 0$

b) The solution contains three species, water molecules, K^+ ions and Cl^- ions. Hence $S = 3$. But $[K^+] = [Cl^-]$.
$R = 1$ and $C = 3 - 1 = 2$.

NOTES

Uttar Pradesh Rajarshi Tandon
Open University

UGCHE-04
Physical Chemistry

Block

4

CHEMICAL EQUILIBRIA AND ELECTROCHEMISTRY

CHEMICAL EQUILIBRIA AND ELECTROCHEMISTRY

In Block 2, we discussed the criteria for equilibria and spontaneity which are applicable to any system. In Block 3, we explained some aspects of physical equilibrium. In this block, we shall apply the principles of thermodynamics to the study of chemical equilibria, ionic equilibria, electrochemical cells and electrolytic cells.

In Unit 14, we shall discuss the main features of chemical equilibrium. We will derive the expressions for equilibrium constants using thermodynamics. We shall explain Le Chatelier's principle and its applications. In Unit 15, we will discuss ionic equilibria. We will derive expressions for the calculation of dissociation constants of acids and bases, the hydrolysis constants of salts and the solubility product constants of sparingly soluble salts.

In Unit 16, we shall explain Faraday's laws of electrolysis and Kohlrausch's law of independent mobility of ions. We will discuss the application of conductance measurements. In Unit 17, we shall explain the importance of single electrode potential values. We will derive Nernst equation. We shall also study the applications of emf measurements.

After studying this block, you should be able to :

- derive expressions for calculating the equilibrium constant in terms of partial pressure, mole fraction and concentration,
- state Le Chatelier's principle and explain its applications,
- define acids and bases on the basis of different concepts,
- calculate dissociation constants of weak acids and weak bases, hydrolysis constants and solubility product constants of salts,
- explain the applications of conductance measurements,
- calculate the cell potential for an electrochemical cell, and
- describe the applications of emf measurements.

UNIT 14 CHEMICAL EQUILIBRIA

Structure

14.1 INTRODUCTION

Three important aspects of a chemical reaction must be studied for a complete understanding of the subject. These are: (i) whether a chemical reaction is feasible at all (the feasibility of the reactions has already been dealt with in Unit 9 of this course) (ii) if the reaction is feasible, at what stage does it stop, and (iii) how fast or slow does the reaction occur. This last aspect we shall be studying under the heading of chemical kinetics in Unit 18. The present unit describes the second aspect of a chemical reaction i.e. upto what stage does a reaction proceed.

We have already defined, in general, the reversible and irreversible processes in Unit 9. However, for chemical reactions, the two processes can be defined as follows. Irreversible reactions are said to go to completion, implying thereby that the reaction proceeds until at least one of the reactants is completely used up. On the other hand, all those reactions which appear not to proceed beyond a certain stage after sometime even when the reactants are still available, are reversible reactions. They have only reached an equilibrium state. The present unit discusses the meaning of this state of equilibrium and how the equilibrium composition of the reactants and products are correlated with change in Gibb's free energy. It also explains the effects of different factors on chemical equilibrium.

Objectives

After studying this unit, you should be able to :

- describe chemical equilibrium,
- differentiate between reversible and irreversible reactions,
- derive an expression for equilibrium constant in terms of Gibb's free energy;
- express the equilibrium constant in different ways and apply it to different systems, and
- predict the shift in equilibrium position with the changes in the concentration, temperature or pressure of the system.

14.2 REVERSIBLE AND IRREVERSIBLE REACTIONS

In general, chemical reactions can be divided into two types — reversible and irreversible. The reversible reactions are those in which the products can combine back to form the reactants. However, in the irreversible reactions, the same reactants cannot be formed back from the products under normal/set of experimental conditions. For the study of equilibrium, we are mainly concerned with reversible reactions, The idea of reversibility of chemical reactions was first realised by Berthollet in 1799. He was trying to explain the cause for substantial amount of deposits of sodium carbonate around some salt lakes of Egypt. He proposed that these deposits are formed due to high concentration of sodium chloride in lake water which reacted with the carbonates present on the shores. Normally, in a laboratory experiment, we find that calcium carbonate is precipitated by the reaction of sodium carbonate with calcium chloride as represented by the equation :

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 \downarrow + 2NaCl$$

What Berthollet proposed was indeed a reverse reaction of the above and the cause for reversibility was in some way connected to the high concentration of dissolved sodium chloride.

Thus, we realise that a chemical reaction such as given above can proceed in both the directions—from left to right or vice-versa—depending on the experimental conditions. Each such reaction is usually written containing two half-arrows pointing in opposite directions (or a sign of equality between reactants and products) emphasising the fact that it is a reversible reaction :

$$Na_2CO_3 + CaCl_2 \rightleftharpoons CaCO_3 + 2NaCl$$

Further studies by Berthelot and Gilles, in 1863, on the reaction between acetic acid and ethyl alcohol giving ester and water, showed that the amount of ester formed varied with the initial concentrations of the reactants at a fixed temperature and pressure.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

In 1864, Guldberg and Wagge showed experimentally that there exists an equilibrium between the reactants and products in a chemical reaction and that this equilibrium can be reached from either direction (starting either from reactants or the products). Furthermore, the relation between the concentrations of the reactants and the products can be expressed by a simple mathematical expression. Let us consider two reactions to clarify these points.

van't Hoff, in 1877, studied the hydrolysis of ethyl acetate.

$$\underset{\text{Ester}}{CH_3COOC_2H_5} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Acid}}{CH_3COOH} + \underset{\text{Alcohol}}{C_2H_5OH}$$

He observed that the ratio of the product of concentrations of the **products** to the product of concentrations of the **reactants** is always constant at equilibrium and is independent of the initial concentrations of the ester. Expressed mathematically,

$$K = \frac{c_{C_2H_5OH} \times c_{CH_3COOH}}{c_{CH_3COOC_2H_5} \times c_{H_2O}}$$

where 'c' represents concentration of a species which is written as subscript.

The constant, K, in the above expression has a fixed value for a particular reaction at a constant temperature and pressure and is a measure of the extent of reaction. A large value of K means numerator is greater than the denominator. This indicates the presence of a larger concentration of products as compared to the concentration of reactants at equilibrium

Consider another example of the reaction involving hydrogen, iodine and hydrogen iodide, all in the gaseous state. If hydrogen and iodine are kept together in a closed vessel at 723 K, they react chemically to give hydrogen iodide. However, if pure hydrogen iodide is taken in a closed vessel and heated to the same temperature of 723 K, it decomposes to give hydrogen and iodine.

Equilibrium is said to be reached if there is no further change in the concentration of reactants and products with respect to time.

The true state of affairs is that, in both cases, after a sufficiently long time, you would find all the three species, hydrogen, iodine and hydrogen iodide—present in the container. At this stage, we say that an equilibrium has been reached between the reactants and the products as shown by the equation, $H_2 + I_2 = 2HI$. Furthermore, at equilibrium, there exists a definite relationship between the concentrations of hydrogen iodide, hydrogen and iodine.

This state of chemical equilibrium can be viewed from a different point of view. The reaction between the two reactants, A and B, to give products, C and D, can be represented as follows :

$$A + B \rightleftharpoons C + D$$

Initially, there are only A and B present but as the reaction proceeds, some amount of C and D are formed. Once the products C and D are formed, they can also react to give A and B, if the reaction is reversible. Since, the concentration of C and D are small in the beginning, it seems logical that the rate of the reverse reaction, $C + D \longrightarrow A + B$, should also be less than the rate of the forward reaction, $A + B \longrightarrow C + D$. However, as the reaction proceeds, more and more of C and D are produced. Consequently, the rate of the reverse reaction would also increase. Ultimately, a situation would be reached when the rate of the reverse reaction would be exactly equal to that of the forward reaction. Since, these are reactions in opposite directions, there is no change in composition with time and it seems as if the reaction has stopped. We then say that the reacting system is in the equilibrium state. Actually the reactions in both directions do take place but rates of forward and reverse reactions are equal. It is said that a state of dynamic equilibrium has been reached. At this stage, no further change in the concentrations of the products and reactants will take place.

Based on such observations, Guldberg and Wagge gave a quantitative formulation known as the law of mass action. This law gives the relationship between equilibrium concentrations of all the substances taking part in a chemical reaction at equilibrium. Instead of just stating this law, we shall derive this relationship with the help of basic principles of thermodynamics.

14.3 DERIVATION OF GENERAL EXPRESSION FOR CHEMICAL EQUILIBRIUM

Even before derivation of equilibrium expression is attempted, we must recapitulate the following conventions in thermodynamics.

1) Any system, to which substances are added or from which they are taken away or in which a chemical reaction takes place, is called an open system.
2) A chemical reaction involving a number of substances is represented by

$$\sum_i \nu_i A_i = 0$$

Where A_i represents a chemical substance at the temperature and pressure of the reaction, and ν_i is called the stoichiometric coefficient of A_i.

ν values are positive for the products and negative for the reactants. This relationship can be explained using the following example :

$$H_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons H_2O(l)$$

can be written as

$$(1)\,H_2O - (1)\,H_2 - \left(\frac{1}{2}\right)O_2 = 0$$

and the values of ν's are :

$$\nu_{H_2O} = 1,\ \nu_{H_2} = -1,\text{ and } \nu_{O_2} = -\frac{1}{2}$$

Again, note that ν is positive for the products, and negative for the reactants.

Let us now consider an open system represented by a general reaction :

$$aA + bB + cC \ldots \rightleftharpoons pP + qQ + rR \ldots \qquad \ldots (14.1)$$

The change in Gibb's free energy, dG, for the reaction is given by Eqs. 9.21, 9.23, 9.68 and 9.69.

$$dG = V dp - S dT + \sum_i \mu_i dn_i \qquad \ldots (14.2)$$

where dn_i = change in the amount of any particular substance, 'i' and μ_i = chemical potential of that substance; all other symbols carry their usual meaning. At constant temperature and pressure, Eq. 14.2 reduces to :

$$dG_{T,P} = \sum_i \mu_i\, dn_i \qquad \ldots (14.3)$$

The symbol $\sum_i$ stands for summation of terms; the terms are obtained by giving different values to i.

As per Eq. 9.68 given in Sec. 9.10 of Unit 9 of this course,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,N} dT + \left(\frac{\partial G}{\partial p}\right)_{T,N} dp + \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_1} dn_2$$

Using Eqs. 9.21, 9.23 and 9.69, this expression can be written as;

$$dG = -S dT + V dp + \mu_1 dn_1 + \mu_2 dn_2$$

Eq. 14.2 is a generalised form of the above equation.

The change in the amount of any substance 'dn_i' can be more conveniently expressed in terms of another quantity ξ_i (pronounced as "xi") which is a measure of the extent of the reaction. For example, $\xi = 0$ for a substance 'i' means that it has not reacted at all; $\xi = 1$ means whole amount of 'i' has reacted and so on. For any reversible reaction the value of ξ should be between zero and unity.

Let us now derive an expression to specify the variation of free energy with respect to the extent of reaction. The number of moles (n_i) of a particular substance i present at different times, as a reaction proceeds, can be expressed by the relation :

$$n_i = n_i^o + \nu_i \xi \qquad \text{... (14.4)}$$

where n_i is the number of moles of the substance i present before the reaction starts, ν_i is the stoichiometric coefficient of the same substance in the balanced chemical equation (with a proper sign) and ξ is the extent of the reaction. Note that n_i^o and ν_i are constants for a substance while n_i varies as ξ changes. The change in n_i can be obtained by differentiating Eq. 14.4 as,

$$dn_i = \nu_i d\xi \qquad \text{... (14.5)}$$

(since n_i^o and ν_i are constants)

Combining Eqs. 14.3 and 14.5, we get,

$$dG_{T,p} = \sum_i^n \mu_i \nu_i d\xi$$

$$\text{Hence, } \left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \sum_i \mu_i \nu_i \qquad \text{... (14.6)}$$

From your study of Unit 9, you can understand that Eq.14.6 represents Gibb's free energy change of the reaction ($\Delta_r G_{T,p}$) at constant temperature and pressure.

In Unit 9, you have studied that $\Delta_r G_{T,p}$ is equal to the sum of the Gibb's free energy of the products minus the sum of the Gibb's free energy of the reactants.

$$\text{i.e., } \left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \sum_i \mu_i \nu_i = \Delta_r G_{T,p} \qquad \text{... (14.7)}$$

Let us apply Eq. 14.7 to two reactions. First, let us consider the formation of water discussed in this section.

$$H_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons H_2O(l)$$

$\Delta_r G_{T,p}$ for the formation of water is given by

$$\Delta_r G_{T,p} = \mu_{H_2O} - \mu_{H_2} - \frac{1}{2}\mu_{O_2}$$

The ν_i values of H_2O, H_2 and O_2 are 1, -1 and $-\frac{1}{2}$, respectively.

As a second example, let us consider the formation of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

For this reaction,

$$\Delta_r G_{T,p} = 2\mu_{NH_3} - \mu_{N_2} - 3\mu_{H_2}$$

Again, note that the ν_i values of NH_3, N_2 and H_2 are 2, -1 and -3, respectively.

A chemical reaction will tend to proceed in a direction of decreasing free energy. At equilibrium, the reaction does not proceed in either direction, implying thereby that there would be an increase in Gibb's free energy of the system if the reaction proceeds in either direction. Hence, the Gibb's free energy of the system will be minimum at equilibrium.

From sec. 9.8 of Unit 9, we know that the Gibb's free energy of the system will be minimum at equilibrium at constant temperature and pressure (see Fig. 14.1). Hence, the derivative of the Gibb's free energy function with respect to the extent of the reaction, which is the slope of the curve in Fig. 14.1, is equal to zero at equilibrium at constant temperature and pressure. In other words,

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p,eq} = \sum_i \mu_i \nu_i = \Delta_r G_{T,p} = 0 \qquad \text{... (14.8)}$$

where 'eq' stands for equilibrium condition.

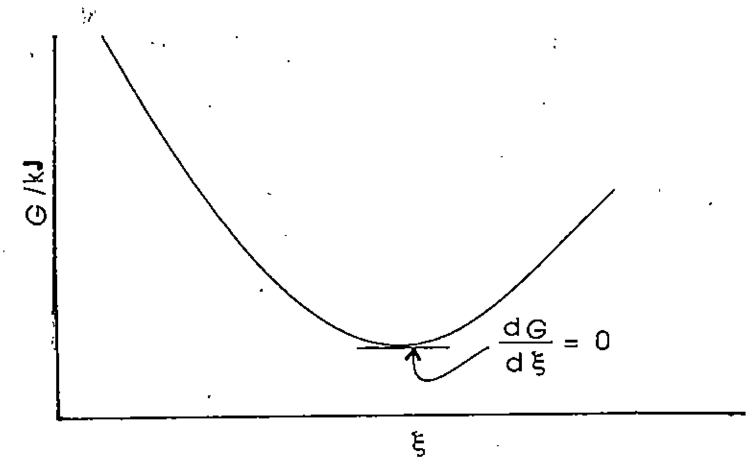


Fig. 14.1 : Change of Gibb's Free Energy and the extent of chemical reaction.

Equation 14.8 is a general expression which is applicable to any reversible chemical reaction under equilibrium conditions at constant temperature and pressure. The equation simply means that the sum of the chemical potentials of the products and reactants is equal to zero at equilibrium.

Equation 14.8 would be most useful if we could express the chemical potential in terms of some experimentally determinable or known quantities. There are a number of ways to express chemical potentials. The next section discusses the substitution for chemical potential in terms of partial pressure, mole fraction and concentration for ideal gas mixtures at equilibrium.

Try the following SAQ which is based on the above discussion.

SAQ 1

For the formation reaction of nitric oxide from nitrogen and oxygen gases, find the value of ν for each of the reactants and products.

....

....

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14.4 CHEMICAL EQUILIBRIUM IN IDEAL GAS MIXTURES

Let us derive an expression for the equilibrium constant in terms of partial pressures for a reaction between ideal gases.

14.4.1 Equilibrium Constant Expression in Terms of Partial Pressure

Consider a general reaction

$$aA + bB + ... \rightleftharpoons lL + mM + ... \qquad ...(14.9)$$

At constant temperature ($dT = 0$) and pressure ($dp = 0$), the free energy change for the above reaction ($\Delta_r G_{T,p}$) is obtained by using Eq. 14.7.

$$\Delta_r G_{T,p} = (l\mu_L + m\mu_M + ...) - (a\mu_A + b\mu_B + ...) \qquad ...(14.10)$$

where μ_L, μ_M, μ_A, μ_B, ..., etc., are the chemical potentials of the products and reactants; and l, m, $(-a)$, $(-b)$, ..., etc., are ν_i values. Remember that the products (such as L and M) have positive ν_i values and the reactants (such as A and B) have negative ν_i values; because of this, there is a negative sign between the two terms on the right hand side of Eq. 14.10.

The Chemical potential, μ_i, of an ideal gas 'i' in a gaseous mixture is given by Eq. 9.83 of Unit 9.

$$\mu_i(p_i) = \mu_i^\circ(p) + RT \ln p_i \qquad \text{... (14.11)}$$

where $\mu_i^\circ(p)$ is the chemical potential of i in the standard state and p_i is its partial pressure.

Using Eq. 14.11 in Eq. 14.10,

$$\Delta_r G_{T,p} = [l(\mu_L^\circ(p) + RT \ln p_L) + m(\mu_M^\circ(p) + RT \ln p_M) + ...] - [a(\mu_A^\circ(p) + RT \ln p_A) + b(\mu_B^\circ(p) + RT \ln p_B) + ...] \qquad \text{... (14.12)}$$

$$\Delta_r G_{T,p} = [(l\mu_L^\circ(p) + m\mu_M^\circ(p) + ...) - (a\mu_A^\circ(p) + b\mu_B^\circ(p) + ...)] + RT \ln \frac{p_L^l\, p_M^m \cdots}{p_A^a\, p_B^b \cdots} \qquad \text{... (14.13)}$$

Note that in the transformation of Eq. 14.12 to Eq. 14.13, we have used the relation :

$lRT \ln p_L = RT \ln p_L^l$; i.e., a coefficient ($l$) of a logarithmic term ($RT \ln p_L$) is taken inside the logarithmic term as a power.

$$\text{But } (l\mu_L^\circ(p) + m\mu_M^\circ(p) + ...) - (a\mu_A^\circ(p) + b\mu_B^\circ(p) + ...) = \Delta_r G^\circ_{T,p} \qquad \text{... (14.14)}$$

where $\Delta_r G^\circ_{T,p}$ is the standard free energy change of the reaction at constant temperature and pressure.

Using Eqs. 14.13 and 14.14, we can write

$$\Delta_r G_{T,p} = \Delta_r G^\circ_{T,p} + RT \ln \frac{p_L^l\, p_M^m \cdots}{p_A^a\, p_B^b \cdots} \qquad \text{...(14.15)}$$

Let us now assume that the above system is under equilibrium. Using Eqs. 14.8 and 14.15, we can write that at equilibrium,

$$\Delta_r G_{T,p} = \Delta_r G^\circ_{T,p} + RT \ln \left[\frac{p_L^l\, p_M^m \cdots}{p_A^a\, p_B^b \cdots} \right]_{eq} = 0$$

The subscript 'eq' stands for equilibrium values of partial pressures.

$$\text{i.e., } \Delta_r G^\circ_{T,p} = -RT \ln \left[\frac{p_L^l\, p_M^m \cdots}{p_A^a\, p_B^b \cdots} \right]_{eq} \qquad \text{... (14.16)}$$

$$\text{or } \Delta_r G^\circ_{T,p} = -RT \ln K_p = -2.303\, RT \log K_p \qquad \text{... (14.17)}$$

where K_p is called the equilibrium constant in terms of partial pressures. The relationship is known as van't Hoff isotherm. K_p is given by the relationship

$$K_p = \frac{p_L^l\, p_M^m \cdots}{p_A^a\, p_B^b \cdots} \text{ at equilibrium} \qquad \text{... (14.18)}$$

$$= \frac{\text{Multiplication of } (p_i)^{\nu_i} \text{ terms of the products}}{\text{Multiplication of } (p_i)^{-\nu_i} \text{ terms of the reactants}} \text{ at equilibrium}$$

It is quite interesting to note that Eq. 14.17 relates equilibrium constant of a reaction to the change in standard free energy that takes place during a reaction. In Unit 9, you have studied the method of calculation of $\Delta_r G^\circ$ from the free energies of formation of the reactants and products; once $\Delta_r G^\circ$ is known at a particular temperature, K_p can be calculated using Eq. 14.17. In Unit 17 on Electrochemical cells, you will study the electrochemical method of calculating the equilibrium constant.

where p_L, p_M, p_A, p_B, ..., etc., are the partial pressures of L, M, A, B, ..., etc., at equilibrium. In subsequent sections, we leave out the subscript 'eq' while referring to equilibrium partial pressures. Eq. 14.18 can also be written as,

$$K_p = p_L^l \cdot p_M^m \cdots p_A^{-a} \cdot p_B^{-b} \cdots \qquad \text{... (14.19)}$$

where p_L, p_M, p_A, p_B, ..., etc., are the equilibrium partial pressures and l, m, $(-a)$, $(-b)$ ..., etc., are the respective ν_i values of L, M, A, B, ..., etc. Eq. 14.19 can also be represented as,

$$K_p = \prod_i p_i^{\nu_i} \qquad \text{... (14.20)}$$

where the symbol $\prod_i$ represents the multiplication of different $p_i^{\nu_i}$ terms given in Eq. 14.19. Again, from Eqs. 14.18 to 14.20, we can see that the dimensions of K_p will depend upon the ν_i values of the reactants and products. This particular aspect will be clear when you study the examples worked out in this unit.

Note that ν_i written as power is positive for the product, NH_3, whereas it is negative for N_2 and H_2, these two being reactants.

Some authors prefer to give K_p as a dimensionless quantity by dividing p_i by p° where $p^\circ = 1$ bar $= 10^5$ Pa. To represent K_p as a dimensionless quantity, Eq. 14.20 is modified as,

$$K_p = \prod_i \left(\frac{p_i}{p^\circ} \right)^{\nu_i} \qquad \text{... (14.21)}$$

Let us apply Eq. 14.19 to ammonia synthesis reaction.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$K_p = (p_{NH_3})^2\ (p_{N_2})^{-1} . (p_{H_2})^{-3}$

$$\text{or } K_p = \frac{p^2_{NH_3}}{p_{N_2}\ \ p^3_{H_2}}$$

Since the partial pressures are expressed in Pa unit, K_p for ammonia synthesis has the unit Pa^{-2}. If K_p for ammonia synthesis is to be dimensionless, then K_p expression is to be written following 14.21 as,

$$K_p = \frac{p^2_{NH_3}(p^\circ)^2}{p_{N_2} \cdot p^3_{H_2}}$$

Let us illustrate the use of Eq. 14.19 with an example.

Example 1

Suppose that, in an experiment at 1000 K, it is found that

$p_{SO_2} = 3.42 \times 10^4$ Pa, $p_{O_2} = 3.13 \times 10^4$ Pa and

$p_{SO_3} = 3.58 \times 10^4$ Pa for the reaction,

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Calculate the value for the equilibrium constant, K_p.

Solution

At the given temperature, K_p is given by the expression

$K_p = p^2_{SO_3} \cdot p^{-2}_{SO_2} \cdot p^{-1}_{O_2}$

$$\text{or } K_p = \frac{p^2_{SO_3}}{p^2_{SO_2} \cdot p_{O_2}} = \frac{(3.58 \times 10^4\ \text{Pa})^2}{(3.42 \times 10^4\ \text{Pa})^2 \times (3.13 \times 10^4\ \text{Pa})}$$

$$= 3.50 \times 10^{-4}\ \text{Pa}^{-1}$$

Note that the unit of K_p as per Eq. 14.19 is given by $(Pa)^{\Sigma\nu_i}$. In the reaction discussed in Example 1, $\Sigma\nu_i = 2 - 2 - 1 = -1$
Hence, the unit of K_p is Pa^{-1}.

Try the following SAQ now.

SAQ 2

Suppose that we write the ammonia synthesis reaction in two different ways :

i) $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightleftharpoons NH_3(g)$

ii) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Would you expect any difference in the expression for K_p in the two cases? (Usually, K_p values are calculated using equations of the type (ii) which have integral stoichiometric coefficients).

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14.4.2 Equilibrium Constant Expression in Terms of Mole Fraction

Since Dalton's law tells us that partial pressure of a gas is equal to the mole fraction times the total pressure, Eq. 14.19 can be written as,

$$K_p = (x_L p_t)^l\ (x_M p_t)^m \ldots (x_A p_t)^{-a}\ (x_B p_t)^{-b}$$

$$K_p = \prod_i (x_i\, p_t)^{\nu_i} \qquad \ldots (14.22)$$

where, x_i = mole fraction of the species i, and p_t = total pressure.

According to Dalton's law of partial pressures, partial pressure (p_i) of an ideal gas, i, is given by,

$p_i = p_t \cdot x_i$

where p_t is the total pressure, and x_i is the mole fraction of the gas in a gaseous mixture.

Example 2

Consider the reaction,

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

If a mixture of NO_2, and N_2O_4 at equilibrium has a total pressure of 1.5×10^5 Pa, calculate the fraction of N_2O_4 that has dissociated at 303 K. K_p for the reaction is 1.4×10^4 Pa at 303 K.

Solution

Suppose that ξ is the fraction of the amount of N_2O_4 which has dissociated at equilibrium or it represents the extent of the reaction. Then, 1-ξ is the fraction of the amount of N_2O_4

remaining at equilibrium and is proportional to the actual number of moles of N_2O_4 present at equilibrium.

From the balanced reaction, it is seen that for each mole of N_2O_4 decomposed, there are two moles of NO_2 produced. Therefore, at equilibrium, 2ξ will be proportional to the actual number of moles of NO_2 produced.

The total number of moles at equilibrium would then be proportional to $1-\xi+2\xi$ or $1+\xi$.

The mole fractions of the two gases at equilibrium can be written as,

$x_{N_2O}=\dfrac{1-\xi}{1+\xi}$ and $x_{NO_2}=\dfrac{2\xi}{1+\xi}$ where x denotes mole fraction.

Using Eq. 14.22, $K_p=(x_{NO_2}\cdot p_t)^2\cdot(x_{N_2O_4}\cdot p_t)^{-1}$

i.e., $K_p=\dfrac{(x_{NO_2}\cdot p_t)^2}{(x_{N_2O_4}\cdot p_t)}$

Substituting for x_{NO_2} and $x_{N_2O_4}$ we get,

$$K_p=\frac{\left(\dfrac{2\xi}{1+\xi}\cdot p_t\right)^2}{\dfrac{1-\xi}{1+\xi}\cdot p_t}$$

$$\text{or } K_p=\frac{4\xi^2}{(1-\xi)(1+\xi)}p_t=\frac{4\xi^2}{1-\xi^2}\cdot p_t$$

Substituting the given values, we get,

$$1.4\times10^4\text{ Pa}=\frac{4\xi^2}{1-\xi^2}\times1.5\times10^5\text{ Pa.}$$

$$\text{or }\frac{1-\xi^2}{\xi^2}=\frac{1.5}{0.14}\times4$$

$$\text{or }\frac{1}{\xi^2}=1+\frac{1.5\times4}{0.14}$$

$$\text{or }\xi^2=0.023$$
$$\xi=0.15$$

The fraction of N_2O_4 dissociated is thus calculated to be 0.15.

Example 3

Consider the reaction,

$CO(g)+2H_2(g)\rightleftharpoons CH_3OH(g)$

where initially 1 mol of CO and 2 mol of H_2 were mixed together. Derive an expression for the equilibrium constant, K_p, in terms of the extent of the reaction, ξ and the total pressure, p_t.

Solution

If the extent of the reaction at equilibrium is represented by ξ then we have,

	$CO(g)\ +$	$2H_2(g)\rightleftharpoons$	$CH_3OH(g)$
Moles at equilibrium	$1-\xi$	$2-2\xi$	ξ
Mole fraction at equilibrium	$\dfrac{1-\xi}{3-2\xi}$	$\dfrac{2-2\xi}{3-2\xi}$	$\dfrac{\xi}{3-2\xi}$

Using Eq. 14.22, $K_p=(x_{CH_3OH}\cdot p_t)^1\cdot(x_{CO}\cdot p_t)^{-1}\cdot(x_{H_2}\cdot p_t)^{-2}$

i.e., $K_p=\dfrac{(x_{CH_3OH}\cdot p_t)}{(x_{CO}\cdot p_t)(x_{H_2}\cdot p_t)^2}$

Hence,

$$K_p = \frac{\left(\frac{\xi}{3-2\xi} \cdot p_t\right)}{\left(\frac{1-\xi}{3-2\xi} \cdot p_t\right)\left(\frac{2-2\xi}{3-2\xi} \cdot p_t\right)^2}$$

$$= \frac{(3-2\xi)^2\,\xi}{(1-\xi)\,(2-2\xi)^2 \cdot p_t^2}$$

You should be able to do the following SAQ, if you have understood the above examples.

SAQ 3

Express the equilibrium constant K_p for the reaction,

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

in terms of (i) partial pressures and (ii) mole fractions of the gaseous species.

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14.4.3 Equilibrium Constant Expression in Terms of Concentration

We know that for an ideal gas,

$$p_i = \frac{n_i RT}{V} = c_i RT$$

where c_i represents molar concentration of a gaseous substance 'i'; other symbols have their usual meaning. Hence we can express Eq. 14.19 in terms of concentrations.

$$K_p = (c_L RT)^l\,(c_M RT)^m \ldots (c_A RT)^{-a}\,(c_B RT)^{-b}$$

$$= \frac{(c_L RT)^l\,(c_M RT)^m \ldots}{(c_A RT)^a\,(c_B RT)^b \ldots} \qquad \ldots (14.23)$$

$$\text{i.e., } K_p = \prod_i (c_i RT)^{\nu_i} \qquad \ldots (14.24)$$

Eqs. 14.18 and 14.26 are the mathematical expressions of the law of mass action.

Where ν_i represents the stoichiometric coefficient (along with proper sign) in the chemical equation.

Eq. 14.23 can be written as,

$$K_p = \frac{c_L^l\,c_M^m \ldots}{c_A^a\,c_B^b \ldots}(RT)^{(l+m+\ldots)-(a+b+\ldots)}$$

$$= \frac{c_L^l\,c_M^m \ldots}{c_A^a\,c_B^b \ldots}(RT)^{\Sigma \nu_i}$$

$$\text{i.e., } K_p = K_c\,(RT)^{\Sigma \nu_i} \qquad \ldots (14.25)$$

where K_c is defined by,

$$= \frac{c_L^l\,c_M^m \ldots}{c_A^a\,c_B^b \ldots} = \frac{\text{Multiplication of } (c_i)^{\nu_i} \text{ terms of the products}}{\text{Multiplication of } (c_i)^{-\nu_i} \text{ terms of the reactants}} \qquad \ldots (14.26)$$

$$\text{i.e., } K_c = \prod_i (c_i)^{\nu_i} \qquad \ldots (14.27)$$

Eq. 14.25 holds good for reactions between ideal gases.

The dimensions of K_c depend of the ν_i values of the reactants and the products. In case K_c is to be expressed as a dimensionless quantity, c_i in Eq. 14.27 is to be replaced by c_i/c_o where c_o is the standard concentration and is equal to 1 mol dm^{-3}.

$$\text{i.e., } K_c = \prod_i \left(\frac{c_i}{c_o}\right)^{\nu_i} \qquad \ldots (14.28)$$

It is important to note that K_p and K_c are functions of temperature; we shall discuss this aspect in Sec. 14.7.

Let us study an application of Eq. 14.26.

Example 4

Calculate the equilibrium concentrations of all the species at 613 K for the reaction,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

if the initial concentrations of the three gases is 0.15 M each and $K_c = 0.800$ M at 613 K. The volume of the vessel is 1 dm^3.

The unit, mol dm^{-3}, is for denoting molarity and is represented by the letter, M.

Note that concentration in

$$\text{molarity} = \frac{\text{Number of moles}}{\text{Volume in } dm^3}$$

The unit of K_c as per Eq. 14.26 is given by $(M)^{\Sigma\nu_i}$. In Example 4, $\Sigma\nu_i = 1+1-1=1$.
Hence, the unit of K_c in this example is M.

Solution

Suppose that x mol of PCl_5 has decomposed at equilibrium. Since volume is 1 dm^3, the concentration expressed in molarity is equal to the number of moles of a particular substance.

	PCl_5	PCl_3	Cl_2
Equilibrium concentration/M	$0.15-x$	$0.15+x$	$0.15+x$

Using Eq. 14.26, we get

$$K_c = \frac{c_{PCl_3} \cdot c_{Cl_2}}{c_{PCl_5}}$$

Substituting the given values, we get,

$$0.800\ M = \frac{(0.15+x) \cdot (0.15+x)}{(0.15-x)}\ M$$

or $0,800\ (0.15-x) = (0.15+x)^2$

or $x^2 + 1.1\ x - 0.0975 = 0$

The solution of a quadratic equation of the form $ax^2+bx+c=0$ is given by

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

Using the principle of solution of standard quadratic equation, we get,

$x = 0.082$ M or

or -1.183 M

We take $x = 0.082$ M, since the second root of the quadratic equation gives the concentrations of PCl_3 and Cl_2 as (0.15 M − 1.83 M =) − 1.033 M which is impossible. Hence, the equilibrium concentrations are :

Square brackets are used to denote the concentration of a species. For example, $[PCl_5]$ is to be read as : concentration of PCl_5

$[PCl_5] = (0.15 - 0.082)\ M = 0.068\ M$

and $[PCl_3] = [Cl_2] = 0.15 + 0.082 = 0.232$ M

We can verify the answer by substituting the values for concentrations in evaluating K_c.

Based on the above discussion, answer the following SAQ.

SAQ 4

How are K_p and K_c related to each other for a reaction between ideal gases?

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14.5 DETERMINATION OF EQUILIBRIUM CONSTANTS

It is now clear from the above examples that if the initial concentrations and the extent of the reaction are known, equilibrium constants can be calculated. In fact, if we want to make use of any of the equations derived in the previous two sections, we must be sure that the equilibrium has indeed been reached. The following two criteria confirm the presence of equilibrium condition :

1) The value of equilibrium constant should be same when the equilibrium is approached from either side.
2) The value of equilibrium constant should be same when the concentrations of the reacting substances are varied greatly.

Once it is established that an equilibrium has been reached, the next step is to find out the equilibrium concentration of at least one of the reactants or products in order to calculate the extent of the reaction. This can be achieved either by chemical analysis or by neasurement of some physical property. The difficulty with the chemical analysis is that the ;oncentration will change during the course of the analysis. Hence, only when the reaction :an be stopped at equilibrium by some means (like sudden cooling), can this method be ısed. Physical methods are more convenient since they do not require stopping of the eaction. The physical properties commonly used for this purpose are density, refractive ndex, electrical conductivity, light absorption etc.

14.6 APPLICATIONS OF EQUILIBRIUM STUDIES

The law of mass action, as represented by Eqs. 14.18 to 14.28, finds many useful pplications in chemical calculations like finding out the amounts of products formed at quilibrium or change in free energy of the system etc. We have already seen a few xamples of the application of these equations; however, to simplify, we shall categorise the roblems into three subsections, namely, homogeneous systems, heterogeneous systems and quid solutions.

4.6.1 Homogeneous Systems

Vhen all the reactants and products are present in the same phase (i.e., gaseous or liquid) 'e call it a homogeneous system. Let us consider a few examples :

xample 5

t 298 K, it was found that $K_p = 7.13$, for the reaction :

$NO_2(g) \rightleftharpoons N_2O_4(g)$

/hat is $\Delta_r G°$ for the reaction?

olution

is worth noting that K_p is given as a dimensionless quantity as per Eq. 14.21.

sing Eq. 14.17, $\Delta_r G° = -RT \ln K_p$

$= -2.303\ RT \log K_p$

ıbstituting the values of R, T and K_p in the above equation, we get,

$G° = (-2.303 \times 8.314 \times 298 \log 7.13)\ \text{J mol}^{-1} = -4.868\ \text{KJ mol}^{-1}$

ample 6

hat is the value of K_p for the ammonia synthesis reaction at 500 K as represented by,

$N_2(g) + \frac{3}{2} H_2(g) \rightleftharpoons NH_3(g)$

$\Delta_r G° = 4.833\ \text{kJ mol}^{-1}$?

lution

$G° = 4833\ \text{J mol}^{-1} = -(2.303 \times 8.314 \times 500 \log K_p)\ \text{J mol}^{-1}$

bstituting the given values, we get, $\log K_p = \frac{-4833}{2.303 \times 8.314 \times 500} = -0.5048$

$\log \frac{1}{K_p} = 0.5048;\ \frac{1}{K_p} = 10^{0.5048}$

$= \text{Antilog of } 0.5048 = 3.197$

ıce, $K_p = \frac{1}{3.197} = 0.3128$

In Example 5, the term inside the log factor is greater than 1; hence the calculation is done as in the case of Example 3 of Unit 6 of this course.

Calculation of K_p from $\Delta_r G°$

If $\Delta_r G°$ is a negative quantity, then $\log K_p$ is a positive quantity. If we assume $\log K_p$ to be equal to x, then K_p can be calculated as follows :

$\log K_p = x$; hence

$K_p = 10^x = \text{Antilog of } x$.

If $\Delta_r G°$ is a positive quantity, then $\log K_p$ is a negative quantity. If we assume $\log K_p$ to be equal to $-x$, then K_p can be calculated as follows :

$\log K_p = -x$; hence $\log \frac{1}{K_p} = x$

$\frac{1}{K_p} = 10^x = \text{Antilog of } x$

or $K_p = \frac{1}{\text{Antilog of } x}$

Example 6 is worked out using this principle.

ample 7

drogen and iodine react at 699 K according to the equation,

$g) + I_2(g) \rightleftharpoons 2HI(g)$

.00 mol of H_2 and 1.00 mol of I_2 are placed in a 1.00 dm^3 flask and allowed to react, at mass of hydrogen iodide will be present at equilibrium? At 699 K, $K = 55.3$.

ution

t thing you should notice in this case is that the equilibrium constant is written with a symbol K and not as K_p or K_c since the total number of moles of the products are equal to those of the reactants (i.e., $\Sigma\nu_i = 0$); so, K_p must be equal to K_c (see Eq. 14.25). Hence, we can write, $K = K_c = 55.3$.

Using Eq. 14.26, $55.3 = \dfrac{c^2_{HI}}{c_{H_2} \cdot c_{I_2}}$

If ξ represents the extent of the reaction, the equilibrium concentrations can be written as, $c_{HI} = 2\xi$, $c_{H_2} = 1 - \xi$ and $c_{I_2} = 1 - \xi$; note that the amount of each material is equal to its concentration since volume is 1 dm^3. Substituting these values in the above equation, we get,

$$55.3 = \frac{(2\xi)^2}{(1-\xi)(1-\xi)}$$

or $\xi = 0.731$ or 1.269; the value, 1.269, is rejected since the value of ξ cannot be greater than one.

Hence, the amount of HI at equilibrium $= 2\xi$ or $2 \times 0.731 = 1.46$ mol; the mass of HI at equilibrium $= 1.46 \times 0.128$ kg $= 0.188$ kg.

14.6.2 Heterogeneous Systems

Chemical reactions may also involve reactants or products in different phases. The most common examples are found where solids and gases are present together at equilibrium. Recall that at standard pressure of 1 bar, the activity of pure solid is unity. Hence, in writing the expression for equilibrium constant the activity or partial pressure terms for solids can be eliminated. Thus, for the reaction,

$$CaCO_3(s) \rightleftharpoons CaO(g) + CO_2(g)$$

as per Eq. (14.19), $K_p = p^1_{CaO}\, p^1_{CO_2}\, p^{-1}_{CaCO_3} = p_{CO_2}$ [since $p_{CaO} = p_{CaCO_3} = 1$]

Again for the reaction,

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

as per Eq. 14.19, $K_p = \dfrac{p_{CO} \cdot p_{H_2}}{p_{H_2O}}$ since $p_C = 1$, carbon being in the solid form.

Let us illustrate the heterogeneous systems with another example.

Example 8

$NH_4HS(s)$ evaporates in an evacuated container at 298 K according to the equation.

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

Find the pressure of each gas at equilibrium if $K_p = 1.10 \times 10^9 Pa^2$ at 298 K.

Solution

We can write for the above reaction,

using Eq. 14.19, $K_p = p_{NH_3} \cdot p_{H_2S}$ (since $p_{NH_4HS} = 1$)

Since the two gases produced in the reaction are in equimolar quantities,

$p_{NH_3} = p_{H_2S}$

or $K_p = p^2_{NH_3} = 1.10 \times 10^9$ Pa^2

$p_{NH_3} = p_{H_2S} = 3.32 \times 10^4$ Pa.

14.6.3 Liquid Solutions

So far we have discussed the reactions which take place in gaseous state or those involving gaseous and solid phases. But the majority of reactions are carried out in liquid solutions.

For example, you have already seen hydrolysis of an ester which can be written as :

Ester + Water $\rightleftharpoons$ Acid + Alcohol

Let us arrive at an expression useful in calculating the equilibrium constants of such reactions.

In an ideal solution, the concentration of each component can be conveniently expressed in terms of molarity. We can use Eq. 14.26 to express K_c of a general reaction (given below) which takes place in a liquid solution; of course, the solution has to exhibit ideal behaviour.

$$aA + bB + \ldots \rightleftharpoons pP + qQ + \ldots$$

In this reaction, A, B, ... etc., and P, Q, ... etc., are the reactants and products; *a, b,* ... etc., and *p, q* ... etc., are the stoichiometric coefficients.

Similar to Eq. 14.26, we can write K_c for the above reaction as,

$$K_c = \frac{c_P^p \cdot c_Q^q \ldots}{c_A^a \cdot c_B^b \ldots} \qquad \ldots (14.29)$$

$$K_c = \frac{m_P^p \cdot m_Q^q \ldots}{m_A^a \cdot m_B^b \ldots} = \frac{[P]^p[Q]^q}{[A]^a[B]^b} \qquad \ldots (14.30)$$

where m_p, m_q, ... etc., are the molarities of substances. In Eq. 14.30, the square brackets denote the concentrations of the species within the brackets.

Eqs. 14.29 and 14.30 can be applied to the solutions showing ideal behaviour. Similarly even in the case of gas phase reactions, equations such as 14.19 or 14.26 can be used only if the reactants and products are ideal gases. In case of deviation from ideal behaviour, whether it is a gas phase or a liquid phase reaction, activities of the substances must be used in the place of partial pressures or concentrations. But the equilibrium constant expressions become more complicated in such cases and we do not discuss them in this course.

Let us work out an example showing the use of Eq. 14.30.

Example 9
Calculate the equilibrium constant for the reaction,

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$
at 298 K if 1.00 mol of acetic acid and 1.00 mol of ethyl alcohol are mixed together. At the equilibrium point, the amount of water is 0.333 mol.

Solution
The concentrations of substances are given below assuming the total volume to be V dm^3:

	$[CH_3COOC_2H_5]$	$[H_2O]$	$[CH_3COOH]$	$[C_2H_5OH]$
Concentration at equilibrium (in mol dm^{-3})	$0.333/V$	$0.333/V$	$(1-0.333)/V$	$(1-0.333)/V$

$$K_c = \frac{(0.667/V)(0.667/V)}{(0.333/V)(0.333/V)} = 4.01$$

Note that K_c is a dimensionless quantity since $\Sigma\ \nu_i$ for this reaction is equal to zero. In cases such as this, volume need not be known as it cancels out in the final expression. If in any reaction $\Sigma\ \nu_i$ is not equal to zero, the final expression would contain volume term and K_c will have suitable dimensions.

SAQ 5
For the reaction,

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

assuming that the reaction has attained equilibrium, calculate the concentration of water at 298 K for a mixture with

$[CH_3COOC_2H_5] = 2.0$ M
$[CH_3COOH] = 0.10$ M and
$[C_2H_5OH] = 0.50$ M
K for this reaction is 4.01 at 298 K.

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14.7 EFFECT OF TEMPERATURE ON CHEMICAL EQUILIBRIUM

The equilibrium constant, K, of a reversible chemical reaction is a constant at a given temperature; but it varies with temperature. Let us derive an expression useful in bringing out the relationship between the equilibrium constant and temperature.

From Eq. 14.17, we get,

$$\Delta_r G^\circ = -RT \ln K_p$$

$$\text{or } \ln K_p = \frac{-\Delta_r G^\circ}{RT}$$

Differentiating this expression with respect to temperature,

$$\text{or } \frac{d \ln K_p}{dT} = -\frac{1}{R}\frac{1}{dT}\left(\frac{\Delta_r G^\circ}{T}\right) \qquad \ldots (14.31)$$

Using Eq. 9.45 we can write

$$\frac{d}{dT}\left(\frac{\Delta_r G^\circ}{T}\right) = -\frac{\Delta_r H^\circ}{T^2} \qquad \ldots (14.32)$$

Combining Eqs. 14.31 and 14.32, we get,

$$\frac{d \ln K_p}{dT} = \frac{\Delta_r H^\circ}{RT^2} \qquad \ldots (14.33)$$

Eq. 14.33 tells us that equilibrium constant varies with temperature and depends on the standard enthalpy of the reaction.

Assuming that the standard enthalpy change ($\Delta_r H^\circ$) of the reaction remains constant over a small range of temperature, the above equation on integration between limits K_{p_1}, K_{p_2}, and T_1, T_2 gives,

$$\int_{K_{p_1}}^{K_{p_2}} d \ln K_p = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ}{RT^2} dT$$

$$\text{or } \ln \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\text{or } \log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta_r H^\circ}{2.303\, R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= \frac{\Delta_r H^\circ (T_2 - T_1)}{2.303\, RT_1 T_2} \qquad \ldots (14.34)$$

Eq. 14.34 correlates the equilibrium constant values K_{p_1} **and** K_{p_2} (expressed in terms of partial pressures) at two different temperatures T_1 and T_2 **to the** standard enthalpy of reaction.

According to Eq. 14.25, which is applicable for ideal gases,

$$K_p = K_c (RT)^{\Delta n}$$

Using this equation and Eq. 14.33, it is possible to relate K_c values to the respective temperatures as,

$$\log \frac{K_{c_2}}{K_{c_1}} = \frac{\Delta_r U^\circ (T_2 - T_1)}{2.303\, RT_1 T_2} \qquad \ldots (14.35)$$

where K_{c_1} and K_{c_2} are the equilibrium constants (in terms of concentrations) at temperatures T_1 and T_2 and $\Delta_r U^\circ$ is the standard internal energy change of the reaction. Since reactions are generally carried out at constant pressure, Eq. 14.34 is of greater importance for us. Eq. 14.35 is known as van't Hoff's isochore.

Example 10

The equilibrium constant for the reaction

$$H_2(g) + S(s) \rightleftharpoons H_2S(g)$$

is 18.5 at 925 K and 9.25 at 1000 K, respectively. Calculate the standard enthalpy of the reaction. Also calculate $\Delta_r G^\circ$ and $\Delta_r S^\circ$ at 925 K.

Solution

Substituting the given values in Eq. 14.34, we get,

$$\log \frac{K_{1000}}{K_{925}} = \frac{\Delta_r H^\circ}{(2.303 \times 8.314)}\left(\frac{1}{925} - \frac{1}{1000}\right)$$

$$\text{or } \log \frac{9.25}{18.5} = \frac{\Delta_r H^\circ}{2.303 \times 8.314}\left(\frac{75}{925 \times 1000}\right)$$

hence $\Delta_r H^\circ = -71.1$ kJ mol^{-1}

Using Eq. 14.17, $\Delta_r G^\circ = -2.303 \times 8.314 \times 925 \log 18.5 = -22.4$ kJ mol^{-1}

Rearranging Eq. 9.15 of Unit 9, $\Delta_r S^\circ = \dfrac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \dfrac{(-71100 + 22400)\ \text{J}}{925\ \text{K}}$

$$= -52.6\ \text{J K}^{-1}\ \text{mol}^{-1}$$

SAQ 6

For the dissociation of mercuric oxide, K_p values are 0.0196 and 0.1794 at 693 K and 723 K, respectively. Calculate the standard enthalpy of the reaction.

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14.8 LE CHATELIER'S PRINCIPLE AND CHEMICAL EQUILIBRIA

The equilibrium expressions derived in Secs. 14.3 to 14.7 are very useful to perform numerical computations of various kinds as we have already seen with different examples given. However, often one is more interested in predicting qualitatively the results of a change brought about by external forces on the system under equilibrium. For instance, if pressure, temperature or volume is changed for a system under equilibrium, what would be its effect, if any, on the equilibrium itself? Of course, we can find out the effect of such factors on the system under equilibrium with the help of expressions such as, Eq. 14.17 or Eq. 14.34. However, it is much more easily predicted with the help of Le Chatelier's principle.

Le Chatelier's principle can be stated as follows :
If a stress is applied to any system under equilibrium, the system would tend to shift in such a way so as to neutralise the effect of that stress (if possible).

The stress for a chemical reaction could be in the form of a change in pressure, temperature or concentration at equilibrium. According to the above principle then, the equilibrium would shift in such a direction so that the effect of these changes is neutralised. We shall consider the effect of each one of these factors on equilibrium separately.

14.8.1 Effect of Change of Concentration

Let us consider the reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

which has attained equilibrium. Now, if we add some H_2 to the equilibrium mixture, it will obviously upset the equilibrium. According to Le Chatelier's principle, the equilibrium would shift in such a way so as to oppose the effect of this excess H_2. It can do so by using up this excess H_2 to react with more I_2 to give more of HI. We describe this process by saying that the final position of equilibrium has shifted to the right of the equation. In this final state of equilibrium, then, more amount of HI is formed as compared to earlier equilibrium state. Just the opposite would be the fate of the reaction if, instead of H_2, some HI is added to the system under equilibrium. In short, by changing the concentration at equilibrium, the reaction will move forward or in the reverse direction so that the equilibrium constant has the same value.

14.8.2 Effect of Change of Pressure

If we consider the above reaction again and suppose that the pressure of the system is increased—perhaps by reducing the volume of the container—the system should react in such a way so as to reduce the effect of the increase in pressure. However, there is no way by which this can be achieved. The forward reaction or the reverse reaction will not be favoured by pressure change since the total number of moles of the reactants is the same as the total number of moles of the products.

However, the situation changes if we consider the synthesis of ammonia :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

If the pressure of the system is increased at the equilibrium as was done in the previous example, the effect of this increase could be eliminated by the formation of more ammonia. This becomes obvious if you realise that the total number of moles of the reactants is four as compared to the moles of product which is two. Four moles will exert greater pressure than two moles; so, if the system wants to reduce the extra pressure, it can do so by moving in the forward direction. On the other hand, if we decrease the external pressure on the system, more of ammonia will decompose to give nitrogen and hydrogen. Thus, if we want to produce ammonia industrially, it is preferable to carry out the reaction at high pressures.

Comparing the two reactions given above, we can conclude that changes in pressure at equilibrium will affect the amounts of products formed for only those reactions where the total number of moles of reactants are different from the total number of moles of products.

14.8.3 Effect of Change of Temperature

Consider once again the synthesis of ammonia from nitrogen and hydrogen which is an exothermic reaction. If the temperature of the system is increased at equilibrium, Le Chatelier's principle tells us that the system should react in such a way so as to neutralise this effect. Let us see how this is possible. We know that the formation of ammonia is an exothermic reaction and, therefore, the reverse reaction of decomposition of ammonia will be endothermic. Thus, the excess heat supplied by raising the temperature of the system can be absorbed by the system if the reaction goes more towards left. This will increase the amounts of N_2 and H_2 and decrease the amount of NH_3 at equilibrium. We can generalise this observation by saying that by raising the temperature of a system undergoing exothermic reaction, we will decrease the amount of the products and increase the amount of the reactants. Just the opposite will be true for all endothermic reactions.

The effect of these factors gains special importance for the production of a substance on large scale. In any industrial production of a substance it is imperative to know the optimum conditions of temperature, pressure and concentrations in order to get the maximum yield at a minimum cost. For instance, in the production of ammonia we know from Le Chatelier's principle that high pressure and high concentration of N_2 and H_2 will favour the reaction. Similarly, the above principle also predicts that the reaction would be more favourable at low temperatures since it is exothermic. However, we cannot carry out the reaction at a very low temperature since another factor comes into the picture. That is, the rate of the reaction becomes too slow at lower temperatures. Hence, the reaction is performed at pressures of several megapascals and temperatures between 650 and 750 K.

You should be able to do the following SAQs which are based on the above discussion.

SAQ 7

Consider the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. How would the equilibrium be affected by,

i) the addition of Cl_2 and
ii) decrease in the volume of the container?

SAQ 8

If $\Delta H^\circ = 41$ kJ mol^{-1} for the reaction,

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

what will be the effect of increase of temperature on the equilibrium?

14.9 SUMMARY

In this unit we have discussed the meaning of chemical equilibrium. A general expression for the equilibrium constant was derived from the basic principles of thermodynamics. Different forms of the general expression were then utilised in understanding the equilibria of homogeneous and heterogeneous systems. We then learnt Le Chatelier's principle and its use in predicting the shift in the position of equilibrium by the changes brought about in concentration, temperature and pressure of the system.

14.10 TERMINAL QUESTIONS

1) In a reaction $A + 2B \rightleftharpoons 2C + D$, A and B are taken in a closed vessel at 300 K. The initial concentration of B is 1.5 times that of A. At equilibrium, the concentration of A and D are equal. Calculate the equilibrium constant at 300 K.

2) At 1000 K for the equilibria,
   i) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $\quad K_p = 4.0 \times 10^3$ Pa
   ii) $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ $\quad K_p' = 2.0 \times 10^5$ Pa

   Solid C, CaO and $CaCO_3$ are mixed and allowed to attain equilibrium at 1000 K. What is the pressure of CO?

3) Show that for the reaction,
   $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$
   the equilibrium constant, K_p, is given by

   $$K_p = \frac{\xi^3 p_t}{(2+\xi)(1-\xi)^2}$$

   where the symbols have their usual meaning.

4. In a 10.0 dm^3 mixture of H_2, I_2 and HI at equilibrium at 698 K, there are 0.100 mol of H_2, 0.100 mol of I_2 and 0.740 mol of HI. If 0.500 mol of HI are now added to this system, what will be the concentrations of H_2, I_2 and HI, once equilibrium has been reestablished?

5. At a certain temperature, $K_c = 7.5$ m^3 mol^{-1} for the reaction,
   $2NO_2(g) \rightleftharpoons N_2O_4(g)$
   i) If 2.0 mol of NO_2 are placed in a 2.0 dm^3 container and allowed to react, what will be the concentrations of NO_2 and N_2O_4 at equilibrium?
   ii) What will be the equilibrium concentration, if the volume of the container is doubled?

6. Find the ν value of the reactants and the products in the following cases :
   i) $C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$
   ii) $2CH_4(g) \rightleftharpoons C_2H_6(g) + H_2(g)$

7. If $K_p > 1$ for a reaction, comment on the sign of standard free energy change of the reaction.

8. At 298.15 K, the standard free energies of formation of $CH_3COOH(aq)$, $CH_3COO^-(aq)$ and $H^+(aq)$ are −396.6, −369.4 and 0 kJ mol^{-1}, respectively. Using this data, calculate the equilibrium constant for the dissociation of acetic acid at 298.15 K.

9. For the reaction,
   $N_2O_4(g) \rightleftharpoons 2NO_2(g)$,
   K_p is 1.4×10^4 Pa at 303 K. Find K_c at this temperature.

14.11 ANSWERS

Self Assessment Questions

1) The formation of nitric oxide can be represented by the equation.

   $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

   ν values are as follows : $\nu_{NO} = 2$; $\nu_{N_2} = -1$ and $\nu_{O_2} = -1$.

2) Let us denote the equilibrium constant for the two equations as K'_p and K_p.

$$K'_p = \frac{p_{NH_3}}{p_{N_2}^{1/2} \cdot p_{H_2}^{3/2}}$$

and

$$K_p = \frac{p_{NH_3}^2}{p_{N_2} \cdot p_{H_2}^3}$$

hence,

$$K_p = (K'_p)^2$$

Remember that generally the equilibrium constant value is obtained from the balanced chemical equation representing the reactants in their normal state of existence.

3) i) $K_p = \dfrac{p_{NO_2}^2}{p_{NO}^2 \cdot p_{O_2}}$

ii) Let us assume that 2 mol of NO and 1 mol of O_2 are mixed together initially. Let the total pressure be p_t.

Let ξ be the fraction of number of moles of O_2 which has reacted at equilibrium.

Total Number of moles
$= (2-2\xi) + (1-\xi) + (2\xi)$
$= (3-\xi)$

	NO	O_2	NO_2
Hence, number of moles at equilibrium	$2-2\xi$	$1-\xi$	2ξ
Mole fraction at equilibrium	$\dfrac{2-2\xi}{3-\xi}$	$\dfrac{1-\xi}{3-\xi}$	$\dfrac{2\xi}{3-\xi}$

$$K_p = 4\xi^2(3-\xi)/(2-2\xi)^2(1-\xi)\, p_t$$

4) $K_p = (RT)^{\Sigma\nu_i} K_c$ [see Eq. 14.25]

where $\Sigma\nu_i$ = {Sum of the stoichiometric coefficients of the products} − {sum of the stoichiometric coefficients of the reactants}

5) Substituting the given values in Eq. 14.29, we get,

$$4.01 = \frac{(2.0)\,(x)}{(0.10)\,(0.50)}$$

$$x = \frac{4.01 \times 0.050}{2.0} = 0.10 \text{ M}$$

Hence, the concentration of water at equilibrium is 0.10 M.

6) Using Eq. 14.34, we get,

$$\Delta_r H^\circ = \frac{2.303 \times 8.314 \times 693 \times 723}{30} \log \frac{0.1794}{0.0196} \text{ J mol}^{-1}$$

$$= 308 \text{ kJ mol}^{-1}$$

7) The equilibrium expression for the reaction,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

can be written as,

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

When,

i) Cl_2 is added, $[PCl_5]$ must increase in order to keep the K_c value constant; i.e., some Cl_2 will combine with PCl_3 to give more of PCl_5. Hence, the equilibrium will shift towards left.

ii) volume of the container is decreased, the pressure will increase. According to Le Chatelier's principle, the equilibrium would shift in such a direction so as to neutralise or reduce this increase. Since the total number of moles on the L.H.S. is less than in R.H.S., the equilibrium has to shift towards left in order to bring about pressure decrease.

8) For endothermic reactions, the increase in temperature will move the equilibrium in the forward direction according to Le Chatelier's principle explained in Sec. 14.8.

1) Let the initial concentration of A be a mol dm^{-3};
then, the initial concentration of B $= 1.5a$ mol dm^{-3}
In the beginning, C and D were not present. Suppose that at equilibrium, x mol dm^{-3} of A has reacted. The equilibrium concentration will be then,

$[A] = (a - x)$ mol dm^{-3}
$[B] = (1.5a - 2x)$ mol dm^{-3}
$[C] = 2x$ mol dm^{-3}
$[D] = x$ mol dm^{-3}.

But it is given that at equilibrium, the concentrations of A and D are equal; hence,

$$(a - x) = x$$

$$\text{or } x = \frac{a}{2}$$

$$\therefore\ [A] = \left(a - \frac{a}{2}\right) \text{ mol dm}^{-3} = \frac{a}{2} \text{ mol dm}^{-3};\ [C] = a \text{ mol dm}^{-3}$$

$$[B] = \left(1.5a - 2 \cdot \frac{a}{2}\right) \text{mol dm}^{-3} = 0.5a \text{ mol dm}^{-3};\ [D] = \frac{a}{2} \text{ mol dm}^{-3}$$

The equilibrium constant is given by the expression;

$$K_c = \frac{[C]^2[D]}{[A]\,[B]^2} = \frac{[C]^2}{[B]^2} \text{ since } [A] = [D]$$

Substituting the values for [C] and [B], we get,

$$K_c = \frac{(a)^2}{(0.5a)^2} = 4;\ K_c \text{ is dimensionless, since } \Sigma\nu_i = 0$$

) For the two reactions (i) and (ii), the equilibrium constants can be expressed as,

$$K_p = p_{CO_2}$$

$$K_p' = \frac{p^2_{CO}}{p_{CO_2}}$$

For the overall reaction; $CaCO_3\,(s) + C(s) \rightleftharpoons CaO(s) + 2CO(g)$, let the equilibrium constant be K_p''.

$$K_p'' = p^2_{CO}$$

$$\text{or } K_p'' = K_p' \times p_{CO_2}$$

$$K_p'' = K_p' \times K_p$$

Substituting the given values, we get,

$$K_p'' = 4.0 \times 10^3 \text{ Pa} \times 2.0 \times 10^5 \text{ Pa}$$
$$= 8.0 \times 10^8 \text{ Pa}^2.$$

$$\therefore\ p_{CO} = \sqrt{K_p''} = \sqrt{8.0 \times 10^8 \text{ Pa}^2}$$
$$= 2.8 \times 10^4 \text{ Pa}.$$

) At equilibrium, the concentration will be given by,

$$\begin{array}{lll} 2H_2S(g) & \rightleftharpoons 2H_2(g) & + S_2(g) \\ 2(1-\xi) & 2\xi & \xi \end{array}$$

Total moles $=$
$2 - 2\xi + 2\xi + \xi = 2 + \xi$

The corresponding mole fractions will be,

$$\frac{2(1-\xi)}{2+\xi} \qquad \frac{2\xi}{2+\xi} \qquad \frac{\xi}{2+\xi}$$

The partial pressures of each substance can be obtained by multiplying the mole fraction by total pressure, p_t. Substituting the proper values in the equilibrium equation,

$$K_p = \frac{p_{S_2} \times p^2_{H_2}}{p^2_{H_2S}}$$

$$= \frac{\left\{\left(\frac{\xi}{2+\xi}\right)p_t\right\}\left\{\left(\frac{2\xi}{2+\xi}\right)p_t\right\}^2}{\left\{\left(\frac{2(1-\xi)}{(2+\xi)}\right)p_t\right\}^2}$$

$$\text{or } K_p = \frac{\xi^2 p_t}{(2+\xi)(1-\xi)^2}$$

4) For the reaction,

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

equilibrium concentrations can be written as,

$[HI] = \frac{0.740}{10.0}$ mol dm^{-3} (since the volume of the container is 10.0 dm^{3})

$[I_2] = \frac{0.100}{10.0}$ mol dm^{-3}

$[H_2] = \frac{0.100}{10.0}$ mol dm^{-3}

Substituting the values in the equilibrium constant expression,

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.0740)^2}{(0.0100)\,.\,(0.0100)}$$

$$= \frac{5.48 \times 10^{-3}}{1.00 \times 10^{-4}} = 54.8$$

Due to the addition of 0.500 mol of HI at equilibrium, the concentration of HI would become (0.074 mol dm^{-3} + 0.05 mol dm^{-3} =) 0.124 mol dm^{-3}. The equilibrium will shift in such a direction so as to reduce the excess of added HI; that is, some more H_2 and I_2 will be formed. Suppose this amount is x mol dm^{-3} for each of these (H_2 and I_2) gases, then the new equilibrium concentrations would be,

$[H_2] = (0.0100 + x)$ mol dm^{-3}
$[I_2] = (0.0100 + x)$ mol dm^{-3}
$[HI] = (0.124 - 2x)$ mol dm^{-3}

Substituting the values in equilibrium expression, we get,

$$54.8 = \frac{(0.124 - 2x)^2}{(0.0100 + x)\,(0.0100 + x)}$$

$$\text{or } 7.40 = \frac{(0.124 - 2x)}{(0.0100 + x)}$$

$$0.0740 + 7.40\,x = (0.124 - 2x)$$

$$\text{or } 9.40\,x = 0.050$$

$$x = 5.3 \times 10^{-3}$$

Hence, $[H_2] = (0.01 + 0.0053)$ M $= 0.0153$ M $= [I_2]$
and $[HI] = 0.113$ M.

5) i) Initial concentration of $NO_2 = \frac{2.0 \text{ mol}}{2.0 \text{ dm}^3} = 1.0$ mol dm^{-3} = 1.0 M

Suppose that at equilibrium, x mol dm^{-3} of N_2O_4 is formed. Then,

$[NO_2] = (1 - 2x)$ M; $[N_2O_4] = x$ M

Substituting in the equilibrium constant expression, we get,

$$7.5 \text{ m}^3 \text{ mol}^{-1} = \frac{x \text{ mol m}^{-3}}{(1-2x)^2 \,(\text{mol m}^{-3})^2}$$

$$\text{or } 7.5 + 30x^2 - 31x = 0$$

$$\text{or } x = \frac{31 \pm \sqrt{(31)^2 - 120 \times 7.5}}{60}$$

$$x = \frac{31 \pm 7.8}{60} = 0.39 \text{ or } 0.65$$

If $x = 0.65$ value is considered, then
$[NO_2]$ at equilibrium $= (1 - 2x)$ M
$= (1 - 1.30)$ M
$= -0.30$ M

This is meaningless and hence is discarded.

M stands for mol dm

We consider only the value, $x = 0.39$, since the second root of the equation has no physical significance.

$[NO_2] = (1 - 2 \times 0.39)$ M $= (1 - 0.78)$ M $= 0.22$ M
$[N_2O_4] = 0.39$ M.

ii) When the volume of the container is doubled, initial concentration of $NO_2 = \dfrac{2.0 \text{ mol}}{4.0 \text{ dm}^3} = 0.5 \text{ mol dm}^{-3} = 0.5 \text{ M}$

Following the same procedure as before, we get,

$$7.5 \text{ M}^{-1} = \frac{x \text{ M}}{(0.5-2x)^2 \text{ M}^2}$$

$7.5(0.25 + 4x^2 - 2x) = x$
$1.875 + 30x^2 - 15x = x$
$30x^2 - 16x + 1.875 = 0$
$x = 0.17$ or 0.36; only the value $x = 0.17$ is considered since the other value has no physical significance.
Hence at equilibrium, $[NO_2] = (0.5-2x) \text{ M} = (0.5-0.34) \text{ M} = 0.16 \text{ M}$
$[N_2O_4] = x \text{ M} = 0.17 \text{ M}.$

6) i) $\nu_{C_2H_5OH} = +1$, $\nu_{C_2H_4} = -1$, and $\nu_{H_2O} = -1$,
ii) $\nu_{C_2H_6} = +1$, $\nu_{H_2} = +1$ and $\nu_{CH_4} = -2$

7) If $K_p > 1$, $\Delta_r G°$ is a negative quantity and the reaction is feasible.

8) The dissociation of acetic acid can be represented by the equation,

$CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

$\Delta_r G°$ = (sum of standard free energies of formation of CH_3COO^- and H^+ ions) − (standard free energy of formation of acetic acid)
$= [(-369.4 + 0) - (-396.6)] \text{ kJ mol}^{-1}$
$= 27.2 \text{ kJ mol}^{-1}$

Let us represent the equilibrium constant for the dissociation of acetic acid as K_a.

$$\log K_a = \frac{-\Delta_r G°}{2.303\,RT}$$
$$= \frac{-27.2 \times 1000 \text{ J mol}^{-1}}{2.303 \times 8.314 \times 298.15 \text{ J mol}^{-1}}$$

$K_a = 1.72 \times 10^{-5}$

9) For the reaction

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$\sum_i \nu_i = +2 - 1 = +1$

According to Eq. 14.25,

$$K_c = K_p(RT)^{-\sum_i \nu_i}$$
$$= K_p(RT)^{-1}$$
$$= \frac{1.4 \times 10^4 \text{ Pa}}{8.314 \times 303 \text{ J mol}^{-1}}$$
$$= 5.56 \text{ mol m}^{-3}.$$

UNIT 15 IONIC EQUILIBRIA

Structure

15.1 INTRODUCTION

We have seen in Unit 14 that for any reversible reaction in a solution, the law of mass action can be applied and the equilibrium constant can be expressed in terms of concentrations of various reactants and products. In this unit we are going to find out how the equilibrium expression can be applied to solve the problems regarding solutions of electrolytes. Solutions as you know consist of a solvent and at least one solute. Since majority of the reactions are carried out in water as a solvent, we shall consider the equilibria in aqueous solutions only. For simplicity we shall study these equilibria in several steps. First we shall apply the equilibrium expression to the solute system where the solute dissociates in water but is not affected otherwise by water. Next we shall consider the equilibrium of water dissociation itself. Finally, those cases will be studied where the two equilibria have to be considered together. These studies find wide applications in the fields of analytical, industrial and biochemistry.

Objectives

After studying this unit, you should be able to :

- define acids and bases on the basis of different concepts,
- write the equilibrium constant expressions for the dissociation of weak acids, weak bases and water,
- define pH scale,
- state the effect of the addition of a substance containing common ion on the dissociation of acids and bases,
- explain the meaning of buffer solutions and their applications,
- state the meaning of hydrolysis and calculate hydrolysis constant,
- find the relationship between solubility and solubility product for different salts, and
- state its application in precipitation reactions.

15.2 ELECTROLYTES AND NONELECTROLYTES : ACIDS, BASES AND SALTS

In this unit, we shall confine our discussion to the solutions of electrolytes. It then becomes necessary that we must first know what are electrolytes and nonelectrolytes. If we put two charged electrodes in pure water, a very small amount of electric current will flow. However, if we add a small quantity of common salt (NaCl) to water, current flows easily; the reason being that the salt dissociates in water into its constituent ions—sodium ions and and chloride ions. Sodium ions which are positively charged will move towards negatively charged electrode and chloride ions will move towards the positively charged electrode. Thus current is carried by these ions in solution. All those substances which on dissolution in water conduct electricity are known as electrolytes; the familiar examples are acids, bases or salts. On the other hand, all those substances which when dissolved in water do not conduct electricity are called nonelectrolytes.

A substance may not necessarily ionise completely in solution. It may ionise to a small extent. We thus further classify qualitatively electrolytes into two groups. All those substances which dissociate almost completely are known as strong electrolytes and the substances which dissociate to a small extent in solution are called weak electrolytes. Most of the acids like acetic acid, oxalic acid, sulphurous acid etc. and a few salts like lead acetate and mercuric chloride are all weak electrolytes. On the other hand, most of the salts and a few acids such as perchloric, nitric, hydrochloric, sulphuric etc. fall in the category of strong electrolytes.

Most of our discussions will be confined to equilibria involving weak acids and weak bases. Presently acids and bases are being defined in many different ways. The application of equilibrium expression remains the same in whatever way one defines these acids and bases; yet, it is advisable to have a clear understanding of these different concepts of acids and bases.

15.2.1 Arrhenius Concept of Acids and Bases

Arrhenius defined acid as a compound which when dissolved in water gives hydrogen ion and a base, as a compound, which dissociates in water to yield hydroxyl ion. When an acid reacts with a base, it gives salt and water and the process is known as neutralisation reaction. Following examples should make the definition quite obvious :

Acids : $HNO_3 \longrightarrow H^+ + NO_3^-$

$HI \longrightarrow H^+ + I^-$

Bases : $NaOH \longrightarrow Na^+ + OH^-$

$KOH \longrightarrow K^+ + OH^-$

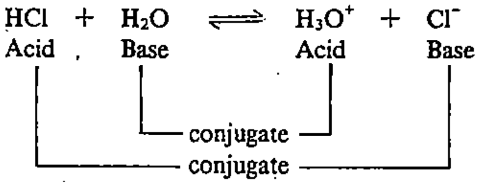
Neutralisation : $\underbrace{H^+ + Cl^-}_{\text{(Acid)}} + \underbrace{Na^+ + OH^-}_{\text{(Base)}} \longrightarrow \underbrace{H_2O}_{\text{(Water)}} + \underbrace{Na^+ + Cl^-}_{\text{(Salt)}}$

This is the most common and frequently used concept. However, there are two main limitations in this concept. First, it does not take into account the role of the solvent in the process. Secondly, there are many substances which do not contain hydrogen ion or hydroxyl ions but behave like acids or bases in their reactions. For examples, ammonia, NH_3, behaves like a typical base in reacting with an acid but does not contain hydroxyl ions. Similarly, BF_3 molecule does not contain hydrogen ions but does act as an acid towards a base like ammonia in the reaction :

$$BF_3 + NH_3 \longrightarrow BF_3 : NH_3$$

15.2.2 Lowry-Brønsted Concept of Acids and Bases

In 1923, two chemists, Lowry and Brønsted, proposed a wider definition of acids and bases. They defined an acid as any substance (molecule or ion) which can act as a proton donor and a base as a substance which can accept a proton. Since a proton cannot exist free in any solvent, it is always found associated with a conjugate base. Thus, any two substances related by the gain or loss of H^+ ion are known as conjugate acid-base pair. For example, HCl is an acid which has a conjugate base, Cl^- ion. Every acid HA has a conjugate base A^- formed by the loss of a proton and every base A^- has a conjugate acid formed when the base accepts a proton. Let us look at the reaction of HCl with water :

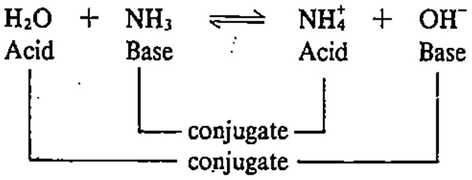


$$\mathrm{HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-}$$

Here, water molecule acts as a base (proton acceptor) towards the acid, HCl (proton donor), producing conjugate acid and base, respectively as H_3O^+ and Cl^-. It can be represented in another way as,

$$\mathrm{Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1}$$

'$Acid_1$' and '$Base_1$' form a conjugate pair just like '$Acid_2$' and '$Base_2$'. Let us consider another case :



$$\mathrm{H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-}$$

In this case H_2O is acting as an acid and NH_3 as a base. Thus, we see that water acts as an acid in one case and a base in another. Further, a stronger base will snatch away the proton associated with a weaker base. Thus, water molecule acts as a stronger base than chloride ion to produce a stronger acid (H_3O^+) and a weaker base, Cl^- ion. Table 15.1 gives a list of a few examples of **Brønsted** acids and bases.

Table 15.1 : Brønsted Acids and their Conjugate Bases

Acid	Base	Acid	Base
H_3O^+	H_2O	HSO_4^-	SO_4^{2-}
H_2O	OH^-	CH_3COOH	CH_3COO^-
HCl	Cl^-	NH_4^+	NH_3
H_2SO_4	HSO_4^-	NH_3	NH_2^-

Two main advantages of this concept are quite obvious. First, any substance which can accept a proton is defined as a base and therefore, it does not have to contain hydroxyl ion to be classified as a base. The obvious example is the above reaction where NH_3 having no OH^- acts as a base towards water. On the other hand, a compound containing a proton can behave like an acid only in the presence of an acceptor. For example, HCl gas cannot behave like an acid unless there is a base like water present to accept the proton. The second advantage is that the acid strength depends on the solvent. Hence, and acid which behaves like a strong acid in water may act as a weak acid in another solvent depending upon the proton accepting ability of the latter. For example $HClO_4$, HBr, HNO_3 etc. are all strong acids in water as shown below :

$$\begin{aligned} \mathrm{HNO_3 + H_2O} &\longrightarrow \mathrm{H_3O^+ + NO_3^-} \\ \mathrm{HClO_4 + H_2O} &\longrightarrow \mathrm{H_3O^+ + ClO_4^-} \\ \mathrm{HBr + H_2O} &\longrightarrow \mathrm{H_3O^+ + Br^-} \end{aligned}$$

These reactions indicate that the equilibrium is shifted almost completely to the right side as their dissociation in water is complete; hence single arrows have been used. Under these conditions, therefore, we cannot differentiate as to which is stronger and which is weaker amongst them. The reason is obvious since water is a strong base for all these acids. Water reduces the strength of all these acids to the same level and these are all called strong acids in water. However, the situation will change if we dissolve all these acids in another solvent which is a weaker base than water, for instance, formic acid. The order of strength found with this base is : perchloric acid > nitric acid > hydrobromic acid. At first the statement sounds ridiculous since we are calling formic acid a base, but a careful examination will clarify this confusion. There is no doubt that formic acid has a proton which can be given off to water;

therefore it is classified as an acid. But, it can also accept a proton from a stronger acid and can thus behave like a base towards a strong acid, as shown by the following reaction :

$$HCOOH + H_2SO_4 \rightleftharpoons HSO_4^- + HCOOH_2^+$$

Thus, Brφnsted definition of acids and bases is much wider than Arrhenius concept.

15.2.3 Lewis Acids and Bases

There are a number of reactions which resemble acid-base neutralisation reactions but where protons are not involved. Obviously, Arrhenius or Brφnsted concepts cannot be utilised for such reactions. Lewis defined acids and bases in a different fashion which has a wider application. According to Lewis, an acid is an electron pair acceptor and a base is an electron pair donor. In other words, any substance which can accept a pair of electrons is an acid and a substance which donates a pair of electrons is a base. A few examples of Lewis acid-base reactions are :

$$BF_3 + NH_3 \rightleftharpoons BF_3NH_3$$
$$H^+ + NH_3 \rightleftharpoons NH_4^+$$
$$H^+ + OH^- \rightleftharpoons H_2O$$

Brφnsted bases like OH^- or NH_3 in the above reactions are also Lewis bases because they react with proton by donating electrons; but Lewis acid is not necessarily Brφnsted acid since Brφnsted acid must contain a proton which can be transferred to a base whereas Lewis acid does not have such a condition.

Though for the sake of simplicity, we write H^+ ion in equation, free H^+ ion cannot exist in solution. It is always associated with solvent molecules. In aqueous solution we represent it by H_3O^+ but it has been shown that it exists as $H_9O_4^+$.

Metal ions in complexes accept electron pairs and act as Lewis acids.

In our discussions, we shall be primarily concerned with aqueous solutions which involve proton transfer and therefore, Lewis concepts are not of so much use in the present context. However, for the sake of completeness and the wide application of Lewis concept, this has been included here.

SAQ 1

Explain with example, the difference between Lewis and Brφnsted acids.

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15.3 IONIC EQUILIBRIA IN WEAK ACIDS AND BASES

Even in dilute solutions, weak electrolytes are dissociated to a very small extent and are never completely dissociated. Thus, for weak acids and bases, the ions produced on dissociation are in equilibrium with the undissociated molecules in solution and the law of mass action can be applied to such an equilibrium. For simplicity, we shall make use of Eq. 14.30 (refer to the Unit 14 on Chemical Equilibria). The equilibrium constants for the dissociation of acids and bases are expressed by the symbols K_a and K_b, respectively. These equilibrium constants, K_a and K_b, are called dissociation constants of acids and bases.

15.3.1 Weak Acids

If HA represents any weak acid, we can write the dissociation reaction as,

$$HA \rightleftharpoons H^+ + A^- \qquad \text{... (15.1)}$$

We have omitted writing H_2O in Eq. 15.1 for the simple reason that the concentration of water remains constant even upto very high concentration of the salt.

and the corresponding dissociation constant expression as,

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (15.2)$$

If the initial concentration of the acid is c_0 and α is the degree of dissociation, then the equilibrium concentrations would be,

	$HA \rightleftharpoons$	H^+ +	A^-
Initial concentration	c_0		
Equilibrium concentration	$(1-\alpha)\,c_0$	αc_0	αc_0

Substituting these values in Eq. 15.2, we get,

$$K_a = \frac{(\alpha c_0)(\alpha c_0)}{(1-\alpha)c_0}$$

$$\text{or } K_a = \frac{\alpha^2 c_0}{1-\alpha} \qquad \text{... (15.3)}$$

Application of Eq. 15.3 can be seen from the following examples.

Example 1

At 298 K, a 0.100 M solution of acetic acid is 1.34% ionised. Calculate the ionisation constant of acetic acid.

K_a and K_b are usually expressed as dimensionless quantities.

Solution

Since $\alpha = 0.0134$, $[H^+] = \alpha c_0 = 0.0134 \times 0.100$ M

$= 0.00134 \text{ M} = [CH_3COO^-]$;

also $[CH_3COOH] = (1 - 0.0134) \times 0.100 \text{ M} = 0.09866$ M

$$\therefore K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(0.00134)^2}{0.09866}$$

or $K_a = 1.82 \times 10^{-5}$

Example 2

Calculate the concentration of H^+ ions in a solution of 1.0 M acetic acid at 298 K ($K_a = 1.8 \times 10^{-5}$).

Solution

As per Eq. 15.1, we can write,

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

Equilibrium concentration $c_0(1-\alpha)$ $\quad c_0\alpha \quad c_0\alpha$

Initial concentration of acetic acid, $c_0 = 1.0$ M.

$\therefore [H^+] = c_0\alpha$ M

$= \alpha$ M

The value of α can be found out by substituting K_a and c_0 values in Eq. 15.3.

$$1.8 \times 10^{-5} = \frac{\alpha^2}{1-\alpha}$$

Solving for α, we get a value of 4.2×10^{-3}; the other value being negative, has no physical significance.

For a monobasic acid like acetic acid, $[H^+] = [\text{acid}] \times$ degree of dissociation

The simplification, $K_a = \alpha^2 c_0$ is valid only when, α is small compared to 1 and may be neglected when subtracted from 1.

Hence, $[H^+]$ in 1 M acetic acid $= \alpha$ M

$= 4.2 \times 10^{-3}$ M

Eq. 15.3 can be simplified further if the degree of dissociation is very small, i.e., if $\alpha << 1$, then $K_a = \alpha^2 c_0$

Multiplying both sides by c_0, we get,

$K_a.c_0 = \alpha^2 c_0^2$

or $c_0\alpha = \sqrt{K_a c_0}$

$$\text{or } [H^+] = \sqrt{K_a c_0} \qquad (15.4)$$

Remember that in deriving Eq. 15.4, we have made two assumptions. First that the degree of dissociation is much smaller than unity and secondly that water which has been used as a solvent has no effect on the equilibrium of the acid.

15.3.2 Weak Bases

For a weak base, BOH, we can write the equations as,

$$BOH \rightleftharpoons B^+ + OH^- \qquad \text{... (15.5)}$$

$$\text{and } K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad \text{... (15.6)}$$

If c_0 is the initial concentration of the base and α is the degree of dissociation, then,

$$K_b = \frac{(\alpha c_0)(\alpha c_0)}{(1-\alpha)c_0} = \frac{\alpha^2 c_0}{1-\alpha} \qquad \text{... (15.7)}$$

$$\text{Also, } [OH^-] = \alpha c_0 = \sqrt{K_b c_0} \; \because \alpha << 1 \qquad \text{... (15.8)}$$

15.3.3 Polyprotic Acids

Those acids which contain more than one hydrogen atom per molecule and can release proton in more than one step are called polyprotic acids. Each ionisation step is associated with an equilibrium constant.

Consider the case of phosphoric acid which is a triprotic acid. It is also called a tribasic acid implying thereby that each mole of the acid can neutralise three moles of a base. The dissociation reactions are written as.

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad \ldots (15.9)$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad \ldots (15.10)$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad \ldots (15.11)$$

Each of these steps of dissociation is connected with an equilibrium constant which can be represented by,

$$K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \qquad \ldots (15.12)$$

$$K_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \qquad \ldots (15.13)$$

and

$$K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \qquad \ldots (15.14)$$

The actual values for the three equilibrium constants have been found to be $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$ and $K_3 = 1.0 \times 10^{-12}$ which follow a decreasing order. This is to be expected since an undissociated molecule, H_3PO_4, can lose its proton more easily than the negatively charged $H_2PO_4^-$ ion, which is turn, can give off its proton more easily than a double-negatively charged HPO_4^{2-} ion. Hence, in a solution of phosphoric acid. the predominant species will be H_3PO_4, H^+ and $H_2PO_4^-$ with lesser amounts of HPO_4^{2-} and still less of PO_4^{3-}.

Another common example is H_2SO_4 which dissociates as,

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-; \quad K_1 = \frac{[H^+][HSO_4^-]}{[H_2SO_4]} = 1.0 \times 10^3$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}; \quad K_2 = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = 1.3 \times 10^{-2}$$

As a test of the understanding of the above concepts, answer the following SAQ.

SAQ 2

Calculate the concentration of OH^- ions in a solution of 1.0 M NH_4OH at 298 K ($K_b = 1.8 \times 10^{-5}$).

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15.4 IONIC PRODUCT OF WATER

Water is the most commonly used solvent and it is amphoteric in character. The dissociation of water can be represented as,

An amphoteric substance can act both as an acid and as a base.

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \ldots (15.15)$$

$$\text{or } 2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad \ldots (15.16)$$

Although Eqs. 15.15 and 15.16 are representations of the same equilibrium, Eq. 15.16 is a better representation in the sense that a free proton having a high charge density and extremely small size is incapable of free existence in solution and, therefore, gets **attached to** a molecule of water. However, since our calculations on equilibrium constant will not be different in case of either representation, for simplicity sake, we represent the water equilibrium by Eq. 15.15 and the equilibrium constant is written as,

$$K = \frac{[H^+][OH^-]}{[H_2O]} \qquad \text{... (15.17)}$$

$$\text{or } K[H_2O] = [H^+][OH^-] \qquad \text{... (15.18)}$$

Mass of 1 dm^3 of water at 298 K is found to be 0.998 kg. Mass of 1 mole of H_2O is 0.018 kg. Hence, the number of moles of H_2O present in 0.998 kg or 1 dm^3 is

$$55.4 \left(= \frac{0.998 \text{ kg}}{0.018 \text{ kg}} \right)$$

which is called the molarity of water.

In pure water the concentration of H_2O molecules is approximately 55.4 M and since the dissociation of H_2O is negligibly small in comparison with its concentration, we can safely assume that the concentration of H_2O at equilibrium is a constant quantity. Thus, $K[H_2O]$ in Eq. 15.18 can be replaced by a new constant, K_w, known as the ionic product of water. Thus,

$$K_w = [H^+][OH^-] \qquad \text{... (15.19)}$$

Experimental determination gives a value of 1.0×10^{-14} for K_w at 298 K. Hence,

$$1.0 \times 10^{-14} = [H^+][OH^-] \qquad \text{... (15.20)}$$

Since the amount of H^+ and OH^- produced by the dissociation of pure water is equal, concentration of each ion in solution is given by,

$$[H^+] = [OH^-] = 1.0 \times 10^{-17} \qquad \text{... (15.21)}$$

$$\text{or } [H^+] = \sqrt{K_w} \text{ (in pure water)} \qquad \text{... (15.22)}$$

In the next section, we shall discuss pH scale which is convenient in expressing the H^+ ion concentration of solutions. Like any equilibrium constant, K_w also depends on temperature.

15.5 pH SCALE

Consider the equilibrium of water as given by Eq. 15.17,

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

Suppose that we add a small quantity of an acid to water, thereby increasing the concentration of H^+ ions at equilibrium. The equilibrium will immediately shift back to oppose the effect of this increase by the combination of the added H^+ ions with some OH^- ions to form undissociated water till Eq. 15.15 is satisfied. Once the equilibrium is reestablished, the concentration of the hydrogen ion will be more than the concentration of the hydroxyl ion in solution. Hence, at 298 K, whenever the concentration of hydrogen ion in water is greater than 1.0×10^{-7} M, we call the solution to be acidic and whenever it is less than 1.0×10^{-7} M, we call it a basic solution. Instead of expressing these small concentrations as negative powers of 10, we can state them more conveniently and as a small number by expressing them in terms of their negative logarithm. Hence, instead of writing H^+ ion concentration as 1.0×10^{-7} M we write it as $-\log[1.0 \times 10^{-7}]$ or simply 7. This number we denote by a symbol pH (small letter, p followed by capital letter, H). Thus,

$$pH = -\log[H^+] \qquad \text{... (15.23)}$$

$$\text{or } [H^+] = 10^{-pH} \qquad \text{... (15.24)}$$

where H^+ ion concentration is expressed in mol dm^{-3}. The concept of negative logarithm can be used for defining the concentration of other ions also. For example, pOH represents the concentration of OH^- ion in solution and pM represents the concentration of the metal ion, M, in solution.

Example 3

Find the concentration of H^+ ions of a solution for which pH value is 4.5.

Solution

Using the equation,

$pH = -\log[H^+]$

we get, $4.5 = -\log[H^+]$

or $\log[H^+] = -4.5$

i.e. $[H^+] = 10^{-4.5}$ M

$= 10^{(-5+0.5)}$ M ... Step (i)
$= 10^{0.5} \times 10^{-5}$ M ... Step (ii)
$= 3.2 \times 10^{-5}$ M ... Step (iii)

To calculate 10^x, see antilog of x.

(i) When x is positive, see antilog straight away.
e.g. (1) $10^{0.5}$ = Antilog of 0.5000 = 3.2
(2) $10^{2.4}$ = Antilog of 2.4 = 2.5×10^2

(ii) When x is negative, follow the steps given below :

Step (i) : The negative exponent (x) is shown as the sum of a negative integer and a positive fraction.

Step (ii) : Write the resultant number as a product of two terms.

Step (iii) : See the antilog of the positive fraction written as power of 10, and multiply this, by 10 raised to the power of negative integer.

These steps are required since while seeing antilogarithm, the mantissa must be positive, although characteristic may be positive or negative. In the light of the above, see Example 3.

Pure water, where H^+ ion and OH^- ion concentration are both equal to 1.0×10^{-7} (at 298 K), will thus have a pH value of 7. An acidic solution means that the pH should be less than 7 and a basic solution should have pH greater than 7.

Let us do a few simple calculations to see quantitatively as to what happens to the self-ionisation equilibrium of water when we add a small quantity of a strong acid to it. Consider a solution containing 0.010 mole of HCl in one dm^3 of water. The concentration of hydrogen ion due to HCl will be 1.0×10^{-2} M. This addition of acid will disturb the water equilibrium and this equilibrium will shift to left so that dissociation of water is suppressed. Thus, the concentration of H^+ ions produced by the self-ionisation of water ($\approx 10^{-7}$ M) is negligible in comparison with the H^+ ion produced by the added acid (10^{-2} M). Hence, the contribution due to water dissociation can be neglected in such a case and the pH of the solution will be 2. The concentration of OH^- ion will then be given by,

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}\ \text{M}$$

or pOH = 12

We can state this in a different way that, in 10^{-2} M acid solution, the concentration of OH^- ion (10^{-12} M in the above example) is less than the concentration of H^+ ion (10^{-2} M) and, the product of the two is always constant, and is equal to 1.0×10^{-14}. This can be expressed as,

$$\text{pH} + \text{pOH} = 14 = -\log K_w \qquad \text{... (15.25)}$$

Thus, in pure water or a dilute solution of an acid or a base, we can express the concentration of H^+ or OH^- by simply stating the pH of the solution. We have also studied that the contribution due to self-ionisation of water is negligible in cases of solution of strong acids and bases as well as of moderately concentrated solutions of weak acids and weak bases. However, dealing with very dilute solutions of weak acids and bases, we cannot neglect the contributions due to self-ionisation equilibrium of water.

To sum up, while calculating $[H^+]$ of an acid,

- $[H^+] = [H^+]$ from acid, if [acid] is far greater than 10^{-6} M.
- $[H^+] = [H^+]$ from acid + $[H^+]$ from water if [acid] is between 10^{-6} and 10^{-8} M.
- $[H^+] = [H^+]$ from water if [acid] is far less than 10^{-8} M.

You try the following SAQs, based on the above concept of pH.

SAQ 3

Calculate the pH of the following solutions :

(a) 1.0×10^{-8} M HCl (b) 1.0×10^{-10} M HCl
(c) 1.0×10^{-10} M NaOH

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15.6 COMMON ION EFFECT

Let us consider the dissociation of a weak acid such as acetic acid,

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

the equilibrium constant for which can be represented as,

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \qquad \text{... (15.26)}$$

$$\text{or } H^+ = K_a \frac{[CH_3COOH]}{[CH_3COO^-]} \qquad \ldots (15.27)$$

Suppose that we add some acetate ions in the form of solid sodium acetate to the above solution. Sodium acetate is added in the solid form so as not to cause any change in the volume of the solution. Sodium acetate being a strong electrolyte will dissociate almost completely to give Na^+ ions and CH_3COO^- ions in solution. The acetate ions so added will disturb the equilibrium of acetic acid. The equilibrium will, therefore, shift to left producing more of undissociated acetic acid in order to counteract the effect of added acetate ions according to Le Chatelier's principle. The net result is that the dissociation of the acid has been suppressed by the addition of a common ion (acetate ion in the present case) at equilibrium. Thus any ion which is involved in a chemical equilibrium and comes from two different sources in solution is known as 'common ion' and its effect finds great use in the study of buffer solutions (sec. 15.7) and the solubility of sparingly soluble salts (sec. 15.11).

On the basis\of the above discussion, answer the following SAQ.

SAQ 4

Addition of NH_4Cl to NH_4OH results in the decrease of OH^- ion concentration. Explain.

15.7 BUFFER SOLUTIONS

A careful examination of Eq. 15.27 reveals that the hydrogen ion concentration (or the pH of the solution) shall have a constant value equal to K_a (or pK_a), if the concentrations of acetate ions and the undissociated acetic acid become equal to each other. In order to find how this condition can be achieved and what are its uses, let us consider a 1.0 M acetic acid solution for which $K_a = 1.8 \times 10^{-5}$. We can write,

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$\text{or } 1.8 \times 10^{-5} = \frac{[H^+]^2}{[CH_3COOH]}$$

since, $[H^+] = [CH_3COO^-]$

Assuming that the amount of acetic acid dissociated is negligible in comparison to the initial concentration of acetic acid (1.0 M), we can write the concentration of undissociated acetic acid as, 1.0 M.

$$\therefore\ [H^+]^2 = 1.8 \times 10^{-5} \times 1.0\ M^2$$

$$\text{or } [H^+] = \sqrt{1.8 \times 10^{-5}}\ M = 4.2 \times 10^{-3}\ M$$

or pH = 2.38; i.e., the pH of 1.0 M acetic acid is 2.38.

To this solution if we add enough of solid sodium acetate to make it 1.0 M in acetate ion concentration, the dissociation of acetic acid will be further suppressed due to common ion effect. Thus, the concentration of acetate ion arising out of the dissociation of acetic acid is negligible in comparision with that supplied by sodium acetate. Hence, we can assume the concentration of acetate ion in solution to be 1.0 M. Similarly, if the dissociation of acetic acid is negligibly small, the concentration of the undissociated acetic acid, $[CH_3COOH]$, can be taken as 1.0 M. Substituting these values in Eq. 15.26, we get,

$$1.8 \times 10^{-5} = \frac{[H^+][1.0]}{[1.0]} = [H^+]$$

or pH = 4.74; i.e., a solution which has 1.0 M acetic acid and 1.0 M sodium acetate has a pH of 4.74.

A solution containing a weak acid and its conjugate base or a weak base and its conjugate acid is called a buffer solution. It resists the change in pH on addition of acids, bases or on dilution.

Such a solution of a weak acid and its salt or a weak base and its salt is known as buffer solution and it has an advantage of maintaining the pH of the solution almost constant even if small quantities of strong acids or bases are added to it. Let us see why this is so.

Assume that to the above solution of acetic acid and sodium acetate, known as acetate buffer, we add hydrochloric acid such that its concentration in the solution becomes 0.01 M. As a result of this, 0.01 M H^+ ions will react with 0.01 M acetate ions to form 0.01 M undissociated acetic acid. Thus, the concentration of the undissociated acetic acid will increase from 1.0 M to 1.01 M. The concentration of acetate ion will correspondingly decrease by 0.01 M and its concentration at equilibrium will be (1.0 M − 0.01 M =) 0.99 M. Substituting these values in Eq. 15.27, we get.

$$[H^+] = \frac{1.8 \times 10^{-5} \times 1.01}{0.99}$$

$$= 1.83 \times 10^{-5}$$

∴ pH = 4.74; hence, we find that by the addition of 0.01 M HCl, there is no change in the pH of the solution.

If the same amount of HCl is added to water, the pH of the solution changes from 7 to 2.

Thus, for any weak acid, HA, in presence of its salt, say, NaA, the following equations can be written :

$$HA \rightleftharpoons H^+ + A^-$$
$$NaA \rightleftharpoons Na^+ + A^-$$

Using Eq. 15.2, we can write,

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\text{or } [H^+] = K_a \frac{[HA]}{[A^-]}$$

The concentration of A^- is mainly due to the dissociation of the salt and negligible due to the dissociation of the acid. Similarly, the concentration of the undissociated acid is the same as the original concentration, since the amount dissociated is negligible.

Hence we can write, $[A^-] = [\text{salt}]$ and $[HA] = [\text{Acid}]$

$$\text{or } [H^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]} \qquad \dots (15.28)$$

By taking logarithms on both l.h.s. and r.h.s. of Eq. 15.28,

$$\log [H^+] = \log K_a + \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

Hence, $-\log [H^+]$

$$= -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

i.e., $pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

This expression is known as Henderson's equation.

In the case of a buffer of a weak base and its salt, we can write an equation similar to Eq. 15.28 as,

$$[OH^-] = K_b \frac{[\text{Base}]}{[\text{Salt}]} \qquad \dots (15.29)$$

For an effective buffer, the ratio of the concentration of the acid (or base) to the concentration of the salt should be between 1/10 and 10/1. Substituting, these values in Eq. 15.28, we get Eqs. 15.30 and 15.31.

Case (i) : $\frac{[\text{Acid}]}{[\text{Salt}]} = \frac{1}{10}$

Using Eq. 15.28, $[H^+] = K_a \frac{1}{10}$

Taking logarithm, $\log [H^+] = \log K_a + \log 1/10$

$$= \log K_a - 1$$

or $-\log [H^+] = -\log K_a + 1$

i.e., $pH = pK_a + 1 \qquad \dots (15.30)$

Case (ii) : $\frac{[\text{Acid}]}{[\text{Salt}]} = 10$

Again using Eq. 15.28, $[H^+] = K_a.10$

Following the steps shown in case (i) we get,

$pH = pK_a - 1 \qquad \dots (15.31)$

Thus, pH is held within a range of unity on either side of pK_a.

Buffers play an important role in nature. For example, blood contains H_2CO_3/HCO_3^- buffer that maintains the pH at 7.4; in the absence of a buffer, the sudden changes in the pH of blood or other cell fluids could cause severe damage to the system. Another example is that the oceans are maintained at about pH = 8.4 by a complex buffering action involving silicates and bicarbonates. In the absence of buffering action, sea-life could be severely affected.

In industrial processes like electroplating, paper manufacturing, alcohol brewing, leather tanning etc. most of the chemical reactions are pH controlled. Applications of buffers in analytical chemistry are innumerable. You should try the following SAQ which is based on the above discussion.

SAQ 5

A solution is prepared by adding 2.05×10^{-3} kg anhydrous sodium acetate to 0.10 dm^3 of 0.10 M HCl solution. What is the pH of the solution?

....

....

....

15.8 HYDROLYSIS

So far we have considered two equilibria—one, of the dissociation of weak acids and bases and the other one, of the self-ionisation of water—and made an assumption that the water equilibrium does not influence the acid-base equilibria since the dissociation of water is negligibly small. We now treat a situation where water equilibria plays an important role The process in which, water not only acts as a solvent but reacts with the solute, is known as hydrolysis.

Suppose we dissolve sodium acetate in water; this being a strong electrolyte, would dissociate completely providing Na^+ ions and CH_3COO^- ions in solution.

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

Acetate ions so produced react immediately with water giving undissociated acetic acid and hydroxyl ions according to the equation,

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \qquad \text{... (15.32)}$$

Since there are free OH^- ions in the solution, it becomes basic.

The question arises as to what happens to the Na^+ ions in solution. The answer is that they do not react with water. Let us see why it is so. For the sake of argument, let us imagine that Na^+ ions also react with water in the same fashion as acetate ion. Accordingly we can write,

$$Na^+ + H_2O \rightleftharpoons NaOH + H^+$$

However, NaOH so produced, will dissociate almost completely giving OH^- ions.

$$NaOH \longrightarrow Na^+ + OH^-$$

The OH^- and H^+ ions would be equal in amount and, these two will produce undissociated water. In other words, Na^+ ions will not affect the water equilibrium.

Salts like sodium acetate can be thought of as a product of the reaction between a weak acid, CH_3COOH, and a strong base, NaOH.

$$NaOH + CH_3COOH \rightleftharpoons CH_3COONa + H_2O$$

Thus our conclusion would be that the salts of a weak acid and a strong base, when dissolved in water, will produce a basic solution.

Let us consider the case of a salt of a weak base and a strong acid like NH_4Cl. Similar to the previous example, in this case only NH_4^+ hydrolyses as:

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

which produces a weak base and excess of hydrogen ions in solution, thus rendering the solution acidic. Hence, we can say that the salt of a weak base and a strong acid will produce an acidic solution.

In case of salts of a weak acid and a weak base, it is not possible to predict qualitatively whether the solution will be acidic or basic. Consider a salt like ammonium acetate, CH_3COONH_4, where both the cation and anion can hydrolyse according to the equations:

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

or $$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Hydrolysis of one ion gives hydrogen ions, whereas that of the other ion gives hydroxyl ions in solution. Therefore, the pH of the solution will depend on the extent of the hydrolysis of the two ions. If NH_4^+ hydrolyses to a greater extent than CH_3COO^- ion, the solution will be acidic and, if the reverse is true, then the solution will be basic. If the extent of hydrolysis is exactly equal, then the solution should be neutral as if no hydrolysis is taking place.

The extent of hydrolysis is given by the equilibrium constant of the hydrolysis reaction which is known as hydrolysis constant. Let us consider the equilibrium represented by Eq. 15.32.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$K = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]\,[H_2O]}$$

Since the concentration of water remains constant, we can write,

$$K_h = K[H_2O] = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} \qquad \text{... (15.33)}$$

where K_h is known as hydrolysis constant.

We can find another expression for K_h using the following equilibria.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-;\ K_a = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]} \qquad \text{... (15.34)}$$

and $$H_2O \rightleftharpoons H^+ + OH^-;\ K_w = [H^+]\,[OH^-] \qquad \text{... (15.35)}$$

From Eqs. 15.34 and 15.35 we get,

$$\frac{K_w}{K_a} = [H^+]\,[OH^-] \times \frac{[CH_3COOH]}{[H^+]\,[CH_3COO^-]} = \frac{[OH^-]\,[CH_3COOH]}{[CH_3COO^-]} \qquad \text{... (15.36)}$$

Comparing Eqs. (15.33) and (15.36) we can write,

$$K_h = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} = \frac{K_w}{K_a} \qquad \text{... (15.37)}$$

Similarly for the hydrolysis of an ion like NH_4^+ which produces a weak base, we can write,

$$K_h = \frac{K_w}{K_b} \qquad \text{... (15.38)}$$

Also, it is possible to show that for the hydrolysis of a salt of a weak acid and weak base,

$$K_h = \frac{K_w}{K_a K_b} \qquad \text{... (15.39)}$$

Thus, we notice that the hydrolysis constant is directly related to K_a or K_b of the weak acid or weak base produced.

Let us now find out the relationship between the hydrolysis constant and the degree of hydrolysis for the reaction given by Eq. 15.32. Suppose that the concentration of sodium acetate is c_0 and its degree of hydrolysis is 'α'. The equilibrium concentrations of OH^- and CH_3COOH will each be $c_0\alpha$ and that of CH_3COO^- will be $(1-\alpha)\,c_0$.

$$\begin{array}{lcccc} & CH_3COO^- + H_2O & \rightleftharpoons & CH_3COOH + & OH^- \\ \text{Equilibrium concentration} & (1-\alpha)\,c_0 & & c_0\alpha & c_0\alpha \end{array}$$

Substituting these values in Eq. 15.33, we get,

$$K_h = \frac{(c_0\alpha)\,(c_0\alpha)}{(1-\alpha)\,c_0} = \frac{c_0\alpha^2}{(1-\alpha)} \qquad \text{... (15.40)}$$

If the degree of hydrolysis is small in comparison to unity, we can write,

$$K_h = c_0\alpha^2 \qquad \text{... (15.41)}$$

or $$c_0 . K_h = (c_0\alpha)^2$$

or $$c_0\alpha = \sqrt{K_h c_0}$$

$$\text{or } [\mathrm{OH}^-] = \sqrt{K_h c_0} \qquad \ldots (15.42)$$

$$\text{or } [\mathrm{OH}^-] = \sqrt{\frac{K_w}{K_a} c_0}, \text{ Since } K_h = \frac{K_w}{K_a} \qquad \ldots (15.43)$$

hence,

$$[\mathrm{H}^+] = \frac{K_w}{[\mathrm{OH}^-]} = \frac{K_w}{\sqrt{\frac{K_w}{K_a} c_0}} = \left(\frac{K_a K_w}{c_0} \right)^{1/2} \qquad \ldots (15.44)$$

Taking logarithms and multiplying by -1, we get,

$$\text{or } -\log[\mathrm{H}^+] = -\frac{1}{2} \log \left(\frac{K_a K_w}{c_0} \right)$$

$$\left[\text{Since } \frac{1}{2} \log \left(\frac{K_a K_w}{c_0} \right) = \frac{1}{2} \log K_a + \frac{1}{2} \log K_w - \frac{1}{2} \log c_0 \right]$$

$$-\log [\mathrm{H}^+] = -\frac{1}{2} \log K_a - \frac{1}{2} \log K_w + \frac{1}{2} \log c_0$$

$$\text{or } \mathrm{pH} = \frac{1}{2} \mathrm{p}K_a + \frac{1}{2} \mathrm{p}K_w + \frac{1}{2} \log c_0 \qquad \ldots (15.45)$$

Example 4

In 0.10 M solution of sodium acetate, calculate

i) K_h

ii) the degree of hydrolysis (α)

iii) $[\mathrm{OH}^-]$

iv) pH at 298 K.

At 298 K, $K_w = 1.0 \times 10^{-14}$ and K_a for acetic acid $= 1.8 \times 10^{-5}$

Solution

i) Using Eq. 15.37, $K_h = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$

ii) Using Eq. 15.41, $\alpha = \sqrt{\frac{K_h}{c_0}}$

$= \sqrt{5.6 \times 10^{-9}}$

$= 7.5 \times 10^{-5}$

iii) Using Eq. 15.42, $[\mathrm{OH}^-] = \sqrt{K_h c_0}$

$= \sqrt{5.6 \times 10^{-11}}$

$= 7.5 \times 10^{-6}$ M

iv) $\mathrm{p}K_a = -\log_{10} 1.8 \times 10^{-5} = 4.74$

$\mathrm{p}K_w = 14$

$\log c_0 = \log 0.10 = -1.0$

Using Eq. 15.45, $\mathrm{pH} = (\frac{1}{2} \times 4.74) + (\frac{1}{2} \times 14) + (\frac{1}{2} \times (-1.0)) = 8.87$

Hence, K_h, α and pH values of a solution of the salt of a weak acid and strong base like sodium acetate can be calculated once c_0, K_a and K_w values are known at a particular temperature.

Now that we have seen the importance of pH in the study of ionic equilibria, we shall turn our attention to a group of compounds for which colour depends on the pH of the solution. They are called indicators and are frequently used in the experimental studies of ionic equilibria. Before proceeding to the next section, answer the following SAQ which is similar to the derivation of Eq. 15.45.

SAQ 6

Show that for the hydrolysis of a salt of a strong acid and a weak base, the pH of the solution is given by

$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log c_0$$

....

....

....

15.9 INDICATORS

There are a number of organic substances (dyes) for which the colour depends on the concentration of hydrogen ion in solution. To put it simply, the pH of the solution governs the colour of the dye. For example, phenolphthalein is an organic compound and it shows a pink colour in basic medium but becomes colourless in acid medium. Such substances are either weak acids or weak bases and when dissolved in water, their dissociated form acquires a colour different from that of the undissociated form. If the concentration of the undissociated form is more in solution we see one colour; on the other hand, if the concentration of the dissociated form is more, we see another colour. The concentration of the dissociated or undissociated form depends on the pH of the solution. Further the dissociation of the indicator is so small that it does not affect the pH of the solution. The equilibrium of an indicator which is a weak acid can be represented by,

$$\underset{\text{Colour I}}{HIn} \rightleftharpoons H^+ + \underset{\text{Colour II}}{In^-} \qquad \text{... (15.46)}$$

when HIn is the undissociated form of the indicator and In^- is the dissociated form. These two forms have different colours I and II, respectively. The pH of the solution determines the ratio of [HIn] to $[In^-]$ in the solution. We can write the equilibrium constant expression for the reaction corresponding to Eq. 15.46 as,

$$K = \frac{[H^+][In^-]}{[HIn]}$$

$$\text{or } \frac{[HIn]}{[In^-]} = \frac{[H^+]}{K} \qquad \text{... (15.47)}$$

The human eye can detect the change in colour if the ratio of the two forms of indicator ranges between 0.1 to 10. Thus, in order to use the indicator effectively in this region, we should have a solution for which H^+ ion concentration is very near to K value of the indicator. It is for this reason that we use different indicators for different systems. The list of some common indicators and the pH ranges in which these are useful are given in Table 15.2.

Table 15.2 : pH Range of Indicators

Indicator	Acid	Alkaline	pH range
Litmus	Red	Blue	5.0 – 8.0
Phenolphthalein	Colourless	Pink	8.3 – 10.0
Methyl Orange	Red	Yellow	2.1 – 4.4
Methyl Red	Red	Yellow	4.2 – 6.3
Bromothymol Blue	Yellow	Blue	6.0 – 7.6

The maximum use of indicators is found in the titrations of acids and bases in analytical chemistry.

15.10 SOLUBILITY AND SOLUBILITY PRODUCT

In Unit 10 you have studied regarding solubility and saturated solutions. One of the most useful applications of chemical equilibria studies is on sparingly or slightly soluble salts like AgCl, CaF_2, Ag_2CO_3, $BaCrO_4$ etc. We shall first derive a relationship between solubility of a salt and a quantity called solubility product. Then we shall study the applications of this relationship to different systems. Let us consider a salt with a general formula A_xB_y, where x

and y are the number of moles of ions A and B, respectively present in one mole of the salt.

e.g., i) for AgCl, $x=1, y=1$.
ii) for Ag_2CrO_4, $x=2, y=1$.
iii) for CaF_2, $x=1, y=2$.

In a saturated solution, there will an equilibrium between the sparingly soluble solid A_xB_y and its ions A and B in solution which can be expressed as given in Eq. 15.48. For the sake of simplicity, we are omitting letters such as *s, aq,* etc., in all such equilibria.

$$A_xB_y \rightleftharpoons xA + yB \qquad \text{... (15.48)}$$

If the solubility is 1×10^{-5} mol dm^{-3} or less, the salt is described as sparingly soluble or insoluble.

Water is not included in Eq. 15.48, because it is neither used up nor produced in the reaction.

For the present moment, we shall neglect counting y^+ charges on the cation A and, x^- charges on the anion B. The equilibrium constant for the reaction given by Eq. 15.48 can be written as,

$$K = \frac{[A]^x [B]^y}{[A_xB_y]} \qquad \text{... (15.49)}$$

$[A_xB_y]$ represents the concentration of the solid A_xB_y; this quantity is constant. Hence, we can introduce a new constant K_{sp} in place of $K[A_xB_y]$, which is known as solubility product constant or simply solubility product. Thus Eq. 15.49 can be written as

$$K_{sp} = [A]^x [B]^y \qquad \text{(15.50)}$$

Expressed in words, Eq. 15.50 says that the solubility product of a saturated solution of a salt is equal to the product of the concentration of ions raised to suitable powers.

Let S mol·dm^{-3} be the solubility of the salt. Then the corresponding concentrations of cation and anion are xS mol dm^{-3} and yS mol dm^{-3}, respectively. Substituting these values of concentration in Eq. 15.50 we get,

$$K_{sp} = (xS)^x (yS)^y$$

$$\text{or } K_{sp} = x^x \cdot y^y \cdot S^{x+y} \qquad \text{... (15.51)}$$

Conductance method for the determination of the solubility of a sparingly soluble salt has been discussed in Unit 16 of this block. The determination of K_{sp} based on emf measurements is discussed in Unit 17.

Let us apply Eq. 15.51 to the sparingly soluble salts such as AgCl, CaF_2 and Ag_2CO_3.

In case of AgCl, $x=1, y=1$.

Hence, Eq. 15.51 gives

$$K_{sp} = S^2 \qquad \text{... (15.52)}$$

Let us examine an alternate method also.

The equilibria between solid AgCl and its ions can be represented as

$$AgCl \rightleftharpoons Ag^+ + Cl^- \qquad \text{... (15.53)}$$

For this reaction, $K = \frac{[Ag^+][Cl^-]}{[AgCl]}$

or $K[AgCl] = [Ag^+][Cl^-]$
or $K_{sp} = [Ag^+][Cl^-]$ ... (15.54)

If the solubility of AgCl is S mol dm^{-3}, then the concentration of Ag^+ and Cl^- ions in solution will each be equal to S mol dm^{-3}. Substitution in Eq. 15.54 gives,
$K_{sp} = S \cdot S = S^2$.

Example 5
At 298 K, the solubility of silver chloride is 1.37×10^{-5} M. Calculate its solubility product.

Solution
Using Eq. 15.52, $K_{sp} = S^2 = (1.37 \times 10^{-5})^2 = 1.88 \times 10^{-10}$

In case of CaF_2, $x=1, y=2$; substituting these values in Eq. 15.51 we get,
$K_{sp} = 1.2^2.S^{(1+2)}$
$K_{sp} = 4S^3$ ... (15.55)

Just like the previous case, the alternative method would be to write the equilibrium between solid CaF_2 and its ions as :

$$CaF_2 \rightleftharpoons Ca^2 + 2F^- \qquad \text{... (15.56)}$$

and for this reaction, $K_{sp} = \frac{[Ca^{2+}][F^-]^2}{[CaF_2]}$

or $K_{sp}[CaF_2] = [Ca^{2+}][F^-]^2$

or $K_{sp} = [Ca^{2+}][F^-]^2$; ... (15.57)

If S is the solubility of CaF_2, then

$[Ca^{2+}] = S$, and $[F^-] = 2S$

substituting these values in Eq. 15.57 we get,

$K_{sp} = S(2S)^2$

or $K_{sp} = 4S^3$

which is the same as we got in Eq. 15.55. As yet another example, let us consider the equilibrium,

$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$

where, $K_{sp} = [Ag^+]^2 [CO_3^{2-}]$

If S is the solubility of Ag_2CO_3, then $[Ag^+] = 2S$ and $[CO_3^{2-}] = S$.

Substituting the proper values, once again we get,

$K_{sp} = 4S^3$

We can get the same result by substituting, $x = 2$ and $y = 1$ in Eq. 15.51.

Finally, let us consider the equilibrium :

$Fe_2S_3 \rightleftharpoons 2Fe^{3+} + 3S^{2-}$

where $x = 2$ and $y = 3$, If S is the solubility of Fe_2S_3, then,

$K_{sp} = 2^2.3^3.S^{2+3}$

or $K_{sp} = 4.27.S^5$

or $K_{sp} = 108\ S^5$

Using the above ideas, answer the following SAQ.

SAQ 7

At 298 K, the solubility product of Bi $(OH)_3$ is 4.0×10^{-31}. Calculate its solubility.

15.11 COMMON ION EFFECT AND THE SOLUBILITY OF A SPARINGLY SOLUBLE SALT

We have already seen that the solubility of AgCl in pure water is 1.37×10^{-5} M and its K_{sp} is equal to 1.88×10^{-10}. Let us now proceed to find out what will happen to the solubility of AgCl if it is dissolved in a solution containing Ag^+ ions. A qualitative answer to this question can be easily found on the basis of Le Chatelier principle. When the concentration of Ag^+ ion is increased, the equilibrium described by Eq. 15.53 will shift towards left forming more of solid AgCl in order to oppose the effect of the increase in concentration of Ag^+ ion. Thus there will be a decrease in the solubility of AgCl in presence of a common ion such as Ag^+ as compared to that in pure water. Let us arrive at expressions useful in calculating the solubility of salts in presence of common ions.

For AgCl, $K_{sp} = S^2$ and $[Ag^+] = [Cl^-] = S$, only if both the ions originate from the dissolution of AgCl in a solvent.

Solubility of silver chloride in presence of silver nitrate

Assume that silver chloride is dissolved in a solution containing c mol dm^{-3} of $AgNO_3$. In solution, then, there will be Ag^+, Cl^- and NO_3^- ions present. The Cl^- ions in solution are provided by the dissolution of AgCl in water only. However, there are two sources for the presence of Ag^+ ions in solution, one is from the dissolution of AgCl and the other from $AgNO_3$. A solution of c molar concentration of $AgNO_3$ will provide c mol dm^{-3} of Ag^+ ions in the solution. Assuming this contribution to be much larger in comparison with Ag^+ ion concentration due to dissolved AgCl, we can write,

There are two assumptions.

(i) sparingly soluble salts in solutions are completely dissociated

(ii) all strong electrolytes are completely dissociated in solution.

$[Ag^+] = c$

Substituting this value in Eq. 15.54, we get

$K_{sp} = c[Cl^-]$

$$\text{or } [Cl^-] = \frac{1.88 \times 10^{-10}}{c} \qquad \ldots (15.58)$$

The chloride ion concentration must be equal to the number of moles of AgCl dissolved in 1 dm^3 of solution (or equal to its solubility). Hence,

$$S = \frac{1.88 \times 10^{-10}}{c} \qquad \ldots (15.59)$$

Example 6

Find the solubility of AgCl in 1 M $AgNO_3$ solution and compare with its solubility in water.

Solution

The solubility of AgCl(s) in presence of 1 M $AgNO_3$(c = 1 M) can be calculated using Eq. 15.59.

$$S = \frac{1.88 \times 10^{-10}}{1} = 1.88 \times 10^{-10}.$$

Hence the solubility of AgCl in presence of 1 M $AgNO_3$ is 1.88×10^{-10} M. You can see that, as compared to the solubility of AgCl in water (1.37×10^{-5} M), its solubility in presence of 1 M $AgNO_3$ is 10^5 times less.

Example 7

Find the solubility of CaF_2 in

i) water ii) 0.10 M NaF iii) 0.10 M $Ca(NO_3)_2$ ($K_{sp} = 4.0 \times 10^{-11}$)

Solution

i) Let us assume that the solubility of CaF_2 in water is S. Since 1 mol CaF_2 can give 1 mole of Ca^{2+} ion and 2 mole of F^- ion in solution, we can write the concentrations of Ca^{2+} and F^- ions as follows :

$$[Ca^{2+}] = S \text{ and } [F^-] = 2S$$

Hence,

$$K_{sp} = [Ca^{2+}]\,[F^-]^2$$

$$\text{or } 4.0 \times 10^{-11} = S(2S)^2 = 4S^3$$

$$\therefore\ S = (1.0 \times 10^{-11})^{1/3} = (10 \times 10^{-12})^{1/3} = 2.2 \times 10^{-4}\ \text{M (approximated to two places)}$$

Note that while taking cube root, 1.0×10^{-11} is changed into 10×10^{-12}. It is easier to take the cube root, if the power of 10 is exactly divisible by 3 (i.e., the remainder is zero). You can see that − 12 is exactly divisible by 3 but not − 11.

Hence the solubility of CaF_2 in pure water is 2.2×10^{-4} M.

ii) In 0.10 M NaF

In presence of NaF, the solubility of $CaF_2 = [Ca^{2+}] = \dfrac{K_{sp}}{[F^-]^2}$

Total $[F^-]$ = $[F^-]$ from CaF_2 + $[F^-]$ from NaF.

Since $[F^-]$ from NaF is much larger than $[F^-]$ supplied by CaF_2, the total fluoride ion concentration is equal to the NaF concentration which is 0.10 M. Substituting the proper values we get,

$$[Ca^{2+}] = \frac{4.0 \times 10^{-11}}{(0.10)^2} = 4.0 \times 10^{-9}\ \text{M}$$

Hence, the solubility of CaF_2 in 0.10 M NaF is 4.0×10^{-9} M.

iii) in 0.10 M $Ca(NO_3)_2$

First we have to find $[F^-]$

$$[F^-]^2 = \frac{K_{sp}}{[Ca^{2+}]} \text{ or } [F^-] = \sqrt{\frac{K_{sp}}{[Ca^{2+}]}}$$

Substituting the given values, we get,

$$[F^-] = \sqrt{\frac{4.0 \times 10^{-11}}{0.10}}\ \text{M} = 2.0 \times 10^{-5}\ \text{M}.$$

Since each mole of CaF_2 produces 2 mole F^- ions in solution, the solubility of CaF_2 will be equal to one half the concentration of the fluoride ion in solution or 1.0×10^{-5} M.

When dealing with problems of this nature, two important points must be remembered.

First, if the solubility of a salt like CaF_2 is given as S, then the concentration of Ca^{2+} ion would be S but the concentration of fluoride ion, would be $2S$. This is so because each mole of CaF_2 which goes in solution gives 1 mole of Ca^{2+} and 2 mole of fluoride ions. The second point which is a source of common confusion and where error can arise is in writing the concentration of one ion in terms of the concentration of the other. For example, the concentration of fluoride ion in a saturated solution of CaF_2 can be expressed as,

$[F^-] = 2[Ca^{2+}]$

but not, $[Ca^{2+}] = 2[F^-]$.

No doubt when 1 mole of CaF_2 goes into slution, it will yield 1 mole of Ca^{2+} ions and 2 mole of fluoride ions, but to find the equivalence, we must write,

$2 \times$ (number of moles of Ca^{2+} ions) = Number of moles of fluoride ions.

or $2[Ca^{2+}] = [F^-]$

Now that we have seen how the presence of a common ion affects the equilibrium of a sparingly soluble salt, we come to the following conclusions regarding the solubility of a sparingly soluble salt.

i) In a saturated solution, K_{sp} = Ionic product

ii) When the product of the concentration of ions raised to suitable powers (i.e., the ionic product) is less than the solubility product value, the concentration of the ions can be increased by dissolving more of the salt. Hence, for an unsaturated solution
$K_{sp} >$ Ionic product

iii) When the concentration of either ion in solution is increased by the addition of a soluble salt containing a common ion, the ionic product increases. Hence, the equilibrium of the sparingly soluble salt is shifted such that it is precipitated. In other words, precipitation will occur when
Ionic product $> K_{sp}$

Here the word 'suitable powers' stands for the number of ions present per formula unit. For example in $Ca_3(PO_4)_2$, the 'suitable power' for Ca^{2+} is 3 and for PO_4^{3-}, it is 2.

Let us see the applications of these generalisations with the help of a few examples.

Example 8

Show that it is impossible to prepare a solution of chromium hydroxide, $Cr(OH)_3$, having 0.1 M concentration of Cr^{3+} ions at pH = 7; K_{sp} for $Cr(OH)_3 = 6.3 \times 10^{-31}$.

Solution

When the ionic product of $Cr(OH)_3$ is equal to its solubility product, the solution will be saturated. That will indicate the state of maximum concentration of Cr^{3+} ions in solution. Thus in a saturated solution,

Solubility product = Ionic Product = $[Cr^{3+}]\,[OH^-]^3$
Substituting the given values we get,

$$6.3 \times 10^{-31} = [Cr^{3+}]\,(1.0 \times 10^{-7})^3$$

$$\therefore\ [Cr^{3+}] = \frac{6.3 \times 10^{-31}}{1.0 \times 10^{-21}}\ \text{M (since at neutral pH, } [OH^-] = 1.0 \times 10^{-7}\ \text{M)}$$

Hence, at pH = 7, the maximum concentration of Cr^{3+} ions in solution would be 6.3×10^{-10} M and it is impossible to prepare a solution having 0.1 M concentration of Cr^{3+} ions at this pH.

An important fact that emerges from this example is that the precipitation or solubility of a hydroxide compound is directly related to OH^- ion concentration or the pH of the solution. It is not only true for the solubility of metallic hydroxides as in the above example, but also for many other cases where OH^- ion is produced due to hydrolysis. For instance, consider the equilibrium of CaF_2 once again. The K_{sp} for CaF_2 is 4.0×10^{-11} and the solubility is 2.2×10^{-4} M. The fluoride ions present in the solution through the dissolution of CaF_2 could further react with water, though to a small extent, according to the equation,

$$F^- + H_2O \rightleftharpoons HF + OH^-$$

If some H^+ ions in the form of an acid are added to the above solution, these will react with the free OH^- ions and the equilibrium will shift to the right. This will reduce the concentration of F^- ions in solution; so, more of CaF_2 will dissolve

Many a times two or more ions are separated from a mixture by means of a technique called selective precipitation. As an example, let us assume that from a solution containing Ag^+, Ni^{2+} and Cu^{2+} ions, Ag^+ ions are to be separated from the other two. This can be achieved by the addition of a substance which will produce a silver salt for which K_{sp} is much low. Thus, the addition of a calculated amount of chloride ion will cause the ionic product of the sparingly soluble AgCl exceed its K_{sp} value; hence, AgCl is precipitated. Under this condition, $NiCl_2$ and $CuCl_2$ remain in solution since their K_{sp} values are larger than their ionic product values. The precipitated solid AgCl can be separated by filtration.

In qualitative analysis of salts, a number of metal ions are precipitated as sulphides using hydrogen sulphide. However, some of these ions are precipitated in acid medium and some others in basic medium. The overall dissociation reaction of H_2S can be represented as

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

The equilibrium constant for this reaction is 1.3×10^{-21} and the concentration of H_2S in a saturated solution is 0.1 M. Substituting these values in the equilibrium constant expression, we get,

$$1.3 \times 10^{-21} = \frac{(H^+)^2\,(S^{2-})}{0.1}$$

$$\text{or } [S^{2-}] = \frac{1.3 \times 10^{-22}}{[H^+]^2}$$

Thus the sulphide ion concentration can be controlled by the adjustment of the pH of the solution. The metallic sulphides which have low K_{sp} values can be precipitated with rather small concentrations of sulphide ions in solution. This is achieved if the solution is acidic. The metallic sulphides which have higher K_{sp} values need higher concentration of sulphide ions for their precipitation and a higher pH (pH > 7) of the solution is to be maintained.

When H_2S is passed through a solution which is basic (pH > 7), H^+ ions obtained from H_2S dissociation is consumed due to the formation of undissociated water. This results in increased dissociation of H_2S and hence, higher concentration of S^{2-} ion.

As an example, let us consider a solution of pH = 3, which contains 0.010 M each of Mn^{2+} and Cu^{2+} ions at pH = 3. Let us pass H_2S through this solution such that $[H_2S] = 0.1$ M. At this pH, the concentration of sulphide ion would be,

$$[S^{2-}] = \frac{1.3 \times 10^{-22}}{(1.0 \times 10^{-3})^2} = 1.3 \times 10^{-16} \text{ (since } [H^+] = 1.3 \times 10^{-3} \text{ M at pH} = 3)$$

and therefore,

$$[Cu^{2+}]\,[S^{2-}] = (1.0 \times 10^{-2})\,(1.3 \times 10^{-16})$$
$$= 1.3 \times 10^{-18}$$

The K_{sp} for CuS = 6.3×10^{-36}. Since, we find that the ionic product (I.P.) > K_{sp}, CuS will precipitate from the solution. However, K_{sp} for MnS is 3×10^{-13} which is much greater than its I.P. (1.3×10^{-18} M); hence MnS remains in solution. After separation of CuS, we can increase the pH of the solution, thereby increasing the concentration of sulphide ion to the limit such that MnS also precipitates out. It is this combined use of the selective precipitation technique and proper control of pH which are the guiding principles in the qualitative analysis of the salts. Try the following SAQ.

SAQ 8

The solubility product of magnesium hydroxide, $Mg(OH)_2$, is 1.8×10^{-11}. What is the pH of a saturated solution of $Mg(OH)_2$?

....

....

....

15.12 SUMMARY

The basic definitions of acids and bases as given by Arrhenius, Lowry-Brønsted and Lewis have been discussed, Strong acids and bases are supposed to dissociate almost completely in water whereas weak acids and bases are not. Equilibrium conditions have been applied to weak acids and weak bases to determine the dissociation constants of these acids and bases in terms of concentrations.

A solution containing a weak acid (or a weak base) and its salt is defined as a buffer solution. The effect of common ion in the form of a salt affects the dissociation equilibrium of weak acids (or weak bases) so that the pH of the solution remains constant. The pH of these solutions changes very little by the addition of small amounts of strong acids and bases.

Some salts of strong acid and weak base, weak acid and strong base or weak acid and weak base undergo hydrolysis. The pH of the solution depends on the dissociation constants, K_a and K_b.

Indicators are weak acids or bases that exhibit different colours in dissociated and undissociated forms. Different indicators change their colour in different pH regions. Hence, the use of a particular indicator for a titration is guided by the range of pH change near the equivalence point.

In case of a sparingly soluble salt, the product of the concentration of ions in a saturated solution raised to their appropriate powers is known as solubility product. The wider differences in the solubility product values of different salts are made use of in analytical chemistry for their separation.

15.13 TERMINAL QUESTIONS

1) Calculate the change in pH that occurs when 1.0×10^{-3} kg of sodium fluoride is added to 0.0025 dm^3 of 0.10 M HF(*aq*). K_a for HF $= 7.2 \times 10^{-4}$.

2) Calculate the H^+ ion concentration of a solution that is 0.050 M in acetic acid and 0.10 M in sodium acetate. Calculate H^+ ion concentration when concentrated HCl is added to this solution such that $[HCl] = 1.0 \times 10^{-3}$ M. Assume that there is not much change in volume.
   (K_a for acetic acid $= 1.8 \times 10^{-5}$)

3) Calculate the concentration of Cl_3CCOOH, Cl_3CCOO^- and H^+ in a 0.25 M solution of trichloroacetic acid.
   (K_a for $Cl_3CCOOH = 0.22$)
   Hint : Note that K_a is not much low.

4) Calculate the molarity of HCN solution that is 0.010% ionised at equilibrium.
   (K_a for HCN $= 6.0 \times 10^{-10}$)
   Hint : Note that K_a is very much low.

5) What is the molarity of an aqueous ammonia solution for which OH^- ion concentration is 1.0×10^{-3} M? $K_b = 1.8 \times 10^{-5}$.

6) Calculate the solubility of
   i) $PbCl_2$ and
   ii) Ag_2CrO_4 at 298 K in mol dm^{-3}
   K_{sp} for the two salts are 1.6×10^{-5} and 9.0×10^{-2}, respectively.

15.14 ANSWERS

Self Assessment Questions

1) Any substance that can accept a pair of electrons is called Lewis acid whereas a Brφnsted acid is defined as any substance which acts as a proton donor. Typical examples of the two classes are given below :
   Lewis Acid : H^+, BF_3, any metal ion in coordination compounds.
   Brφnsted Acid : HCl, HNO_3, H_2SO_4 etc.

2) The equation for the dissociation of NH_4OH is,

$$\begin{array}{ccc} NH_4OH & \rightleftharpoons & NH_4^+ + OH^- \\ c_0(1-\alpha) & & c_0\alpha \quad\quad c_0\alpha \end{array}$$

   where c_0 = Initial concentration of ammonium hydroxide solution
   α = Degree of dissociation of ammonium hydroxide

Proceeding as per subsec. 15.3.2, we can write, $K_b = \dfrac{\alpha^2 c_0}{1-\alpha}$

By substituting the values of K_b and c_0, we get $\alpha = 4.2 \times 10^{-3}$.
Hence, $[OH^-] = \alpha c_0 = 4.2 \times 10^{-3}$ M
Alternatively, since NH_4OH is a weak base,

Using Eq. 15.8, $[OH^-] = \sqrt{K_b c_0}$

$$= \sqrt{1.8 \times 10^{-5}}$$
$$= \sqrt{18 \times 10^{-6}}$$
$$= 4.2 \times 10^{-3} M$$

3) a) We have to consider $[H^+]$ from both the sources, namely from the dissociation of HCl and water.
Let H^+ concentration as also OH^- concentration due to dissociation of water be x.
Since $[HCl] = 1.0 \times 10^{-8}$ M,
total $[H^+] = (x + 1.8 \times 10^{-8})$ M
But $[H^+]\,[OH^-] = K_w = 1.0 \times 10^{-14}$
i.e., $(x + 1.0 \times 10^{-8})\,(x) = 1.8 \times 10^{-14}$
Solving for x, we get, $x = 9.5 \times 10^{-8}$
$\therefore\ [H^+] = (9.5 \times 10^{-8} + 1.0 \times 10^{-8})\ M = 1.05 \times 10^{-7}$ M
$pH = -\log_{10}(1.05 \times 10^{-7}) = 6.98$
Note that pH of 1.0×10^{-8} M HCl is in the acidic range (<7).

b) Concentration of H^+ provided by $HCl = 1.0 \times 10^{-10}$ M
Concentration of H^+ due to $H_2O = 1.0 \times 10^{-7}$ M.
Since the $[H^+]$ ion due to the dissociation of water molecule is much greater than the hydrogen ions provided by HCl, the concentration of H^+ ions due to HCl can be neglected in comparison with that from water. Thus, we can write,

$[H^+] = 1.0 \times 10^{-7}$ M and pH = 7.

c) As in the above case (OH^-) from water is far greater than (OH^-) from NaOH.
Hence $[OH^-] = [OH^-]$ from water $\simeq 10^{-7}$ M

Hence $(H^+) = \dfrac{K_w}{(OH^-)} = 10^{-7}$ M and pH = 7.

4) Ammonium chloride, being a strong electrolyte, dissociates almost completely to give NH_4^+ ions and Cl^- ions. The NH_4^+ ions so produced suppresses the dissociation of the weak electrolyte, NH_4OH, due to common ion effect.

5) Moles of sodium acetate added $= \dfrac{\text{Mass}}{\text{Molar mass}} = \dfrac{2.05 \times 10^{-3}\ \text{kg}}{0.082\ \text{kg mol}^{-1}} = 0.025$ mol

Moles of HCl in solution $= 0.10\ \text{mol dm}^{-3} \times 0.10\ \text{dm}^3 = 0.010$ mol
Since HCl and CH_3COONa react in the ratio of 1 : 1 as per equation,

$$CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl,$$

0.010 mol HCl will react with 0.010 mol CH_3COONa to give 0.010 mol CH_3COOH.
Hence, moles of CH_3COONa remaining in solution after reaction
$= (0.025 - 0.010)$ mol
$= 0.015$ mol
$[CH_3COONa]$ in solution after the reaction

$$= \frac{0.015\ \text{mol}}{0.10\ \text{dm}^3} = 0.15\ M$$

[Acid] = Acetic acid concentration = $[CH_3COONa]$ reacted

$$= \frac{0.010\ \text{mol}}{0.10\ \text{dm}^3} = 0.10\ M$$

Substituting the proper values in Eq. 15.28, we get,

$$[H^+] = \frac{K_a\,[\text{acid}]}{[\text{salt}]} = \frac{1.8 \times 10^{-5} \times 0.10}{0.15}\ M$$

$$= 1.2 \times 10^{-5}\ M$$

$\therefore\ pH = -\log(1.2 \times 10^{-5}) = 4.9$

) Consider a salt of a weak base and a strong acid, BX. Let c_0 be the initial concentration of the salt BX and α be the degree of hydrolysis. The cation B^+ hydrolyses as follows :

$$\begin{array}{lcccccc} & B^+ & + & H_2O & \rightleftharpoons BOH & + & H^+ \\ \text{Equilibrium concentration} & c_0(1-\alpha) & & & c_0\alpha & & c_0\alpha \end{array}$$

The hydrolysis constant, K_h, can be expressed as,

$$K_h = \frac{(c_0\alpha)^2}{(1-\alpha)\,c_0} = \frac{\alpha^2 c_0}{(1-\alpha)}$$

If $\alpha << 1$ then,

$K_h c_0 = (c_0\alpha)^2$

or $c_0\alpha = (K_h c_0)^{1/2}$

We also know that

$$K_h = \frac{K_w}{K_b}$$

Hence, $[H^+] = \left(\dfrac{K_w c_0}{K_b}\right)^{1/2}$

$$-\log [H^+] = -\frac{1}{2}[\log K_w + \log c_0 - \log K_b]$$

$$\text{or pH} = \frac{1}{2}\,pK_w - \frac{1}{2}\log c_0 - \frac{1}{2}\,pK_b$$

7) For $Bi(OH)_3$, $x=1, y=3$

Using Eq. 15.51, $K_{sp} = 1^1.3^3.S^{1+3}$

$= 27\,S^4$

Since $K_{sp} = 4.0 \times 10^{-31}$,

$$S^4 = \frac{4.0 \times 10^{-31}}{27}$$

$$\therefore S = \left(\frac{4.0 \times 10^{-31}}{27}\right)^{1/4}$$

$= (0.148 \times 10^{-31})^{1/4}$

$= (1.48 \times 10^{-32})^{1/4}$

$= 1.1 \times 10^{-8}$

Hence the solubility of $Bi(OH)_3$ is 1.1×10^{-8} mol dm^3.

8) From Eq. 15.51

$K_{sp} = 1^1.2^2.S^{2+1} = 4S^3$.

$$S = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{1.8 \times 10^{-11}}{4}\right)^{1/4}$$

$= (4.5 \times 10^{-12})^{1/3}$

$= 1.7 \times 10^{-4}$ mol dm^{-3}

$[OH^-] = 2S = 3.4 \times 10^{-4}$ mol dm^{-3}.

$$[H^+] = \frac{10^{-14}}{3.4 \times 10^{-4}} = 2.9 \times 10^{-11}$$

pH = 10.5

Terminal Questions

1) pH of 0.10 HF can be calculated by using the equation,

$[H^+] = \sqrt{c_0 K_a}$

$$\text{or } -\log [H^+] = -\frac{1}{2}(\log c_0 + \log K_a) = -\frac{1}{2}(\log 0.1 + \log 7.2 \times 10^{-4})$$

$$= -\frac{1}{2}(-1.0 - 3.14)$$

pH = 2.07

$$0.0010 \text{ kg of NaF} = \frac{0.0010}{0.042} \text{ mol of NaF} = 0.0238 \text{ mol}$$

$\therefore$ Concentration of NaF $= \dfrac{0.0238 \text{ mol}}{2.5 \times 10^{-3} \text{ dm}^{-3}} = 9.5$ M

Substituting the proper values in the equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]},$$

$$\text{pH} = -\log K_a + \log \frac{9.5}{0.1}$$

$$= 3.14 + 1.98 = 5.12$$

2) i) Using Eq. 15.28,

$$[\text{H}^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$= 1.8 \times 10^{-5} \times \frac{0.050}{0.10} = 9.0 \times 10^{-6} \text{ M}$$

ii) Again using Eq. 15.28,

$$[\text{H}^+] = 1.8 \times 10^{-5} \times \frac{(0.050 + 0.001)}{(0.10 - 0.001)}$$

$$= 9.3 \times 10^{-6} \text{ M}$$

3) Since K_a for trichloroacetic acid is not much low, α will not be much low. Thus we use Eq. 15.3 only.

Dissociation of the acid can be written as

$Cl_3CCOOH \longrightarrow H^+ + Cl_3CCOO^-$

$0.25\,(1-\alpha) \quad 0.25\,\alpha \quad 0.25\,\alpha$

where α is the degree of dissociation of the acid. Hence,

$$K_a = \frac{c_0 \alpha^2}{1-\alpha}$$

$$0.22 = 0.25 \frac{\alpha^2}{1-\alpha}$$

or $0.25\,\alpha^2 = 0.22 - 0.22\,\alpha$

or $0.25\,\alpha^2 + 0.22\,\alpha - 0.22 = 0$

$$\alpha = \frac{-0.22 \pm \sqrt{(0.22)^2 + 4 \times 0.22 \times 0.25}}{2 \times 0.25}$$

$= 0.60$ (leaving the negative value)

Hence, $[\text{H}^+] = [Cl_3CCOO^-] = 0.25\,\alpha = 0.25 \times 0.60 = 0.15$ M

and $[Cl_3CCOOH] = c_0\,(1-\alpha) = 0.25 \times 0.4 = 0.10$ M

4) Since K_a is much low, α can also be expected to be much low. Hence we can write following subsec. 15.3.1,

$K_a = \alpha^2 c_0$

Since $\alpha = 0.010\% = 1.0 \times 10^{-4}$

or $c_0 = \dfrac{K_a}{\alpha^2} = \dfrac{6.0 \times 10^{-10}}{1.0 \times 10^{-8}}$ M $= 6.0 \times 10^{-2}$ M

Hence the molarity of HCN solution is 6.0×10^{-2} M.

5) Since NH_4OH solution is a weak base, we can use Eq. 15.8.

Hence $[\text{OH}^-] = \sqrt{K_b c_0}$

$$c_0 = \frac{[\text{OH}^-]^2}{K_b}$$

$$= \frac{1.0 \times 10^{-6}}{1.8 \times 10^{-5}}$$

$$= 5.6 \times 10^{-2}$$

Hence the molarity of ammonia solution is 5.6×10^{-2} M.

6) i) Solubility of $PbCl_2 = \left(\dfrac{1.6 \times 10^{-5}}{4}\right)^{1/3} = (4.0 \times 10^{-6})^{1/3} = 0.016$ mol dm^{-3}

ii) Solubility of $Ag_2CrO_4 = \left(\dfrac{9.0 \times 10^{-2}}{4}\right)^{1/3} = (22.5 \times 10^{-3})^{1/3} = 0.28$ mol dm^{-3}.

UNIT 16 ELECTROLYTIC CONDUCTANCE OF SOLUTIONS

Structure

16.1 INTRODUCTION

We have already seen in Unit 15 that an electrolyte on dissolution in water dissociates to give positive and negative ions which may carry single or multiple charges. For example, when sodium chloride is dissolved in water, the sodium ions, Na^+, and chloride ions, Cl^- are formed and get dispersed throughout the solution homogeneously. These ions are responsible for the passage of current through sodium chloride solution. In order to find the amount of current carried by these ions and the changes brought about by the passage of current through a solution, we should learn more about the nature and properties of the solvent. For instance, depending on the nature of the solvent, there are many kinds of interactions possible in an electrolyte solution. Two of these are ion-dipole and ion-ion interactions. We shall study a few possible interactions which influence the passage of current through aqueous solution, since water is a commonly used solvent. We shall then look into some of the useful applications of conductance studies. In the next unit, we shall study the designing and the applications of electrochemical cells.

Objectives

After going through this unit, you should be able to :

- describe the nature of ions in solution and the possible interactions among them,
- state Faraday's law of electrolysis and apply the same to a few systems,
- define specific and molar conductance of a solution,
- describe the dependence of conductance on concentration,
- state Kohlrausch's law of independent mobility of ions,
- state the applications of conductance measurements,
- explain the conductance method for titrations, and
- describe the method of determination of ionic product of water, dissociation constant of weak acids and weak bases and solubility of sparingly soluble salts.

16.2 INTERACTIONS IN SOLUTIONS

Since water is the most commonly used solvent, our studies are mainly confined to reactions in water. It is desirable that we refresh our memory about the nature and structure of water. The structure of water has been dealt with in Units 3 and 6 of Atoms and Molecules course, in

Unit 9 of Inorganic Chemistry course and in Unit 3 of this course. Based on a number of physico-chemical studies, the water molecule may be represented as shown in Fig. 16.1.

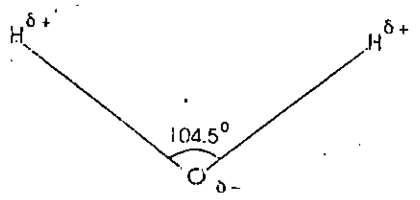

Fig. 16.1 : Structure of water molecule.

It is a bent molecule, H—O—H bond angle being approximately 104.5°. It shows polar character due to a large difference in the electronegativities of oxygen and hydrogen atoms. It thus has a permanent dipole moment. We should, therefore, expect water molecules to interact with each other. This kind of interaction between permanent dipoles is called dipole-dipole interaction. Due to this interaction, there is net force of attraction between the molecules. In addition, there will be hydrogen bonds present between oxygen atom of one molecule and hydrogen atoms of other molecules. When a salt is dissolved in water, it will produce ions in solution. As a result, there will be additional interactions between ions and water as well as between the ions themselves. We shall now consider such interactions in detail.

Ion-Solvent Interaction

An ion in solution will create an electrical field around it and solvent molecules with dipole moment will strongly interact with the field due to the ion. The water molecules will thus orient themselves in such a way that the dipoles lie along the field direction in order to minimise the energy of the system. The negative end of the water dipole will point towards the cation and the reverse will be true for the anion. Thus, each ion will be surrounded by a number of water molecules. Of course, generally, this number will depend on the size and charge of the ion and the nature of the solvent molecules. These ions are then called 'solvated ions'; in case of water, they are known as hydrated ions. The ion-solvent interaction is strong enough to hold a certain fixed number of solvent molecules (called coordination number) around a particular ion; however, the interaction is not so strong as to always produce different chemical species in solution. Whenever the interaction is strong enough to give different product, we define it as solvolysis and, in case of water, it is called hydrolysis. Solvent molecules so held by the central ion are known to form the first solvation shell. The first hydration shell for most of the cations usually contains either four or six molecules of water. For example, Cr^{3+} or Ni^{2+} is present as $[Cr(H_2O)_6]^{3+}$ or $[Ni(H_2O)_6]^{2+}$ in aqueous solution. The solvent structure far away from the ion differs little from the bulk structure of the solvent. In between these two extremes, there is a region of solvent structure where solvent molecules are under the influence of two forces, one from the ions present in the solution and the other due to intermolecular forces of the solvent. The solvent molecules in this region are consequently oriented randomly. To sum up, we can say that an electrolyte on dissolution in a solvent produces solvated ions. There is an inner or a primary solvent shell in which the solvent molecules are bound through the strong ion-dipole interaction. There is an outer or secondary solvent layer where molecules are not aligned in any particular fashion either by the field of the ion or by the forces that act in bulk solvent. The solvation number of an ion is defined as the mean number of solvent molecules in the primary solvation shell.

Ion-Ion Interactions

Any two ions present in a solution will interact with each other. Like charges will repel each other whereas unlike charges will attract each other. The electrostatic forces between any two ions is governed by Coulomb's law. Thus a sodium ion in a solution of sodium chloride will be repelled by other sodium ions in its vicinity but it will be attracted by chloride ions. However in solutions, a well-ordered structure as found in the solids—where each ion is surrounded by a definite number of oppositely charged species at a fixed distance—is not possible. In solutions, the thermal motion will not leave the ions at fixed positions. The net result is that at any given moment on an average, there will be an atmosphere of excess of

Coulomb's law states that the force of attraction between two oppositely charged particles is directly proportional to the product of the charges and inversely proportional to the square of the distance between them. Mathematically it is expressed as :

$$F \propto \frac{q_1 \cdot q_2}{r^2}$$

where q_1 and q_2 are the charges on the two particles, r is the distance between them and F is the force of attraction.

negative ions around each positive ion and the reverse will be true for the negative ion as shown in Fig. 16.2

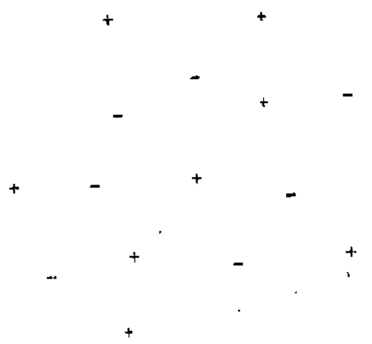

Fig. 16.2 : Atmosphere of oppositely charged ions around each cation and anion.

The measure of the electrostatic interaction is given by a term called, ionic strength, I. The ionic strength depends on the concentration of the ions present and the charge carried by the ions. It is given by the expression,

$$I = \frac{1}{2} \sum_i m_i z_i^2 \qquad \text{..... (16.1)}$$

where m_i is the molal concentration of ion 'i' in solution and z_i is the charge associated with the same ion.

In the case of a dilute solution (of density, d), its molarity (c_i) is related to its molality (m_i) as per Eq. 16.2.

$$c_i = m_i d \qquad \text{..... (16.2)}$$

Substituting the value of m_i from Eq. 16.2 into Eq. 16.1 we get,

$$I \simeq \frac{1}{2d} \sum_i c_i z_i^2 \qquad \text{..... (16.3)}$$

Eq. 16.3 indicates that the electrostatic interaction between any two ions in solution is directly proportional to concentration of the solution. This has been experimentally verified in terms of a quantity called ion-atmosphere radius. It is defined as the effective radius at which the atmosphere of opposite charges is situated around an ion. The radii of ion-atmosphere around sodium ion in 1.0×10^{-2} M, 1.0×10^{-4} M and 1.0×10^{-6} M sodium chloride solutions have been calculated to be in the ratio of 1:10:100. Thus, we see that ion-atmosphere radius increases with dilution. Hence, it can be concluded that at very low concentrations or at infinite dilution, an ion would be free from inter-ionic interactions. The concepts developed so far form the basis for the theory of ionic solutions as given by Debye and Hückel. However, our immediate concern is to study the effects of passage of current through an electrolyte solution but not the theory of electrolytic conductance. Next four sections are devoted to these studies only.

16.3 FARADAY'S LAWS OF ELECTROLYSIS

A process in which a chemical change is brought about by the passage of current through a solution is called electrolysis. The apparatus in which electrolysis is carried out is known as electrolytic cell. Consider a solution of an electrolyte into which two metal plates are dipped. The metal plates do not chemically react with the solution. On connecting the plates to the two terminals of a battery, a current starts flowing through the solution due to movement of ions in solution. The negatively charged plate is called cathode and the positively charged plate is known as anode. The ions which move towards cathode and anode are known as cations and anions, respectively. The combined name for the two plates is electrodes. As the ions reach the two electrodes, a chemical reaction takes place at each electrode; oxidation at the anode and reduction at the cathode. Suppose that an electric current is passed through a solution of copper sulphate into which two copper electrodes are dipped. Then the following reactions occur at the electrodes:

At the anode : $Cu \longrightarrow Cu^{2+} + 2e^-$ (oxidation)

At the cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$ (reduction)

For simplicity we have represented the net reaction at the anode as oxidation of Cu to Cu^{2+}. However, the anodic reaction may be a complicated one involving sulphate ions.

The battery pushes electrons to one electrode and takes away from the other. In other words, electrons are transferred between the electrodes and ions. The current in the solution is due to migration of ions. Suppose that a current (I) is passed through an electrolyte solution for a time t. Then the quantity of electric current (q) passed is given by the product of current and time.

$$q = I \, . \, t \qquad \text{..... (16.4)}$$

The units of quantity of electricity, current and time are coulomb (C), ampere (A) and second (s), respectively. Hence,

$$1 \text{ C} = 1 \text{ A s}$$

An electrolytic cell designed to measure the quantity of electric current that has passed through the solution is called a coulometer (see Example 1). For example, a silver coulometer uses platinum electrodes and a solution of silver nitrate as an electrolyte. On electrolysis the following reaction occurs at the cathode and silver gets deposited.

$$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag} \qquad \text{..... (16.5)}$$

By measuring the increase in mass of the cathode, one can calculate the quantity of electric current that has passed during electrolysis. To understand the calculations involving coulometer, we must study Faraday's laws of electrolysis.

In 1813, Faraday made certain useful observations on the decomposition of electrolyte solutions by the passage of electric current. These are known as Faraday's laws of electrolysis and are stated below :

1) The mass (w) of a product formed at an electrode is directly proportional to the quantity of electricity (q) passed i.e.

$$w \propto q \qquad \text{..... (16.6)}$$

2) The masses of different products (say w_1 and w_2 for two substances 1 and 2) formed at the electrodes by the passage of the same quantity of electricity are directly proportional to their equivalent weights. Thus the quantity of electricity that has passed through the electrolytic cell can be measured by the extent of the chemical reaction which has taken place in a cell or vice-versa.

Before seeing the usefulness of these laws let us explain the term **faraday**. The quantity of electricity carried by 1 mole of electrons is called **faraday** and given the symbol, F. The charge on one electron is 1.602×10^{-19} C. Hence, the charge on one mole of electrons would be $1.602 \times 10^{-19} \times 6.022 \times 10^{23}$ C or 96489 C. It is usual to approximate one faraday as being equal to 96500 C.
Consider an electrode reaction :

$$\text{X}^{n+} + ne^- \longrightarrow \text{X}$$

The quantity of electricity required for the deposition of 1 mole of X will be equal to nF, where n is the number of moles of electrons required for the reaction. Let M be the mass of 1 mole atoms of an element X. Therefore, for the deposition of M kg (or 1 mole) of the element, we require nF or $n \times 96500$ C of electricity. It can also be expressed as follows :
$n \times 96500$ C of electricity deposits M kg (or 1 mole) of an element. Hence, q coulomb of electricity deposits $\dfrac{M \, . \, q}{n \, . \, 96500}$ kg of the element.

$$\text{or } w = \frac{M \, . \, q}{n \, . \, 96500} \text{ kg} \qquad \text{..... (16.7)}$$

where w = mass of an element deposited by the passage of q coulomb of current.

Substituting the value of q from Eq. 16.4 into Eq. 16.7 we get

$$w = \frac{M \, . \, I \, . \, t}{n \, . \, 96500} \qquad \text{..... (16.8)}$$

This equation is useful in calculating the mass of an element deposited by the passage of known quantity of current. Let us make use of Eq. 16.8 in solving some problems.

Example 1

n is equal to the charge on an ion.

A current of 5.0×10^{-3} A is passed for 100 minutes through a silver coulometer. Calculate the mass of silver deposited on the cathode. Atomic mass of Ag = 107.9
(or M = 0.1079 kg mol^{-1}).

Solution

Substituting the given values in Eq. 16.8 we get,

$$w = \frac{0.1079 \text{ kg mol}^{-1} \times 5.0 \times 10^{-3} \text{ A} \times (100 \times 60) \text{ s}}{1 \times 96500 \text{ C mol}^{-1}} \quad (n = 1, \text{ since 1 mole of Ag}^{+} \text{ ions needs 1 mole of electrons})$$

$$w = 3.4 \times 10^{-5} \text{ kg}$$

Example 2

Two electrolytic cells, one containing silver nitrate solution and the other copper sulphate solution as electrolytes were connected in series. A steady current of 1.50 A was passed through them until 0.00145 kg of silver was deposited at the cathode of the first cell. How long did the current flow? What mass of copper was deposited in the second cell?

Solution

1 C = 1 A s

Let t second be the time for which the current flowed through the cells.

For the deposition of Ag,

$n = 1, I = 1.50$ A, $w = 0.00145$ kg, $M = 0.1079$ kg mol^{-1}

Rearranging Eq. 16.8 and substituting the given values we get,

$$t = \frac{w\, n\, 96500}{M I}$$

$$t = \frac{0.00145 \text{ kg} \times 1 \times 96500 \text{ A s mol}^{-1}}{0.1079 \text{ kg mol}^{-1} \times 1.50 \text{ A}} = 865 \text{ s}$$

Since the electrolytic cells containing $AgNO_3$ and $CuSO_4$ are connected in series, same quantity of current is passed through both the cells. Hence, for the deposition of Cu, we have, $I = 1.50$ A and $t = 865$ s. But $n = 2$ in the electrolysis of $CuSO_4$ solution, since

$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

Further, mass of one mole atoms of Cu = 0.06354 kg.

Substituting these values in Eq. 16.8 we get,

$$\left.\text{mass of copper deposited}\right\} = \frac{0.06354 \text{ kg mol}^{-1} \times 1.50 \text{ A} \times 865 \text{ s}}{2 \times 96500 \text{ C mol}^{-1}} = 4.27 \times 10^{-4} \text{ kg}$$

You should now be able to apply the laws of electrolysis in solving the following SAQs.

SAQ 1

If a 5 A current is passed through an electrolytic cell containing molten magnesium chloride, how long would it take to prepare a mole of magnesium metal?

[**Hint** : $Mg^{2+} + 2e^{-} \longrightarrow Mg$]

....

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SAQ 2

1 dm^3 of a solution of 2.0 M $CuSO_4$ is electrolysed using platinum electrodes by passing 4.50 A current for 9000 s.

Calculate

i) the mass of Cu deposited, and

ii) the amount of Cu^{2+} in the solution at the end of the electrolysis.

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16.4 ELECTROLYTIC CONDUCTANCE

We shall now turn our attention to a property of the electrolyte solution, called, conductivity. The electrical resistance (R) of a sample is directly proportional to its length (l) and inversely proportional to its cross-sectional area (A). It can be expressed as,

$$R \propto \frac{l}{A}$$

$$\text{or } R = \rho \cdot \frac{l}{A} \qquad \text{..... (16.9)}$$

The proportionality constant, ρ, is known as its electrical resistivity. The unit of resistance is ohm (Ω) while the unit of resistivity is ohm metre (Ω m). The electrical conductance is defined as the inverse of electrical resistance. Similarly, conductivity or specific conductance (κ) of a material is defined as the reciprocal of its electrical resistivity. Hence, Eq. 16.9 can be written as

$$R = \frac{1}{\kappa} \cdot \frac{l}{A} \qquad \text{..... (16.10)}$$

$$\text{or } \kappa = \frac{l}{AR} \qquad \text{..... (16.11)}$$

Since the resistance is expressed in ohm, the reciprocal ohm (Ω^{-1}) was earlier used as the unit for conductance. However, in SI system, the unit for conductance is 'siemens' and, given the symbol 'S'. Hence, the unit for conductivity will be S m^{-1}. (1 S = 1 Ω^{-1}).

For the measurement of electrical resistance (R_x) of a sample, we use a set-up known as Wheatstone bridge. It consists of two wires R_1, R_2, of known resistance values, and a third resistance, R_s, the value of which can be adjusted. These are all connected to a battery source, E, as shown in Fig. 16.3. R_s is adjusted until points a and b are exactly at the same potential. This can be tested by momentarily connecting a sensitive ammeter (A) between a and b. If the two points are exactly at the same potential, there will be no deflection in the ammeter.

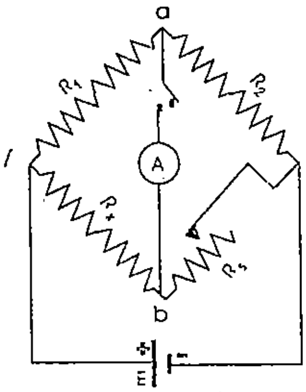

Fig. 16.3 : Wheatstone bridge.

Under these conditions, the following relation will hold good :

$$\frac{R_1}{R_2} = \frac{R_x}{R_s}$$

$$\text{or } R_x = \frac{R_s \cdot R_1}{R_2} \qquad \text{..... (16.12)}$$

For finding the resistance of a solution (R_{cell}), we make slight alterations in the Wheatstone bridge described above. Instead of a battery, we use an alternating current source to prevent electrolysis. The electrolysis that occurs when current passes in one direction is reversed when it passes in the other direction. The direction of current changes so rapidly that the build-up of charge at the electrode is not possible

Finally, instead of an ammeter, we use an alternating current detector as shown in Fig. 16.4.

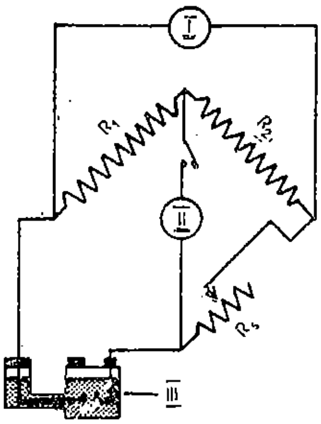

Fig. 16.4 : Wheatstone bridge where electrolytic cell occupies one arm of the bridge :
I) AC source of frequency;
II) Alternating current detector;
III) Test cell (R_{Cell})

At the balance point,

$$R_{cell} = R_s\left(\frac{R_1}{R_2}\right) \qquad ..... (16.13)$$

The relationship between specific conductance and resistance is given by Eq. 16.11 as

$$\kappa = \frac{l}{A}.\frac{1}{R}$$

$$\text{or } \kappa = k_{cell}\ \frac{1}{R} \qquad ..... (16.14)$$

where k_{cell} is the cell constant representing $\frac{l}{A}$ ratio; it is a constant as far the same cell is used for measurements. Since the conductivities of certain standard solutions have been carefully measured, we could use such a solution in a cell and measure its resistance. Thus knowing κ and R, we can calculate the value of k_{cell} the cell constant. Once k_{cell} is determined, we can use the same cell for the measurement of conductivity of other electrolyte solutions. Using these ideas, work out the following SAQ.

Nowadays, conductivity bridges facilitate direct reading of the resistance and conductance values, without having to use Eq. 16.13. In CHE-03(L) laboratory course, experiments involving conductivity bridges have been included.

SAQ 3

A conductance cell filled with 0.020 M KCl has a resistance of 195.96 Ω at 298 K. When filled with a 0.050 M $AgNO_3$ solution, it has a resistance of 94.2 Ω. The specific conductance of 0.020 M KCl is 0.2768 S m^{-1}. What is the specific conductance of 0.050 M $AgNO_3$ solution?

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16.5 MOLAR AND EQUIVALENT CONDUCTANCE

In order to compare the conductivities of different electrolytes, we must use the same concentration. It is because the conductivity of the solution depends on the number of ions present. Therefore, instead of specific conductance, we use molar conductivity, Λ_m, which is the conductivity per unit molar concentration and is given by the expression :

$$\Lambda_m = \frac{\kappa}{c} \qquad ..... (16.15)$$

where c is in mol m^{-3} units. The molar conductivity is usually expressed in S m^2 mol^{-1} or S cm^2 mol^{-1}. It may be remembered that, S m^2 mol^{-1} = 10000 S cm^2 mol^{-1}.

It might be thought that Λ_m should be a quantity independent of concentration. However, it is an experimental fact that Λ_m for NaCl, KBr. etc. in aqueous solution does vary with concentration. This is due to the ionic interactions which change with concentration. This, in turn, affects the conductivity, κ.

If we plot the molar conductivities of a large number of electrolytes against the concentrations we find that these fall into two distinct categories. In one class of electrolytes, there is a small increase in molar conductivities with the decrease in concentration. Such electrolytes are called 'strong electrolytes'. Since these electrolytes dissociate almost completely even in concentrated solution, the number of ions do not change much with concentration. The conductivity should not vary much since it is directly related to the number of ions present in solution. The minor changes observed are due to interionic interactions. The second class of compounds, known as 'weak electrolytes', are those where ionisation is incomplete. The ionisation will increase with dilution, and hence, the molar conductivity increases with dilution. Thus the conductivity is directly proportional to the degree of dissociation of a weak electrolyte.

It is to be remembered that c in Eq. 16.15 is to be expressed in mol m^{-3} units. If the concentration is given in terms of molarity (mol dm^{-3}), then the following conversion is to be carried out :

$$c(\text{mol m}^{-3}) = \text{Molarity} \times 1000 \qquad \dots (16.16)$$

Earlier, equivalent conductivity (Λ_{eq}), which is given by the following expression, was in use.

$$\Lambda_{eq} = \frac{1000\kappa}{c'}$$

where c' is the concentration expressed in terms of normality of the solution.

However, IUPAC recommends the use of molar conductivity only.

Example 3

At 298 K, the resistance of 2.00×10^{-2} M KCl is 195.96 Ω and that of 2.50×10^{-3} M K_2SO_4 is 775.19 Ω. The specific conductance (κ) of 2.00×10^{-2} M KCl at 298 K is 0.2768 S m^{-1}. Calculate molar conductivity of K_2SO_4 solution.

Solution

First we have to find out the cell constant. From Eq. 16.14

$$k_{cell} = \kappa \times R$$

Substituting the given values for 2.00×10^{-2} M KCl, we get,

$$k_{cell} = 0.2768 \text{ S m}^{-1} \times 195.96\ \Omega$$
$$= 54.24 \text{ m}^{-1}.$$

Next, we have to calculate the κ of K_2SO_4 solution.

$$\kappa = \frac{k_{cell}}{R} = \frac{54.24 \text{ m}^{-1}}{775.19\ \Omega}$$
$$= 0.06997 \text{ S m}^{-1}.$$

The concentration of K_2SO_4 is given in molarity. Hence, its concentration in mol m^{-3} units may be obtained by using Eq. 16.16.

$$c = 1000 \times 2.50 \times 10^{-3} \text{ mol m}^{-3}$$
$$= 2.50 \text{ mol m}^{-3}$$

We can calculate Λ_m using Eq. 16.15,

$$\Lambda_m = \frac{\kappa}{c} = \frac{0.06997}{2.50} \text{ S m}^2 \text{ mol}^{-1}.$$
$$= 0.028 \text{ S m}^2 \text{ mol}^{-1}.$$

16.6 MOLAR CONDUCTANCE AT INFINITE DILUTION

We have already seen that the molar conductance of an electrolyte increases with decreasing concentrations as is apparent from the values given in Table 16.1.

Table 16.1 : Molar Conductance at 298 K

Concentration	Λ_m/S m^2 mol^{-1}			
M	HCl	KCl	CH_3COOH	$AgNO_3$
1.000	0.03328	0.01119	—	—
0.100	0.03913	0.01289	0.00052	0.01091
0.010	0.04120	0.01413	0.00162	0.01248
0.001	0.04214	0.01469	0.00486	0.01305
0.0005	0.04227	0.01478	0.01350	0.01314

Many of the books tabulate Λ_m in terms of S cm^2 mol^{-1}.

Moreover, as a consequence of interionic interactions, every ion in solution has a diffused ionic atmosphere of opposite charges. The motion of an ion under the influence of an electric field would be least affected by the interionic forces when the solution is very dilute. Indeed the value of molar conductance extrapolated to zero concentration should be independent of interionic interactions. It is called limiting molar conductivity or molar conductance at infinite dilution and given the symbol, Λ_m^0. Kohlrausch gave an empirical formula on the basis of his experimental results, which connects the molar conductivites with concentration, for strong electrolyte:

$$\Lambda_m = \Lambda_m^0 - Ac^{1/2} \qquad ..... (16.17)$$

Where A is constant; its value depends on the nature of the electrolyte rather than on the identity of the specific ions. For example, electrolytes of the type KCl, NaOH, NaCl etc. have the same value of A whereas $BaCl_2$ $CuSO_4$ etc, have a different value.

Kohlrausch's Law of the Independent Migration of Ions

On the basis of conductivity measurements on a series of strong electrolytes, Kohlrausch discovered that the molar conductance at infinite dilution is the sum of the contributions from each ion. It is known as the law of independent migration (or mobility) of ions. This law can be expressed as :

$$\Lambda_m^0 = \nu_+\lambda_+^0 + \nu_-\lambda_-^0 \qquad ..... (16.18)$$

where ν_+ and ν_- are numbers of cations and anions per formula unit, respectively and λ_+^0 and λ_-^0 are the corresponding molar conductivities of the ions at infinite dilution. For example, Table 16.2 gives Λ_m^0 values for a number of salts. If you compare the values for any pair of salts having a common ion, it always shows a constant difference between Λ_m^0 values. These values can be explained if we assume that Λ_m^0 is the sum of two terms, one arising due to cation and the other due to anion. Thus the first set of values gives the difference due to the different contributions of K^+ and Na^+, the second due to K^+ and Li^+ and the third due to Cl^- and NO_3^-.

Table 16.2 : Λ_m^0 values for Some Electrolytes

Electrolyte	Λ_m^0 S m^2 mol^{-1}	Electrolyte	Λ_m^0 S m^2 mol^{-1}	Electrolyte	Λ_m^0 S m^2 mol^{-1}
KCl	0.01498	KOH	0.02715	KNO_3	0.01450
NaCl	0.01264	NaOH	0.02481	$NaNO_3$	0.01216
Difference	0.00234		0.00234		0.00234
KCl	0.01498	KNO_3	0.01450	$KClO_4$	0.01400
LiCl	0.01150	$LiNO_3$	0.01101	$LiClO_4$	0.01051
Difference	0.00348		0.00349		0.00349
LiCl	0.01150	KCl	0.01498	NaCl	0.01264
$LiNO_3$	0.01101	KNO_3	0.01450	$NaNO_3$	0.01216
Difference	0.00049		0.00048		0.00048

Ostwald's Dilution Law

In the case of weak electrolytes, it is not possible to obtain the limiting molar conductance value, Λ_m^0, by extrapolation of molar conductance value to zero concentration since there is a large increase in molar conductance and the experimental measurements become unreliable. This can be seen from the values given for acetic acid in Table 16.1. For weak electrolytes, Ostwald derived a relationship between the molar conductivity and the limiting molar conductance. This relationship is known as Ostwald's dilution law.

The molar conductivity of weak electrolyte can be expressed as the product of degree of ionisation of the electrolyte and its limiting molar conductance:

$$\Lambda_m = \alpha \, . \, \Lambda_m^0 \qquad ..... (16.19)$$

where α is the degree of ionisation.

If c is the molar concentration of the electrolyte, we can express the ionisation of a weak electrolyte as follows :

$$\begin{array}{ccccc} MA & \rightleftharpoons & M^+ & + & A^- \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

So, $$K = \frac{[\mathrm{M}^+][\mathrm{A}^-]}{[\mathrm{MA}]} = \frac{(\alpha c)(\alpha c)}{(1-\alpha)c} = \frac{\alpha^2 c}{1-\alpha} \quad \text{..... (16.20)}$$

Eq. 16.20 can be rearranged as

$$\frac{1-\alpha}{\alpha^2 c} = \frac{1}{K}$$

or $\dfrac{1-\alpha}{\alpha} = \dfrac{\alpha c}{K}$ (multiplying both sides of the equation by αc)

or $\dfrac{1}{\alpha} - 1 = \dfrac{\alpha c}{K}$

$$\text{or } \frac{1}{\alpha} = 1 + \frac{\alpha c}{K} \quad \text{..... (16.21)}$$

But from Eq. 16.19, we know that

$$\frac{1}{\alpha} = \frac{\Lambda_m^0}{\Lambda_m}$$

Substituting the value of $\dfrac{1}{\alpha}$ in Eq. 16.21, we get

$$\frac{\Lambda_m^0}{\Lambda_m} = 1 + \frac{c}{K} \cdot \frac{\Lambda_m}{\Lambda_m^0}$$

Dividing throughout by Λ_m^0 we get,

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{c\,\Lambda_m}{K\,(\Lambda_m^0)^2} \quad \text{..... (16.22)}$$

It is found that for concentrations higher than 0.1 mol dm^{-3}, Ostwald's law is not followed strictly. We can use Kohlrausch's law of independent mobility of ions to calculate indirectly Λ_m^0 value for weak electrolytes as illustrated by the following example :

$$\Lambda_m^0(\mathrm{CH_3COOH}) = \Lambda_m^0(\mathrm{CH_3COONa}) + \Lambda_m^0(\mathrm{HCl}) - \Lambda_m^0(\mathrm{NaCl})$$

Notice that all the terms on the right hand side are for strong electrolytes and are known; thus, we can calculate the value for the weak electrolyte, $\mathrm{CH_3COOH}$, as shown below :

The values of molar conductance at infinite dilution for sodium acetate, hydrochloric acid and sodium chloride are 0.009101, 0.04261 and 0.01264 S m^2 mol^{-1}, respectively.

$$\begin{aligned}\text{Hence, } \Lambda_m^0(\mathrm{CH_3COOH}) &= [(0.009101 + 0.04261) - 0.01264]\ \mathrm{S\ m^2\ mol^{-1}} \\ &= 0.03907\ \mathrm{S\ m^2\ mol^{-1}}.\end{aligned}$$

16.7 IONIC MOBILITIES AND TRANSPORT NUMBER

Potential gradient is the voltage drop for unit length. Its unit is V m^{-1}. Ionic mobility (u) can be defined as the velocity of an ion under unit potential gradient.

Unit of ionic mobility

$$= \frac{\text{Unit of velocity}}{\text{Unit of potential gradient}}$$

$$= \frac{\mathrm{m\ s^{-1}}}{\mathrm{V\ m^{-1}}} = \mathrm{m^2\ V^{-1}\ s^{-1}}$$

Transport number of an ion indicates the fraction of the total current carried by it.

$$t_+ + t_- = 1$$

If the total quantity of electricity is q while the transport numbers of cation and anion are t_+ and t_-, then,

$$\left.\begin{array}{l}\text{quantity of electricity}\\ \text{carried by cation } (q_+)\end{array}\right\} = t_+ q = t_+ It \text{ and}$$

$$\left.\begin{array}{l}\text{quantity of electricity}\\ \text{carried by anion } (q_-)\end{array}\right\} = t_- q = t_- It$$

The above is true only if two ions are present in the solution.

The next question which arises in this connection is why should there be a difference between the values of limiting molar conductivities of similarly charged ions, if these ions are just acting as carriers of electric charges only?

The answer lies in the fact that different ions have different mobilities in solution. The mobility of an ion in solution is mainly dependent upon the size of the hydrated ion. The ionic mobility is defined as the velocity with which an ion would move under a potential gradient of 1 V m^{-1} in a solution. It provides a link between theoretical and measurable quantities. For instance, ionic mobility, (u) is related to molar ionic conductivity by the following equations :

$$\lambda_+^0 = z_+ u_+ F \ \ and \ \ \lambda_-^0 = z_- u_- F \quad \text{..... (16.23)}$$

where z_+ and z_- are the valency of the ions, u_+ and u_- represent the ionic mobilities and F is the faraday. In the above equation, if one of the two quantities, λ or u, is known, the other can be calculated.

To find the values of λ_+^0 or λ_-^0 we define yet another quantity, called transport of transference number of an ion indicated by the symbol t_+ or t_-. It is defined as the fraction of the total current carried by an ionic species and can be expressed mathematically as,

$$t_+^0 = \frac{\lambda_+^0}{\Lambda_m^0} \text{ and } t_-^0 = \frac{\lambda_-^0}{\Lambda_m^0} \quad \text{..... (16.24)}$$

The transport number and the limiting molar conductance are measurable quantities. Hence, the molar ionic conductivity value can be calculated from Eq. 16.24. Finally, once the molar ionic conductivity value is obtained, we can then make use of Eq. 16.23 to calculate the ionic mobility.

Example 4

Calculate the ionic mobility of the cation in an infinitely dilute solution of KBr at 298 K. Given that the transport number of K^+ is 0.48 and the molar conductance of KBr at infinite dilution is 1.52×10^{-2} S m^2 mol^{-1}.

t_+ and t_- stand for transport numbers of the ions at any given concentration, whereas t_+^0 and t_-^0 are the transport numbers at infinite dilution. The methods of determination of t_+ and t_- are discussed in the next section. The transport numbers measured at low concentrations are exptrapolated to zero concentration to obtain t_+^0 and t_-^0.

From the definitions, we know that,

$$S = \frac{1}{\Omega} \text{ and } C = A\,s$$

$$\frac{S}{C} = \frac{1}{\Omega\, A\, s} = \frac{1}{V\, s}$$

since 1 V = 1 Ω A

(emf = Resistance × current as per ohm's law)

Solution

From Eq. 16.24 we can write

$$t_+^0 = \frac{\lambda_+^0}{\Lambda_m^0}$$

or $\lambda_+^0 = t_+^0\, \Lambda_m^0$

Substituting the value λ_+^0 in Eq. 16.23 we get,

$$t_+^0\, \Lambda_m^0 = z_+\, u_+\, F$$

Hence,

$$u_+ = \frac{t_+^0\, \Lambda_m^0}{z_+\, F}$$

Substituting the given values in the above equation we get,

$$u_+ = \frac{0.48 \times 1.52 \times 10^{-2}\ \text{S m}^2\ \text{mol}^{-1}}{1 \times 96500\ \text{C mol}^{-1}} = 7.6 \times 10^{-8}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}$$

We shall now look into the methods of determination of transport number.

16.8 DETERMINATION OF TRANSPORT NUMBER

There are mainly two methods for the determination of transport number. Let us discuss Hittorf method first.

Hittorf Method

An electrolytic cell of the type shown in Fig. 16.5 is divided into three compartments. Each one has a stop-cock at the bottom so that the solution can be drained from any compartment for analysis. It is connected in series with a sensitive ammeter (M), silver coulometer (C) and a battery (E). K is the connecting key.

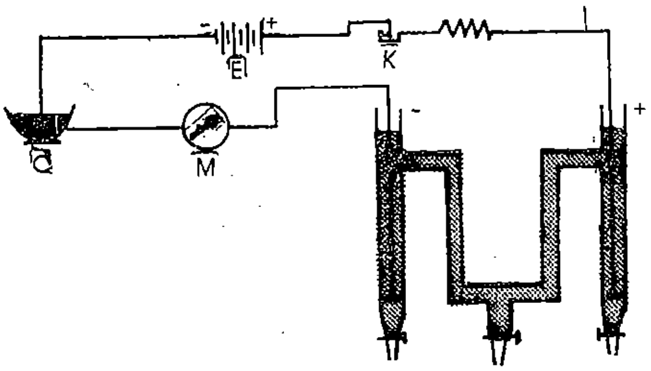

Fig. 16.5 : Transport number determination by Hittorf method.

The cell is filled with the electrolyte solution of known concentration. A known amount of electricity (≈ $I\,t$) is passed through the cell, where I is the current and t is the time interval. At the end of electrolysis, a known volume of the electrolyte is drained out from the cathode compartment and analysed to find the concentration of the electrolyte. Knowing the initial amount of the electrolyte and its amout at the end of electrolysis, we can find the change in its amount. At the same time, by determining the amount of silver deposited in the coulometer, the exact quantity of electricity passed can be accurately determined. Let us see how transport number is calculated from these measurements.

From Eq. 16.7, the number of moles of cations discharged at the cathode by the passage of I ampere current for t second, is given by

$$\text{Number of moles of cations discharged} = \frac{\text{Mass of the element deposited}}{\text{Mass of one mol atoms of the element}}$$

$$= \frac{w}{M} = \frac{q}{nF}$$

If z_+ is the electrovalency of the cation of the element, then $n = z_+$.

$$\text{Hence, the number of moles of cations discharged} = \frac{w}{M} = \frac{It}{z_+F} \quad \text{..... (16.25)}$$

Quantity of electricity carried by the cations $\Big\} = q_+ = t_+It$;
Hence, the number of moles of cations moving into the cathode compartment as per Eq. 16.7
$= \frac{w}{M} = \frac{q_+}{z_+F} = \frac{t_+It}{z_+F}$

At the same time, when these cations are getting discharged, some cations from the middle compartment will move into the cathode compartment to keep the solution in the cathode compartment electrically neutral. Just the opposite reaction will take place in the anode compartment. Now the moles of cations that move into the cathode compartment would be $t_+\left(\frac{It}{z_+F}\right)$. Due to this, there would be a change in the amount of the electrolyte in the cathode compartment; this change can be calculated as shown below:

Change in the amount of the electrolyte around the cathode, = (Moles of cations entering into the cathode compartment) – (moles of cations discharged at the cathode)

$$= t_+\frac{It}{z_+F} - \frac{It}{z_+F} = (t_+ - 1)\frac{It}{z_+F} \quad \text{..... (16.26)}$$

Note that the r.h.s. of Eq. 16.26 is a negative quantity since t_+ is less than 1 and $(t_+ - 1)$ is a negative quantity. The physical significance of Eq. 16.26 is that the change in the amount of the electrolyte around the cathode is negative. In other words, there is a decrease in the amount of the electrolyte (as a result of electrolysis) around the cathode.

This change in the amount of the electrolyte can be found out after stopping the current and draining out a known volume of the solution from the cathode compartment for chemical analysis. At the same time, q can be calculated by knowing the difference in masses of the cathode in the coulometer before and after passing current. Thus, one can find the value of transport number.

Note that the amount of a substance $= \frac{\text{Mass of the substance}}{\text{Its molar mass}}$
Also, molar mass of HCl = 0.0365 kg mol^{-1}

Example 5

A solution of HCl was electrolysed between Pt electrodes in a Hittorf cell. The analysis of the solution from the cathode compartment before and after the electrolysis indicated the masses of HCl as 1.82×10^{-4} kg and 1.67×10^{-4} kg. The silver deposited at the cathode of the coulometer in the same circuit was 2.52×10^{-4} kg. Calculate the transport number of both the ions.

Solution

According to Eq. 16.26, change in the amount of HCl around the cathode,

$$(t_+ - 1)\frac{It}{z_+F} = \frac{(1.67 \times 10^{-4} - 1.82 \times 10^{-4})\ \text{kg}}{0.0365\ \text{kg mol}^{-1}}$$

$$(t_+ - 1)\left(\frac{It}{z_+F}\right) = -\frac{0.15 \times 10^{-4}\ \text{kg}}{0.0365\ \text{kg mol}^{-1}} = -\,4.1 \times 10^{-4}\ \text{mol}$$

But as per Eq. 16.25

$$\text{number of moles of cations discharged} = \frac{It}{z_+F} = \frac{2.52 \times 10^{-4}\ \text{kg}}{0.108\ \text{kg mol}^{-1}}$$

$$= 23.33 \times 10^{-4}\ \text{mol}$$

Hence,

$(t_+ - 1)(23.33 \times 10^{-4}) = -\,4.1 \times 10^{-4}$

$t_+ - 1 = -\,0.18$

$t_+ = 1 - 0.18 = 0.82$ and $t_- = 1 - 0.82 = 0.18$.

Moving Boundary Method

Suppose that the transference number of the cation, M^{z+}, of a salt MA is to be determined. A solution of MA is introduced into a tube with known uniform bore, where it forms an upper layer over a solution of another electrolyte M_1A, having a common anion, A. The two electrolytes are so chosen such that the mobility of M^{z+} is much greater than M_1^{z+} and the two solutions form a sharp boundary between them (Fig. 16.6).

Fig. 16.6 : Apparatus for moving boundary method
I) Cathode;
II) boundary after passing the current for time t;
III) initial boundary;
IV) anode.

The boundary can be observed by the use of any physical property. For instance the difference in the refractive index of the two electrolytes can be utilised. When a current I is passed through the cell for a time t, the boundary will move. M_1^{z+} will neither be able to overtake M^{z+}

nor lag behind it; therefore the boundary between the electrolytes will be preserved. Suppose that the boundary moves a distance x and the concentration of the electrolyte MA is c. If the cross-section area of the tube is a, than $xa = V$, where V is the volume of the column of electrolyte between the boundaries before and after the experiment. Hence, the number of moles of electrolyte in this volume will be equal to Vc. Each mole of cation M^{z+} carries a charge, z_+F. Thus, the charge carried by Vc mole of the cation is Vcz_+F; but, the total quantity of charge supplied is It.

Hence,

$$\text{Transport number, } t_+ = \frac{\text{Charge carried by cation}}{\text{Total charge}}$$

$$= \frac{Vcz_+F}{It} = \frac{xacz_+F}{It} \qquad \text{..... (16.27)}$$

SAQ 4

In a moving boundary experiment with 0.020 M NaCl solution, a current of 0.0016 A moved the boundary through a distance of 0.060 m in 2070 s. The radius of the tube is 1.884×10^{-3} m. Calculate the transport number of both the ions.

Hints : 1) The tube is cylindrical and its cross-sectional area $(a) = \pi \times (\text{radius})^2$

2) Concentration (c) = Molarity $\times 10^3$
[since $1\ \text{dm}^{-3} = 10^3\ \text{m}^{-3}$]

....

....

....

16.9 APPLICATIONS OF CONDUCTIVITY MEASUREMENTS

The conductance measurements on electrolyte solutions can provide a lot of useful information. We have already seen that we can divide the electrolytes into strong and weak categories on the basis of the magnitude of molar conductance. This classification helps us in understanding the behaviour of different substances in solution. Further, these measurements can lead us to evaluate the degree of ionisation and the ionisation constants for weak electrolytes. We can also determine the solubility of sparingly soluble salts. Finally, the conductance experiments can be performed to find the equivalence points in acid-base or precipitation titrations. Let us see how it is actually done in each case.

Determination of the Ionic Product of Water

We can determine both the degree of dissociation and the ionic product of water using conductivity measurements. For this purpose, conductivity water is prepared by repeated distillation of water containing a small quantity of NaOH and $KMnO_4$. Experimentally determined value for conductivity on such samples of distilled water is

$$\kappa(H_2O) = 5.50 \times 10^{-6}\ \text{S m}^{-1}$$

To find out the molar conductance, we must know the concentration of water since from Eq. 16.15,

$$\Lambda_m = \frac{\kappa}{c}$$

$$\text{But the concentration } (c) \text{ of water} = \frac{\text{Amount of water}}{\text{Volume}}$$

$$= \frac{\text{Mass of water}}{\text{Molar mass of water}} \times \frac{1}{\text{Volume}}$$

$$= \frac{1\ \text{kg}}{0.018\ \text{kg mol}^{-1}} \times \frac{1}{10^{-3}\ \text{m}^3}$$

$$c = 5.56 \times 10^4\ \text{mol m}^{-3}.$$

The concentration of water is calculated using the fact that 1 dm^3 (i.e., $10^{-3}\ \text{m}^3$) of water has a mass of 1 kg. Also the molar mass of water is 0.018 kg mol^{-1}.

Substituting the values of κ and c we get,

$$\Lambda_m = \frac{5.50 \times 10^{-6}}{5.56 \times 10^{4}} \text{ S m}^2 \text{ mol}^{-1}$$

$$\Lambda_m = 9.90 \times 10^{-11} \text{ S m}^2 \text{ mol}^{-1}$$

The molar conductance at infinite dilution, Λ_m^0, can be calculated on the basis of law of independent mobility of ions. In the present case, since water dissociates to a small extent into H^+ and OH^- ions we can write,

$$\Lambda_m^0 (H_2O) = \lambda^0 (H^+) + \lambda^0 (OH^-)$$

The values of $\lambda^0(H^+)$ and $\lambda^0 (OH^-)$, as determined experimentally are, 3.498×10^{-2} S m^2 mol^{-1} and 1.980×10^{-2} S m^2 mol^{-1}, respectively. Hence,

$$\Lambda_m^0 = (3.498 + 1.980) \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$$
$$= 5.478 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$$

From Eq. 16.19, we know that

$$\Lambda_m = \alpha \, \Lambda_m^0$$

$$\text{or } \alpha = \frac{\Lambda_m}{\Lambda_m^0}$$

where α is the degree of dissociation of water.

Substituting the proper values obtained above, we get

$$\alpha = \frac{9.90 \times 10^{-11} \text{ S m}^2 \text{ mol}^{-1}}{5.478 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}}$$
$$= 1.81 \times 10^{-9}$$

Thus, the degree of dissociation of water is found to be 1.81×10^{-9}.

1m = 10 dm
$(1 \text{ m})^{-6} = (10 \text{ dm})^{-6}$
$= 10^{-6} \text{ dm}^{-6}$
Hence, $1.01 \times 10^{-8} \text{ m}^{-6}$
$= 1.01 \times 10^{-8} \times 10^{-6} \text{ dm}^{-6}$
$= 1.01 \times 10^{-14} \text{ dm}^{-6}$
Also $1.01 \times 10^{-8} \text{ mol}^2 \text{ m}^{-6}$
$= 1.01 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

Further, we have already learnt in Unit 15 of this block that the ionic product of water is given by the equation :

$$K_w = [H^+][OH^-] = (c\alpha)(c\alpha) = \alpha^2 c^2 \qquad \text{..... (16.28)}$$

Substituting c and α values in this equation, we get

$$K_w = (1.81 \times 10^{-9})^2 (5.56 \times 10^4 \text{ mol m}^{-3})^2$$
$$= 1.01 \times 10^{-8} \text{ mol}^2 \text{ m}^{-6}$$
$$= 1.01 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

Thus we see that the degree of dissociation and the ionic product of water can be calculated.

Dissociation Constant of a Weak Acid

We have learnt in Unit 15 of this block that the dissociation of a weak acid can be represented as,

$$\begin{array}{ccc} HA & \rightleftharpoons & H^+ + A^- \\ c(1-\alpha) & & c\alpha \quad c\alpha \end{array}$$

where the symbols have their usual meaning. The dissociation constant is written as

$$K_a = \frac{\alpha^2 c}{(1-\alpha)} \qquad \text{..... (16.29)}$$

From Eq. 16.19 we know,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0}$$

Hence, Eq. 16.29 can be written as

$$K_a = \frac{(\Lambda_m/\Lambda_m^0)^2 \, c}{\left(1 - \dfrac{\Lambda_m}{\Lambda_m^0}\right)} = \frac{\Lambda_m^2 \, c}{\Lambda_m^0 (\Lambda_m^0 - \Lambda_m)} \qquad \text{..... (16.30)}$$

Following the steps shown in Example 3, we can calculate the molar conductance of a weak acid at any given concentration, if its resistance is known. The molar conductance at infinite dilution, Λ_m^0, can be calculated from the principle of independent migration of ions. Thus for HA we can write

$$\Lambda_m^0 (HA) = \lambda^0(H^+) + \lambda^0(A^-) \qquad \text{..... (16.31)}$$

λ^0 values for most of the common ions have been determined and given in Table 16.3.

It is thus possible to calculate the dissociation constant of a weak acid or any other weak electrolyte.

Table 16.3 : Ion Conductances at Infinite Dilution at 298 K

Ion	$10^4 \times \lambda_+^0$/S m^2 mol^{-1}	Ion	$10^4 \times \lambda_-^0$/S m^2 mol^{-1}
H^+	349.8	OH^-	198.0
K^+	73.52	Cl^-	76.34
Na^+	50.11	NO_3^-	71.46
Ag^+	61.9	CH_3COO^-	40.9
NH_4^+	73.6	Br^-	78.14

Let us consider an example for the determination of dissociation constant of a weak acid.

Example 6

Calculate the dissociation constant for acetic acid at 298 K if 0.040 M solution of the acid ias a molar conductance of 8.59×10^{-4} S m^2 mol^{-1}.

Solution

The principle of independent migration of ions gives

$$\Lambda_m^0 = \lambda^0(H^+) + \lambda^0(CH_3COO^-)$$

Substituting the proper values from Table 16.3 gives,

$$\Lambda_m^0 = (349.8 + 40.9) \times 10^{-4}\ \text{S.m}^2\ \text{mol}^{-1}$$
$$= 390.7 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$$

rom Eq. 16.30, we get

$$K_a = \frac{\Lambda_m^2\, c}{\Lambda_m^0 (\Lambda_m^0 - \Lambda_m)}$$

r

$$K_a = \frac{(8.59 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1})^2 \times 0.040\ \text{mol dm}^{-3}}{(390.7 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1})(390.7 \times 10^{-4} - 8.59 \times 10^{-4})\ \text{S m}^2\ \text{mol}^{-1}}$$

$$K_a = 1.98 \times 10^{-5}\ \text{mol dm}^{-3}$$

Note that concentration is expressed in mol dm^{-3} units while calculating K_a or any equilibrium constant values (as per Unit 14).

he value so obtained is in close agreement with the accepted standard value of 1.8×10^{-5}.

etermination of Solubility of a Sparingly Soluble Salt

he solubility of a sparingly soluble salt can be determined using conductance method. By iding Λ_m and κ values of the salt and substituting the same in the rearranged form of q. 16.15, the concentration, c, of a sparingly soluble salt in its solution can be calculated:

$$= \frac{\kappa(\text{salt})}{\Lambda_m(\text{salt})} \qquad \text{..... (16.32)}$$

is to be noted that κ(salt) is the conductivity of the salt alone and is given by the equation,

$$\text{salt}) = \kappa(\text{solution}) - \kappa(\text{water}) \qquad \text{..... (16.33)}$$

ence, κ (salt) is calculated by subtracting κ (water) from κ (solution), which are both termined experimentally.

irther, we know that the sparingly soluble salts are at extremely low concentrations even in a turated solution. Hence, the molar conductivity of a saturated solution of a sparingly soluble t can be assumed to be equal to the molar conductivity at infinite dilution.

$$_m(\text{salt}) = \Lambda_m^0(\text{salt}) \qquad \text{..... (16.34)}$$

using Eq. 16.18,

$$^0_m(\text{salt}) = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0 \qquad \text{..... (16.35)}$$

iere ν_+ and ν_- are the numbers of cations and anions per formula unit of the salt.

mbining Eqs. 16.32, 16.33 and 16.35, we get

$$= \frac{\kappa(\text{solution}) - \kappa(\text{water})}{\nu_+ \lambda_+^0 + \nu_- \lambda_-^0} \qquad \text{..... (16.36)}$$

Substituting the values of quantities in Eq. 16.36, the concentration of the sparingly soluble salt in its saturated solution can be determined.

Example 7

Specific conductances (κ) at 298 K of a saturated solution of AgCl and of water used for dissolving the salt are 2.850×10^{-4} S m^{-1} and 5.50×10^{-6} S m^{-1}, respectively. The ionic conductances at infinite dilution for Ag^+ and Cl^- ions are 61.9×10^{-4} S m^2 mol^{-1} and 76.34×10^{-4}S m^2 mol^{-1}. Calculate the solubility of AgCl in kg m^{-3}.

Solution

Substituting the given values in Eq. 16.36, we get,

$$c = \frac{(2.850 - 0.055) \times 10^{-4}\,\mathrm{S\,m^{-1}}}{(61.9 + 76.34) \times 10^{-4}\,\mathrm{S\,m^2\,mol^{-1}}} \quad (\text{since } \nu_+ = \nu_- = 1)$$

$$= \frac{2.795 \times 10^{-4}\,\mathrm{S\,m^{-1}}}{138.24 \times 10^{-4}\,\mathrm{S\,m^2\,mol^{-1}}}$$

$$= 2.022 \times 10^{-2}\,\mathrm{mol\,m^{-3}}$$

$$= 2.022 \times 10^{-2} \times 0.143\,\mathrm{kg\,m^{-3}} (\text{since molar mass of AgCl} = 0.143\,\mathrm{kg\,mol^{-1}})$$

$$= 2.89 \times 10^{-3}\,\mathrm{kg\,m^{-3}}$$

Conductometric Titrations

Acid-base or precipitation titrations can be performed with the help of conductivity measurements. In acid-base titrations, three different situations can arise:

a) titration between a strong acid and a strong base
b) titration of a weak acid with a strong base and
c) titration of a weak acid with a weak base.

Let us consider each one of them separately.

i) Suppose we titrate a strong acid, say, HCl, with a strong base, NaOH:

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$

Actually, the addition of NaOH results in replacing H^+ ions by Na^+ ions in solution as shown by the above equation. The ionic conductance of H^+ is more than that of Na^+ ion. As a result, the conductivity of the solution will decrease with the addition of NaOH. At the equivalence point, the conductivity will have the lowest value since all the H^+ ions have been replaced by Na^+ ions in solution. After the equivalence point, addition of NaOH will produce excess of Na^+ ions as well as fast moving OH^- ions. Again there will be a rise in the conductivity of the solution. A typical plot of conductance ($1/R$) against the volume of the base (V) added for a strong acid-strong base titration is shown in Fig. 16.7 a. The decrease in conductance before the equivalence point is much sharper than the increase after the equivalence point. The reason is that H^+ ions are far more mobile than OH^- ions. The equivalence point, B, is obtained by the intersection of the two lines. AB and BC.

ii) In the case of titration between a weak acid and a strong base, we get a titration curve as shown in Fig. 16.7 b.

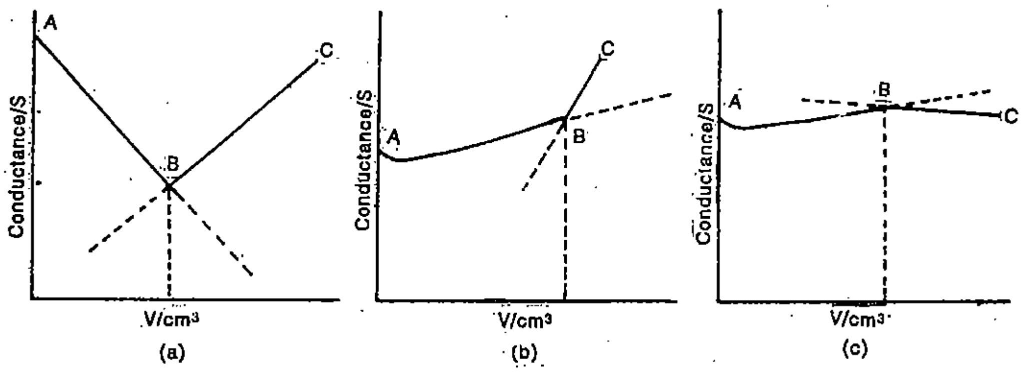

Fig. 16.7 : a) Conductometric titration of a strong acid with a strong base; b) conductometric titration of a weak acid with a strong base; c) conductometric titration of a weak acid and a weak base.

Initially the conductance will be low, since the dissociation of a weak acid is low and smaller number of H^+ ions is produced. On addition of NaOH, H^+ ions combine with OH^- ions to produce water; but, at the same time, some fresh H^+ ions are produced in the solution. As soon as H^+ ions are removed in the form of water, the equilibrium

$$HA \rightleftharpoons H^+ + A^-$$

will shift to the right. In addition to these H^+ ions, we will also have some Na^+ ions in solution. The net result is that there is a slight increase in conductivity. This trend will be seen till the equivalence point is reached. However, after the equivalence point, there will be a sudden increase in the conductivity due to the presence of Na^+ ions and OH^- ions. Since NaOH is a strong electrolyte, it dissociates completely in solution. So even a small excess will produce enough of fast moving OH^- ions. The equivalence point in this case may not be very sharp; but the extrapolation of the curves before and after the equivalence point will cut at a point which will be the equivalence point.

iii) When the titration between a weak acid and a weak base is carried out (Fig. 16.7 c), the initial nature of the titration curve obtained will be similar to that found in (ii). This means the conductivity will slowly increase before the equivalence point. After the equivalence point, further addition of a base will not make much of a difference in the conductivity since the base itself is very weak, having low dissociation constant value.

Conductometric Titration of a Precipitation Reaction

Let us consider a typical precipitation reaction between the solutions of NaCl and $AgNO_3$ which is expressed as,

$$Na^+ + Cl^- \xrightarrow{AgNO_3} AgCl + Na^+ + NO_3^-$$

Initially we have Na^+ ions and Cl^- ions in solution. The slow addition of $AgNO_3$ gives solid AgCl and Na^+ and NO_3^- ions in solution. Thus as the titration proceeds, we are replacing Cl^- ions by NO_3^- ions in solution. Since there is not much of a difference in the conductance of Cl^- ions and NO_3^-, this part of the curve (AB) in Fig. 16.8 remains almost horizontal, without much of a change in the slope, After the equivalence point, B, there will be a continuous increase in the conductance with the addition of $AgNO_3$. This is so because each addition of $AgNO_3$ will give more Ag^+ and NO_3^- ions which would increase the conductance.

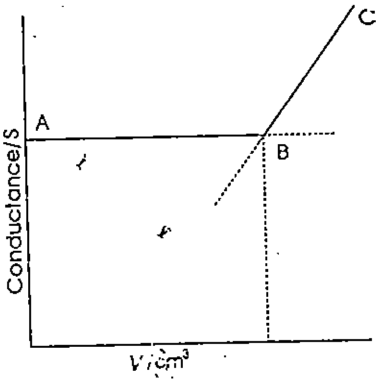

Fig. 16.8 : Conductance against volume plot for precipitation titration.

16.10 SUMMARY

In the present unit, we have discussed the behaviour of electrolytes in solution under the influence of an electric field. Since the ions produced by the dissolution of an electrolyte are charged particles, these are bound to interact with each other. However, these interactions will not be as strong as in solid state due to the thermal motion of the ions. At the same time, the ions will interact with polar molecules of the solvent, water.

After explaining the nature of these interactions, we then analysed in brief as to what happens to these solutions at the electrodes when we pass an electric current through them. This has been summed-up in the two laws of Faraday

Different ions, even when they carry same charge, will move at different rates under the influence of an electric potential. The mobility of an ion is defined in terms of a quantity known as transport number. Two common methods for the experimental determination of transport number have been discussed.

The utility of conductance studies has been discussed in the determination of the dissociation constant of a weak electrolyte and the solubility of sparingly soluble salts. The conductance methods of acid-base and precipitation titrations have been discussed.

16.11 TERMINAL QUESTIONS

1) The specific conductance at 298 K of a saturated solution of $BaSO_4$ is 4.580×10^{-4} S m^{-1} and that of water is 5.50×10^{-6} S m^{-1}. The molar conductance at infinite dilution of $BaSO_4$ is 2.86×10^{-2} S m^2 mol^{-1}. What is the solubility of $BaSO_4$ at 298 K?

2) 1000 C of electricity is passed through a NaOH solution in an electrolysis apparatus. Calculate the volume of hydrogen and oxygen liberated at S.T.P.

3) A moving boundary experiment is carried out with 0.100 M solution of HCl at 298 K. Sodium ions are caused to follow the hydrogen ions. The cross-sectional area of the tube is 3.0×10^{-5} m^2. With 3.0 milliampere current, the boundary moves 3.08×10^{-2} m in an hour. Calculate the transport number of the hydrogen ion.

4) Calculate the time required to discharge all the Cr^{3+} ions from 500 cm^3 of 0.270 M $Cr_2(SO_4)_3$ by a current of 3.00 A.

5) The limiting molar conductivities of KCl, KNO_3, and $AgNO_3$ are

   1.499×10^{-2} S m^2 mol^{-1}
   1.450×10^{-2} S m^2 mol^{-1}, and
   1.334×10^{-2} S m^2 mol^{-1}, respectively.

   What is the limiting molar conductivity of AgCl at this temperature?

6) A solution of $AgNO_3$ was electrolysed with silver electrodes. 1.74×10^{-4} kg silver was deposited on the cathode. If the transport number of Ag^+ ion is 0.37, calculate the decrease in the amount of $AgNO_3$ around the cathode compartment.

16.12 ANSWERS

Self Assessment Questions

1) To reduce each Mg^{2+} ion to magnesium metal, two electrons are required,

   $Mg^{2+} + 2e^- \longrightarrow Mg$

   Hence $n = 2$

   Rearranging Eq. 16.8, we get, $t = \dfrac{96500\ nw}{IM}$

   Since 1 mol magnesium is to be prepared, $\dfrac{w}{M} = 1$ mol.

   Also, $I = 5$ A

   Hence $t = \dfrac{96500 \times 2 \times 1}{5} s = 38600\ s.$

2) i) To reduce each Cu^{2+} ion to copper metal, two electrons are required.

   $Cu^{2+} + 2e^- \longrightarrow Cu$

   Hence $n = 2$

   According to Eq. 16.8, $w = \dfrac{MIt}{96500n}$

   Substituting for *M, I, t* and *n* we get,

   $w = \dfrac{0.06354 \times 4.50 \times 9000}{96500 \times 2}$ kg [since $M = 0.06354$ kg mol^{-1}]

   $w = 1.33 \times 10^{-2}$ kg.

ii) Amount of Cu deposited $= \frac{w}{M} = 0.21$ mol

Amount of Cu initially present = 2.0 mol
(since 1 dm^3 of 2.0 M solution contains 2.0 mol of copper)
Amount of Cu at the end of the electrolysis = (2.0 − 0.21) mol
= 1.79 mol

This must also be equal to the amount of Cu^{2+} ions present in the solution at the end of electrolysis.

3) Substituting the given values for 0.020 M KCl in Eq. 16.14, we get,

$$\kappa = k_{cell} \times \frac{1}{R}$$

$$0.2768\ S\ m^{-1} = k_{cell} \times \frac{1}{195.96\ \Omega}$$

$$k_{cell} = 0.2768 \times 195.96\ m^{-1}$$

Using this value of k_{cell} for 0.050 M $AgNO_3$ solution in Eq. 16.14 we get

$$\kappa(AgNO_3) = 0.2768 \times 195.96\ m^{-1} \times \frac{1}{94.2\ \Omega}$$

$$= 0.576\ S\ m^{-1}.$$

4) According to Eq. 16.27,

transport number, $t_+ = \frac{x\,a\,c\,z_+\,F}{It}$

where the symbols have their usual meaning.
Substituting the given values we get,

$$t(Na^+) = \frac{0.060\ m \times 3.14 \times (1.884 \times 10^{-3}\ m)^2 \times (0.020 \times 10^3\ mol\ m^{-3}) \times (1 \times 96500\ C\ mol^{-1})}{0.0016\ A \times 2070 s}$$

$$= 0.39$$

Hence, $t(Cl^-) = (1 - t(Na^+)) = 0.61$

i) $A = \pi r^2 = 3.14 \times (1.884 \times 10^{-3}\ m)^2$
ii) concentration in mol m^{-3} units
= Molarity × 10^3
iii) $z_+ = 1$

Terminal Questions

1) According to Eq. 16.36,

$$c = \frac{\kappa(solution) - \kappa(water)}{\nu_+ \lambda_+^0 + \nu_- \lambda_-^0}$$

but $\nu_+ \lambda_+^0 + \nu_- \lambda_-^0 = \Lambda_m^0(salt)$ according to Eq. 16.35. Hence, combining the two equations we get,

$$\frac{\kappa(solution) - \kappa(water)}{\Lambda_m^0(salt)}$$

Substituting the given values we get,

$$c = \frac{(4.580 \times 10^{-4} - 0.0550 \times 10^{-4})\ S\ m^{-1}}{(2.86 \times 10^{-2})\ S\ m^2\ mol^{-1}}$$

$$= 1.58 \times 10^{-2}\ mol\ m^{-3}.$$

2) According to the equations,
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ and $4\ OH^- \rightleftharpoons 2H_2O + O_2 + 4e^-$, we find that for the production of 1 mole each of H_2 and O_2, we require 2 and 4 faradays of electricity respectively.

Hence $n = 2$ for the production of hydrogen, whereas for the production of oxygen, $n = 4$.

Using Eq. 16.7, the amount of hydrogen produced,

$$n^{H_2} = \frac{w}{M} = \frac{q}{nF}$$

Also as per gas law, volume of hydrogen,

$$V_{H_2} = \frac{n_{H_2} RT}{p} \quad [\text{At STP, } p = 1.013 \times 10^5\ Pa,\ T = 273.15\ K]$$

using the above two expressions,

$$V_{H_2} = \frac{qRT}{nFp}$$

$$= \frac{1000\ \text{C} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 273.15\ \text{K}}{2 \times 96500\ \text{C mol}^{-1} \times 1.0132 \times 10^{5}\ \text{Pa}}$$

$$= 1.162 \times 10^{-4}\ \text{m}^3$$

Similarly, $V_{O_2} = \frac{qRT}{nFp}$ [Note that $n = 4$ in the case of oxygen evolution]

$$= 5.81 \times 10^{-5}\ \text{m}^3$$

3) $t_+ = \frac{x\,a\,c\,z_+\,F}{It}$ (as per Eq. 16.27)

$$= \frac{3.08 \times 10^{-2}\ \text{m} \times 3.0 \times 10^{-5}\ \text{m}^2 \times 0.100 \times 10^{3}\ \text{mol m}^{-3} \times 1 \times 96500\ \text{C mol}^{-1}}{3.0 \times 10^{-3}\ \text{A} \times 1 \times 60 \times 60\ \text{s}}$$

$= 0.83.$

4) 1000 cm³ of 1 M $Cr_2(SO_4)_3$ solution contains 2 mol of Cr^{3+} ions. Amount of Cr^{3+} in the given solution ($n_{Cr^{3+}}$)

$$= \frac{500\ \text{cm}^3}{1000\ \text{cm}^3} \times \frac{0.270\ \text{M}}{1\ \text{M}} \times 2\ \text{mol}$$

$= 0.270$ mol

From the following equation,

$$Cr^{3+} + 3e^- \rightleftharpoons Cr$$

we find that for producing each mole of Cr, we require 3F of electricity (i.e., $n = 3$)
From Eq. 16.7

$$n_{Cr^{3+}} = 0.270\ \text{mol} = \frac{w}{M} = \frac{q}{nF} = \frac{It}{nF} = \frac{(3.00\ \text{A})\ t}{(3 \times 96500)\ \text{C mol}^{-1}}$$

$$t = \frac{0.270 \times 3 \times 96500}{3.00}\ \text{s} = 2.61 \times 10^{4}\ \text{s}.$$

5) We can write

$$\Lambda_m^0(\text{AgCl}) = \Lambda_m^0(\text{AgNO}_3) + \Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{KNO}_3)$$

Substituting the given values we get,

$$\Lambda_m^0(\text{AgCl}) = (1.334 + 1.499 - 1.450) \times 10^{-2}\ \text{S m}^2\ \text{mol}^{-1}$$
$$= 1.383 \times 10^{-2}\ \text{S m}^2\ \text{mol}^{-1}$$

6) As per Eq. 16.25,
number of moles of Ag^+ ions discharged

$$= \frac{It}{z_+F} = \frac{w}{M} = \frac{1.74 \times 10^{-4}\ \text{kg}}{0.108\ \text{kg mol}^{-1}} = 0.0016\ \text{mol}$$

As per Eq. 16.26, change in the amount of $AgNO_3$ around the cathode compartment $= (t_+ - 1)\frac{It}{z_+F}$

$= (-0.63) \times (0.0016)$ mol
$= -0.0010$ mol

Hence, the decrease in the amount of $AgNO_3$ around the cathode compartment = 0.0010 mol.

UNIT 17 ELECTROCHEMICAL CELLS

Structure

17.1 INTRODUCTION

In Unit 16, we have seen that on passing electric current through an electrolyte solution, a chemical reaction takes place. In other words, an electric current can cause a chemical reaction to take place under suitable conditions. Is the reverse process also possible? Or by means of a chemical reaction, can we produce electricity? The answer is yes and in both the processes, we make use of a group of reactions where electron transfer takes place.

In an electrolytic cell, a chemical reaction takes place by passing electricity through an electrolyte in a fused state or in solution. On the other hand, when an electrochemical cell is used to generate electricity by the use of a chemical reaction, it is called a galvanic or voltaic cell. In this unit, we shall mainly study different types of galvanic cells, the electrodes used and their effect on the voltage generated. We shall also look at the relationship between the free energy change for the reaction and the electrical potential generated by the cell. Common practical cells will also be discussed as well as the applications of emf measurements. Finally there will be a discussion on the applications of electrolytic cells also.

Objectives

After reading this unit, you should be able to :

- explain the terms used in electrochemistry such as anode, cathode, oxidation, reduction and emf,
- calculate the cell potential for a given cell,
- correlate the electrical energy generated by the cell with the free energy change for the cell reaction,
- correlate the dependence of the cell potential on the temperature and the concentration of the electrolytes,
- describe the characteristics and the half-cell reactions of various kinds of electrodes used,
- differentiate between primary and secondary cells,
- list different types of dry cells in common use, and
- describe the use of electrolytic cells.

17.2 GALVANIC OR VOLTAIC CELLS

Let us recapitulate the definitions of the terms, oxidation and reduction. Oxidation is the loss or release of electrons. Reduction is the gain or addition of electrons. These two processes are illustrated below :

Oxidation

$A \longrightarrow A^{n+} + ne^-$

Reduction

$B + me^- \longrightarrow B^{m-}$

Usually oxidation and reduction reactions take place together. Such reactions are also called **redox reactions.**

Electrochemical cells make use of spontaneous oxidation-reduction reactions to produce electricity. These cells are known as galvanic or voltaic cells in recognition of the work by Italian scientists, Galvani and Volta. Let us explain the functioning of a volatic cell.

In any spontaneous redox reaction, the two processes,

$A \longrightarrow A^+ + e^-$ (oxidation)

$B + e^- \longrightarrow B^-$ (reduction)

take place without doing any useful work, if we just mix them together. The energy released by such a reaction is in the form of heat. However, if we devise a means of performing oxidation and reduction in separate compartments rather than mixing the two together, we can force the electrons to flow from oxidation to reduction compartment through an external wire, thus producing current. Part of the energy of the reaction is thus converted into electrical work. Let us take the example of the most common and familiar galvanic cell, known as Daniell cell. It consists of a container divided into two compartments by a porous plug. The function of the porous plug is not to allow the free mixing of the electrolyte solutions in the two compartments but to allow the flow of ions. In one compartment, a strip of zinc metal is immersed in a solution of zinc sulphate whereas, the other compartment holds a solution of copper sulphate with a copper strip immersed in the solution. The two metal strips, henceforth called the electrodes, are connected to an ammeter through copper wires as shown in Fig. 17.1. The moment the two electrodes are connected, a current starts flowing as shown by the deflection in the ammeter. As the current flows through the circuit, zinc strip dissolves while copper deposits at the other electrode.

When zinc metal goes into solution as Zn^{2+} ion, it leaves behind an excess of electrons on the zinc electrode; hence this electrode is assigned a negative charge as shown in Fig. 17.1. On the other hand, the electrons from copper electrode are picked up by the copper ions in solution thereby resulting in a positive charge on the cathode.

Metals in their normal mode of existence are assigned an oxidation state of zero.

In a galvanic cell, cathode is assigned a positive sign and the anode, a negative sign. However, in an electrolytic cell, these electrodes acquire charges opposite to the above. However, in both the cases, oxidation takes place at anode and reduction takes place at cathode.

It is commonly said that the current flows from positive electrode to the negative in the circuit; however, the flow of electrons in the connecting wire is from the negative electrode (anode) to the positive electrode (cathode) in the galvanic cell.

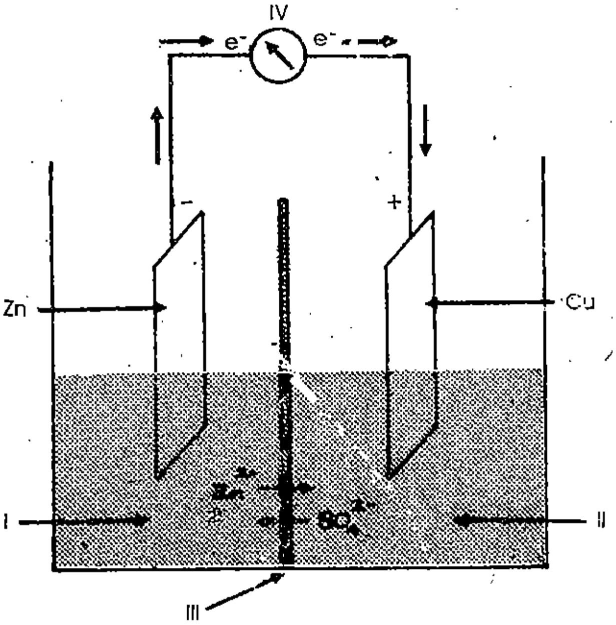

Fig. 17.1 : Daniell Cell :

I) $ZnSO_4$ solution; II) $CuSO_4$ solution; III) porous plug; IV) ammeter.

The overall reaction in Daniell cell can be represented as

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$$

whereas the reactions taking place in the two compartments known as half-cell reactions can be written as :

$Zn \rightleftharpoons Zn^{2+} + 2e^-$ ...... oxidation
and $Cu^{2+} + 2e^- \rightleftharpoons Cu$ ...... reduction

The capacity to do electrical work by a cell is called the cell potential.

There is always an equilibrium between the atoms in the electrode and the ions present in the solution as represented by the above equations. The electrode at which oxidation takes place is called anode; it is at a lower potential than the cathode at which reduction takes place. Zinc metal dissolves as Zn^{2+} ion leaving behind an excess of electrons at this electrode. Thus anode gets negatively charged and attains relatively lower potential. On the other hand, ions in solution around the cathode withdraw electrons from it causing it to become positively charged and attain relatively higher potential. By convention, we regard the current through the connecting wire to flow from positive to negative, that is from cathode to anode in the present context. However, we should not forget that the flow of electrons in the wire is in the opposite direction, that is, from zinc to copper. However, in an electrolytic cell, the situation will be just the opposite. The anode would acquire a positive charge and the cathode, a negative charge. In order to avoid any confusion, we shall always refer to an electrode, where oxidation takes place, as anode, and the electrode, where reduction takes place, as cathode, irrespective of whether the cell is galvanic or electrolytic.

SAQ 1

How do we define anode and cathode? What sign — positive or negative — would you assign to anode and cathode in (a) a galvanic cell (b) an electrolytic cell?

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17.3 EXPERIMENTAL MEASUREMENT OF EMF

The capacity to do electrical work by a cell is called the cell potential. It is expressed in volt (V). We could use a voltmeter to measure the cell potential. However, this would not give us the correct value of cell potential. The reason is that the cell potential is dependent upon the concentration of the electrolyte which would change if we allow the current to flow in the circuit through the voltmeter. Hence, we must measure the potential difference between the two half-cells when the cell is held at almost constant composition and no current is flowing.

The potential difference of a cell when no current is drawn out and when the cell is operating reversibly is called the emf (electromotive force) of the cell. The measurement of the emf can be done by using a potentiometer. More recently emf is found with the help of an electronic digital voltmeter which draws negligible current.

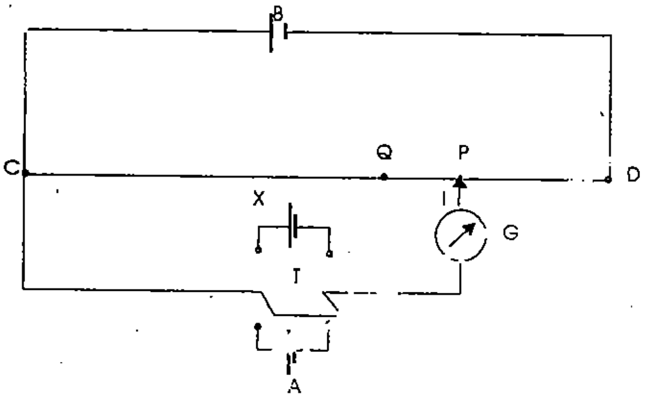

Fig. 17.2 : Potentiometric measurement of emf of a cell.

Fig. 17.2 shows a simple set-up to measure the emf of a cell. The potentiometer consists of a wire of uniform cross-section and high resistance. This wire is stretched between two terminals, C and D. It is connected to a storage battery, B. The terminal C is connected to a sliding point I which can be moved from C to D. In between C and D, there is a double throw-switch T and a galvanometer G. The function of the switch is to bring either a standard (weston) cell, A, or the test cell X (for which emf is to be determined) in the circuit. First, we connect A in the circuit and move I to such a position P that there is no deflection in the galvanometer. The exact length of the wire from C to P is recorded. Let us suppose this length is l_1. Next by means of the switch T, we remove A but bring cell X in the circuit. The emf of A and X may not be the same, hence on replacement of A by X, the galvanometer will show a deflection. We move the contact point to such a position Q that there is again no deflection in the galvanometer. Measure the length of the wire l_2, from C to Q. Under the conditions of no deflection, the drop in potential of the battery B across the slide wire is balanced by the emf of the cell (A or X). Hence, we can write,

$$\frac{\text{emf of X}}{\text{emf of A}} = \frac{\text{Drop in potential from C to Q } (E_2)}{\text{Drop in potential from C to P } (E_1)} = \frac{\text{Resistance due to wire length CQ}}{\text{Resistance due to wire length CP}} = \frac{l_2}{l_1}$$

$$\frac{E_2}{E_1} = \frac{l_2}{l_1}$$

$$\text{In general, } E_2 = E_1 . \frac{l_2}{l_1} \qquad \text{..... (17.1)}$$

where E_2 and E_1 are the emf values of the test cell and the standard cell, respectively.

We make use of a standard cell in the procedure described above for the standardisation of a potentiometer. We describe here, Weston cadmium cell, which is a commonly used standard cell.

Weston Cell

The most commonly used standard cell is called Weston cell. Its voltage remains constant for a long period of time and is reproducible. The change in voltage with temperature is also small. Due to these advantages, Weston cell is widely used as a standard cell. The basic cell reaction can be represented as

$$Cd + Hg_2SO_4 \rightleftharpoons CdSO_4 + 2Hg$$

It is prepared in the form of a H—shaped container as shown in Fig. 17.3

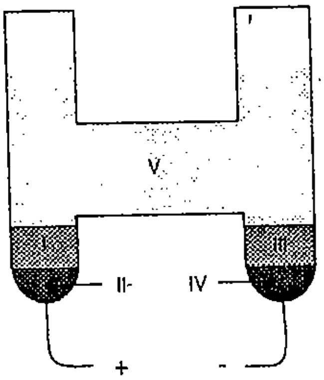

Fig. 17.3 : Weston cell : I) Paste of Hg and Hg_2SO_4 II) Mercury III) $3CdSO_4 . 8H_2O$ crystals IV) Cd (Hg) (V) Saturated $CdSO_4$ solution

In one arm of the container, mercurous sulphate — mercury paste is in contact with mercury. In the other arm, some crystals of cadmium sulphate are dropped over the surface of cadmium amalgam (12.5%). The container is then filled with a saturated solution of cadmium sulphate. The cell produces an emf of 1.01845 V at 293 K.

17.4 STANDARD ELECTRODE POTENTIAL

Consider a strip of zinc metal immersed into an aqueous solution of zinc sulphate at constant temperature and pressure. Both metal and the solution contain zinc ions which can be transferred between the two phases. If some zinc ions from the metal enter into the solution, there would be a net negative charge on the electrode due to the excess of electrons left behind. On the other hand, zinc ions already in solution attract electrons from the electrode and the resulting zinc atoms would stick to the surface of the electrode. This process will leave a positive charge on the electrode. In a short time, however, the rate of escape and of return of zinc ions become equal and an equilibrium is established as expressed by

$$Zn^{2+} + 2e \rightleftharpoons Zn$$

Depending upon whether the equilibrium lies towards left or right, the net charge on the electrode will arise.

Thus we see that there will be a potential difference developed at the junction of the metal and the solution. However, the potential difference between the two phases cannot be readily measured. Therefore, instead of measuring the electrode potentials, we usually measure the total cell potential. The cell potential can be written as the sum of the two electrode potentials neglecting other effects which contribute to the potential difference between the phases. Thus,

$$E_{cell} = E_{cathode} + E_{anode} \qquad ..... (17.2)$$

The total cell potential is a measure of the driving force of a chemical reaction whereas $E_{cathode}$ and E_{anode} are representative of oxidising and reducing capabilities of the concerned reactants, respectively. Hence, in order to obtain a large cell potential, we must use a strong oxidising agent along with a strong reducing agent. Now the question arises as to how do we decide which is a better oxidising agent and which is a better reducing agent. To determine the comparative oxidising or reducing capacity of any substance, we must use some standard against which all other electrode potentials are measured. We shall now explain the necessity of having such a standard.

Let us consider an example, say Daniell cell, the standard cell potential of which is 1.1 V. It just tells us that zinc is a better reducing agent than copper since zinc gets oxidised to Zn^{2+} ion and it reduces Cu^{2+} ions to metallic copper. However, it will not tell us whether a third substance, say, Fe is a better reducing agent than zinc or copper. In order to get some idea regarding the relative oxidising and reducing abilities of different substances, we must measure the cell potentials keeping one-half-cell the same in every case. This is necessary since we cannot measure directly the potential of a half-cell. It is like saying that for a reducing agent to give off its electrons, surely you must have an oxidising agent to accept that electron. It cannot function as an oxidising agent on its own without the presence of a reducing agent. Further, for comparing the reducing powers of different substances, we must use the same oxidising agent. The standard against which all other potentials are measured is a hydrogen electrode. We now describe a standard hydrogen electrode.

The chemical reaction taking place at the hydrogen electrode is given by the equation :

$$2H^+ + 2e^- \longrightarrow H_2$$

The electrode potential for the standard hydrogen electrode is arbitrarily assigned a value of zero. Fig. 17.4 shows a standard hydrogen electrode where hydrogen gas is bubbled through a glass hood (*B*) over the surface of Pt electrode (*A*) at a pressure of 1 bar (≃ 1 atm). The electrode is immersed in an acid in which $[H_3O^+] = 1$ M. The whole set-up is kept at 298 K.

Recent redefinition of the standard state for the pressure of the gas is 1 bar. But 1 bar is not much different from 1 atm. Therefore, we specify the pressure in terms of atm only.

1×10^5 Pa = 1 bar ≃ 0.987 atm

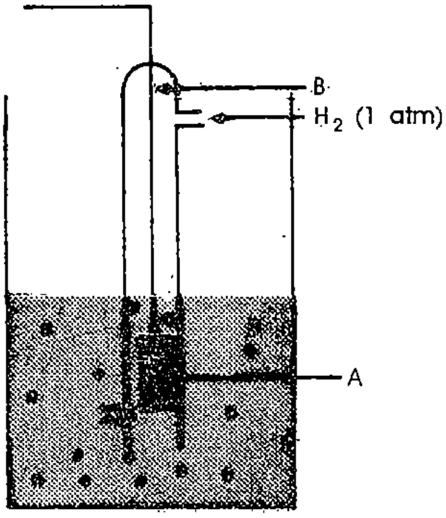

Fig. 17.4 : Standard hydrogen electrode.

In view of the confusion that existed in literature regarding the sign convention in reporting the standard state half-cell potentials ($E°$), IUPAC has set down the following rules in this regard:

1) All electrode reactions are written as reduction reactions.
2) All reactions that produce better reducing agents than hydrogen are given a negative reduction potential value.
3) The most negative reduction potential values are written at the top of the table of standard reduction potentials (Table 17.1).

Table 17.1 : The Standard Reduction Potentials ($E°$) for Some Half-Cell Reactions

Half-cell reactions	$E°$/V
$Li^+ + e^- \longrightarrow Li$	− 3.05
$K^+ + e^- \longrightarrow K$	− 2.93
$Ca^{2+} + 2e^- \longrightarrow Ca$	− 2.87
$Mg^{2+} + 2e^- \longrightarrow Mg$	− 2.36
$Al^{3+} + 3e^- \longrightarrow Al$	− 1.66
$Zn^{2+} + 2e^- \longrightarrow Zn$	− 0.76
$Fe^{2+} + 2e^- \longrightarrow Fe$	− 0.44
$Sn^{2+} + 2e^- \longrightarrow Sn$	− 0.14
$Pb^{2+} + 2e^- \longrightarrow Pb$	− 0.13
$Fe^{3+} + 3e^- \longrightarrow Fe$	− 0.04
$2H^+ + 2e^- \longrightarrow H_2$	0.00
$Cu^{2+} + 2e^- \longrightarrow Cu$	+ 0.34
$Cu^+ + e^- \longrightarrow Cu$	+ 0.52
$I_2 + 2e^- \longrightarrow 2I^-$	+ 0.54
$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$	+ 0.59
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+ 0.77
$Ag^+ + e^- \longrightarrow Ag$	+ 0.80
$Br_2 + 2e^- \longrightarrow 2Br^-$	+ 1.09
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+ 1.33
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+ 1.36
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+ 1.49
$F_2 + 2H^+ + 2e^- \longrightarrow 2HF$	+ 3.03

Standard reduction potential indicates the willingness of a species to be reduced under standard conditions. Larger the reduction potential, greater is the ease with which a particular species can be reduced; in other words, it is a powerful oxidising agent. This is so because, in an oxidation—reduction reaction, an oxidising agent gets reduced and a reducing agent gets oxidised.

These $E°$ values represent the driving force or spontaneity of the reactions under standard conditions. For example, the reaction,

$F_2 + 2H^+ + 2e^- \longrightarrow 2HF$

has a strong tendency to go in the forward direction since it has a high positive potential value, whereas, the reaction,

$Li^+ + e^- \longrightarrow Li$

has the least tendency to go in the forward direction; rather, it has strong tendency to go in the reverse direction. These observations are in accordance with our basic knowledge of chemistry. Fluorine shows a strong tendency to become fluoride ion; thus, fluorine should act as a powerful oxidising agent. The same reasoning tells us that lithium metal should act as a strong reducing agent. These conclusions are borne out by experimental results. Now that we have a set of values for the standard half-cell potentials, we can use them to calculate the standard cell potential for any cell.

$E^o_{anode} = -E°$ and $E^o_{cathode} = E°$, where $E°$ is the standard reduction potential as per Table 17.1

There are, however, a few points to be kept in mind before we set out to calculate the standard cell potentials.

- Since the cell potentials are a measure of the tendency of a particular reaction to go in a particular direction, these potentials are cited in volt and not as volt per mole.
- The calculation of the standard cell potential from the standard potentials of the two half-cells will not be affected by the stoichiometric coefficients used to balance the overall reaction.

- You must remember that Table 17.1 gives the standard reduction potentials for some half-cell reactions. But at the anode, a particular species gets oxidised. In order to get the standard potential for the oxidation reaction at the anode, the sign of the standard reduction potential for that reaction must be reversed.
  i.e., $E^{\circ}_{anode} = -E^{\circ}$ as per Table 17.1.

For example, let us calculate the standard cell potential for the reaction :

$Cu + 2Ag^{+} \longrightarrow Cu^{2+} + 2Ag$

for which the half-cell reactions and corresponding potentials are given below :

$Cu \longrightarrow Cu^{2+} + 2e \qquad E^{\circ}_{anode} = -E^{\circ}_{Cu^{2+}/Cu} = -0.34\ V$

$Ag^{+} + e \longrightarrow Ag \qquad E^{\circ}_{cathode} = E^{\circ}_{Ag^{+}/Ag} = 0.80\ V$

we shall not multiply the Ag^{+}/Ag cell potential by two which is a number used to balance the overall reaction. Secondly, we must keep in mind that in the overall reaction, copper metal is getting oxidised to Cu^{2+} ion. Hence, when we are adding the cathodic and anodic potentials to find the total cell potential, we must reverse the sign of the potential for Cu^{2+}/Cu couple.

An alternative method to arrive at the cell potential value is as follows:

$E^{\circ}_{cell} = [\,E^{\circ}_{reduction}$ (r.h.s. electrode)]
$\quad - [\,E^{\circ}_{reduction}$ (l.h.s. electrode)]
$\quad = [0.80 - (+0.34)]\ V = 0.46\ V$

If the sign of E°_{cell} is negative, then anode and cathode are interchanged. Note that r.h.s. and l.h.s. stand for right hand side and left hand side, respectively.

Thus the standard cell potential for the reaction would be

$$E^{\circ}_{cell} = E^{\circ}_{anode} + E^{\circ}_{cathode}$$
$$= -E^{\circ}_{Cu^{2+}/Cu} + E^{\circ}_{Ag^{+}/Ag}$$
$$= [(-0.34) + (0.80)]\ V$$
$$= 0.46\ V$$

A positive E°_{cell} value indicates that the reaction is spontaneous under standard conditions.

But, if any reaction is written in such a way that on calculation, the cell potential has a negative sign, it should be inferred that the reaction is non-spotaneous. For example, under standard conditions,

$2Fe^{3+} + 2Cl^{-} \longrightarrow 2Fe^{2+} + Cl_2 \qquad E^{\circ}_{cell} = -0.59\ V$

is not a spontaneous reaction. On the other hand, the following reaction is spontaneous :

$2Fe^{2+} + Cl_2 \longrightarrow 2Fe^{3+} + 2Cl^{-} \qquad E^{\circ}_{cell} = +0.59\ V$

And the above is the cell reaction that takes place when a galvanic cell is designed using Fe^{2+}, Fe^{3+} and Cl^{-}, Cl_2 as reacting species.

SAQ 2

Predict which of the following reactions will be spontaneous with the help of standard potential values :

i) $Fe + 2H^{+} \longrightarrow Fe^{2+} + H_2$

ii) $Cu + 2H^{+} \longrightarrow Cu^{2+} + H_2$

iii) $2Fe^{3+} + 2I^{-} \longrightarrow 2Fe^{2+} + I_2$

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17.5 ELECTROCHEMICAL CELL REPRESENTATION AND CELL REACTION

An abbreviated way of representing the Daniell cell is

$Zn \mid Zn^{2+}(c_1) \parallel Cu^{2+}(c_2) \mid Cu$

The anodic reaction is always written on the left and, the cathodic reaction on the right. Also by convention, within the half-cell, the reactants are written before the products. A single vertical line is used to indicate a phase boundary and, a double vertical line represents the elimination of potential at the junction of two electrolyte solutions. Finally, the concentrations of aqueous solutions may be written in parenthesis after the symbol of the ions. The line notation, therefore, corresponds to the direction of the flow of electrons.

In the Daniell cell, when electrons from the anode travel through the wire, it will create an excess of positive charge (Zn^{2+}) around the electrode. Simultaneously, excess negative charge (SO_4^{2-}) will accumulate around cathode. To maintain electroneutrality in both the cells and the continuous flow of electric current, the negative ions (Cl^- or NO_3^-) from the salt bridge would flow into the anode compartment and the positive ions (K^+) will move into the cathode compartment. Since the sizes of K^+ and Cl^- or NO_3^- ions are almost equal, their speeds will also be equal.

Many a times, instead of separating the two solutions by means of a porous plug, the two separate half-cells are connected by means of a salt-bridge. It consists of a U-tube filled with a saturated solution of a strong electrolyte such as KCl, NH_4NO_3 etc. The two ends of the U-tube are plugged by cotton-wool or the whole solution is set in agar-agar gel to prevent the free flow of KCl into the two cells. (see Fig. 17.5).

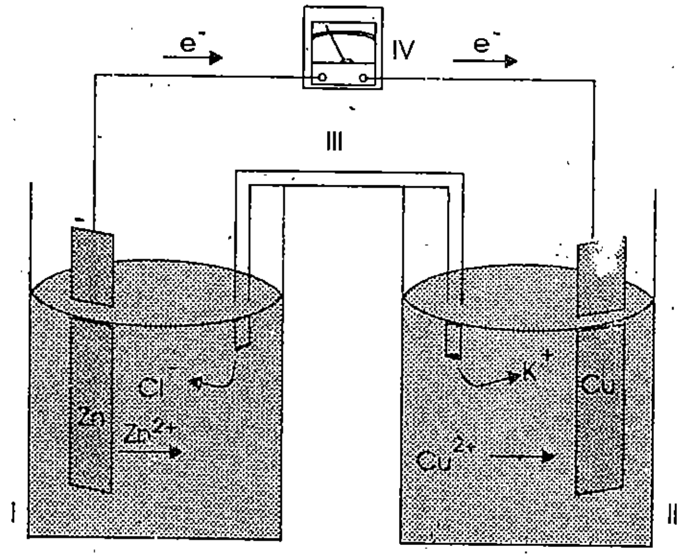

Fig. 17.5 : Daniell cell with salt bridge:
I) anodic compartment
II) cathodic compartment
III) salt bridge
IV) voltmeter.

When we draw current from the cell, the negatively charged Cl^- ion will flow out from the salt-bridge to neutralise the excess of positive charge due to production of Zn^{2+} ion in the anode compartment. Similarly K^+ ion will flow into the other compartment to neutralise the excess of sulphate ions. Thus the electroneutrality of the solution in the two compartments is maintained.

Cell construction from cell reaction

Now we shall discuss the steps involved in constructing a cell from a given chemical reaction:

Step (i) : From the given chemical equation, write the balanced ionic equation.

Step (ii) : Separate this ionic equation into two parts, one in which oxidation takes place and, another, in which reduction takes place. Balance each part using electrons. Sometimes H^+, OH^- or H_2O also may have to be added to either side of the equation for proper balancing.

Step (iii) : The oxidation part must appear on the left side of the cell. The reduction part must appear on the right side of the cell. Usually electrons and H_2O are not indicated in the representation of the cell. Also stoichiometric numbers must not appear in the representation.

Step (iv) : The electrodes are shown at the extreme left and right positions. These are shown distinctly separated from the corresponding electrolytes by means of single vertical lines. In case of gas electrodes and many redox systems (which we shall study in detail in Sec. 17.8), inert electrodes such as Pt wire or carbon rod are used for electrical contact.

Step (v) : A pair of vertical lines or a dotted line must be used to show the barrier between the left side and right side parts. Two vertical lines indicate the use of a salt bridge and a dotted line shows a porous barrier.

Step (vi) : It is usual to represent the pressure of the gases, the concentration of the electrolytes and the physical state of the electrodes within parenthesis.

Example 1

Using the above steps, let us try to construct a cell for the reaction:

$Cu + 2AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag$

Let us assume that the concentrations of $Cu(NO_3)_2$ and $AgNO_3$ are c_1 and c_2, respectively.

Solution

Step (i) : The balanced ionic equation is :

$Cu + 2Ag^+ —— Cu^{2+} + 2Ag$

Note that the NO_3^- ions do not appear on both the sides due to cancellation.

Step (ii) : Oxidation : $Cu \longrightarrow Cu^{2+} + 2e^-$

Reduction : $2Ag^+ + 2e^- \longrightarrow 2Ag$

Step (iii) :	Left side	Right side
	Cu, Cu^{2+}	Ag^+, Ag

Step (iv) : $Cu \mid Cu(NO_3)_2\ AgNO_3 \mid Ag$

Step (v) : $Cu \mid Cu(NO_3)_2 \mid\mid AgNO_3 \mid Ag$

We assume that there is a salt bridge between the two parts.

Step (vi) : $Cu(s) \mid Cu(NO_3)_2\,(c_1) \mid\mid AgNO_3\,(c_2) \mid Ag\,(s)$

Example 2

As another example, let us construct a cell in which the following reaction takes place:

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

Let us assume that the concentrations of $ZnSO_4$ and H_2SO_4 are c_1 and c_2, and the pressure of hydrogen gas is p_1.

Solution

Step (i) : The balanced ionic equation is :

$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

Note that SO_4^{2-} ions do not appear in this equation.

Step (ii) : Oxidation :

$Zn \longrightarrow Zn^{2+} + 2e^-$

Reduction :

$2H^+ + 2e^- \longrightarrow H_2$

Step (iii) :	Left side	Right side
	Zn, Zn^{2+}	H^+, H_2
Step (iv) :	$Zn \mid ZnSO_4$	$H_2SO_4 \mid H_2 \mid Pt$

Note that in the right side, Pt is used for electrical contact.

Step (v) : $Zn \mid ZnSO_4 \mid\mid H_2SO_4 \mid H_2 \mid Pt$

Step (vi) : $Zn\,(s) \mid ZnSO_4\,(c_1) \mid\mid H_2SO_4(c_2) \mid H_2\,(g, p_1) \mid Pt\,(s)$

So far we studied the method of arriving at a cell from cell reaction. Now we shall study the steps involved in writing the cell reaction, once the cell is known.

Steps for writing the cell reaction for a galvanic cell

i) Write the half-cell reaction corresponding to oxidation taking place at the anode.

ii) Similarly write the half-cell reaction for the reduction taking place at the cathode.

iii) Combine the above two half-cell reactions so that the number of electrons released at the anode is equal to the number of electrons used at the cathode.

Alternatively, the following steps can be used for writing the cell reaction for a galvanic cell.

(i) Write reduction reactions at both the electrodes

(ii) Write the equations so that both electrodes use the same number of electrons.

(iii) The overall reaction is the oxidation reaction on the l.h.s. electrode and the reduction reaction on r.h.s. electrode. By subtracting the l.h.s. reduction reaction from the r.h.s. reduction reaction, this is obtained.

Example 3

Let us illustrate the above steps using the following example:

Let us consider the cell,

$Al\,(s) \mid Al^{3+}\,(c_1) \mid\mid Cu^{2+}\,(c_2) \mid Cu\,(s)$

Using the above steps, Example 3 can be worked out as follows :

Step (i) :
L.h.s. electrode:
$Al^{3+} + 3e^- \longrightarrow Al$
R.h.s. electrode:
$Cu^{2+} + 2e^- \longrightarrow Cu$

Step (ii) :
For both the electrodes, write the equations involving same number of electrons.
$2Al^{3+} + 6e^- \longrightarrow 2Al$
$3Cu^{2+} + 6e^- \longrightarrow 3Cu$

Step (iii) :
Cell reaction = (Reduction reaction at the r.h.s. electrode) − (Reduction reaction at the l.h.s. electrode)
$3Cu^{2+} + 6e^- - 2Al^{3+} - 6e^- \longrightarrow 3Cu - 2Al$
i.e., $2Al + 3Cu^{2+} \longrightarrow 2Al^{3+} + 3Cu$

Solution

Step (i) : **Oxidation at the anode**

$Al \longrightarrow Al^{3+} + 3e^-$ ..... (1)

Step (ii) : **Reduction at the cathode**

$Cu^{2+} + 2e^- \longrightarrow Cu$ ..... (2)

Step (iii) : Before combining Eqs. (1) and (2), we have to multiply (1) by 2 and (2) by 3 so that six mole electrons (same number of electrons) are exchanged between the two electrodes.

Hence, (1) X 2 gives,

$2Al \longrightarrow 2Al^{3+} + 6e^-$ ..... (3)

(2) × 3 gives,

$3Cu^{2+} + 6e^- \longrightarrow 3Cu$ ..... (4)

Adding (3) and (4), we get

$2Al + 3Cu^{2+} \longrightarrow 2Al^{3+} + 3Cu$ ..... (5)

Using the principles explained above, answer the following SAQ.

SAQ 3

Draw a diagram of a Galvanic cell where the following reaction takes place:

$2Al + 3ZnSO_4 \longrightarrow Al_2(SO_4)_3 + 3Zn$

Label the electrodes and indicate the flow of electrons in the cell. Assume that the concentrations of $Al_2(SO_4)_3$ and $ZnSO_4$ solutions are c_1 and c_2, respectively.
(Hint : You may draw this diagram using Fig. 17.5.)

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17.6 NERNST EQUATION

As mentioned in Table 1.3 of Unit 1;

Cell potential = $\dfrac{\text{Electrical energy or work}}{\text{Quantity of charge}}$ ..... (17.3)

It was discussed in Sec. 9.3 of Unit 9 that the decrease in Gibbs free energy ($-\Delta G$) for any reaction would be equal to the maximum useful work ($-W_{net}$) that can be obtained from the system at constant temperature and pressure. The only kind of work done in an electrochemical cell is the electrical work which can be calculated from Eq. 17.4

Electrical work done by the system = $-W_{net}$
= Quantity of electricity × cell potential ..... (17.4)

The standard state conditions have been defined in Unit 9 of Block 2 of this course.

The quantity of electricity carried by 1 mol of electrons is 1F. Hence the quantity of electricity carried by n mol of electrons is nF. If the cell potential is E, then Eq. 17.4 can be written as,

Electrical work = $-W_{net} = nFE$ ..... (17.5)

Hence, $-\Delta G = nFE$ ..... (17.6)

Under standard state conditions,

$-\Delta G^\circ = nFE^\circ$ ..... (17.7)

For a general reaction of the type,

$a\text{A} + b\text{B} + \ldots\ldots \rightleftharpoons c\text{C} + d\text{D} + \ldots\ldots$

We can adopt Eq. 14.15 of Unit 14 of this block and write.

$\Delta G = \Delta G^\circ + RT \ln Q$ ..... (17.8)

where $Q = \dfrac{a_C^c\, a_D^d \ldots.}{a_A^a\, a_B^b \ldots.}$ ..... (17.9)

In Eq. 17.9, a_C, a_D, . . . etc., refer to the activities of the substances.

Substituting the values of ΔG and ΔG° from Eqs. 17.6 and 17.7 in Eq. 17.8, we get

$-nFE = -nFE^\circ + RT \ln Q$ ..... (17.10)

Dividing throughout by $-nF$,

$$E = E^\circ - \frac{RT}{nF} \ln Q \qquad \text{..... (17.11)}$$

or $$E = E^\circ - \frac{2.303\,RT}{nF} \log Q \qquad \text{..... (17.12)}$$

At 298 K, the numerical value of $\frac{2.303\,RT}{F}$ is 0.059.

Hence, at 298 K,

$$E = E^\circ - \frac{0.059}{n} \log Q \qquad \text{..... (17.13)}$$

Eqs. 17.12 and 17.13 are known as Nernst Equation in honour of Nernst who in 1889 first derived this equation. If activity coefficients are equal to unity, the activities given in Eq. 17.9 can be replaced by concentrations. Then, Eqs. 17.12 and 17.13 can be written as,

$$E = E^\circ - \frac{2.303\,RT}{nF} \log \frac{[\mathrm{C}]^c[\mathrm{D}]^d\ldots}{[\mathrm{A}]^a[\mathrm{B}]^b\ldots} \qquad \text{..... (17.14)}$$

At 298 K, $$E = E^\circ - \frac{0.059}{n} \log \frac{[\mathrm{C}]^c[\mathrm{D}]^d\ldots}{[\mathrm{A}]^a[\mathrm{B}]^b\ldots} \qquad \text{..... (17.15)}$$

Eqs. 17.14 and 17.15 are better known forms of Nernst Equation. Nernst equation brings out the dependence of emf on the concentrations of the substances taking part in the cell reaction.

17.7 APPLICATIONS OF NERNST EQUATION

Let us consider some applications of Nernst equation.

Equilibrium constant of the cell reaction

We can calculate the equilibrium constant of a given reaction from the standard emf of the cell. For this purpose, we derive Eq. 17.17.

At equilibrium, $\Delta G = 0$ and hence, Eq. 17.8 becomes, $0 = \Delta G^\circ + RT \ln K$ [At equilibrium, Q is replaced by K]

or $$\Delta G^\circ = -RT \ln K \qquad \text{..... (17.16)}$$

Eq. 17.17 is interesting due to the fact that the equilibrium constant of a reaction is related to standard emf of the cell where the reactants and products are in their standard states. Eq. 17.17 can also be written to the following way : $K = e^{nE^\circ F/RT}$

Combining Eqs. 17.7 and 17.16,

$-nFE^\circ = -RT \ln K$

$$\left.\begin{aligned} &\text{Hence, } E^\circ = \frac{RT}{nF} \ln K \\ &\text{or } E^\circ = \frac{2.303\,RT}{nF} \log K \end{aligned}\right\} \qquad \text{..... (17.17)}$$

Hence from E° value, the equilibrium constant can be calculated.

Example 4

Calculate the equilibrium constant at 298 K for the cell reaction taking place in the cell,

$\mathrm{Al}(s) \mid \mathrm{Al}^{3+}(c_1) \parallel \mathrm{Cu}^{2+}(c_2) \mid \mathrm{Cu}(s)$

Solution

n Example 3, we have arrived at the cell reaction for this cell.

$\mathrm{Al} + 3\mathrm{Cu}^{2+} \longrightarrow 2\mathrm{Al}^{3+} + 3\mathrm{Cu}$

Also we have mentioned, that six mole electrons are exchanged between the electrodes; i.e., $= 6$.

$E^\circ_{\text{cell}} = E^\circ_{\text{anode}} + E^\circ_{\text{cathode}}$

$= (-E^\circ_{\mathrm{Al^{3+}/Al}}) + E^\circ_{\mathrm{Cu^{2+}/Cu}}$

$= [-(-1.66) + 0.34]$ V

$= 2.0$ V

At 298 K, Eq. 17.17 becomes, $E^\circ = \dfrac{0.059}{n} \log K$

$$\log K = \frac{12.0}{0.059} = 203.390$$

Hence, $K = 2.5 \times 10^{203}$

Calculation of E_{cell} from the Concentration of Electrolytes

Consider the half-cell reaction:

$$M^{n+} + ne \longrightarrow M$$

Applying Nernst equation (Eq. 17.12) to the above reaction,

$$E_{M^{n+},M} = E^\circ_{M^{n+},M} - \frac{2.303\ RT}{nF} \log \frac{1}{[\,M^{n+}\,]} \qquad \text{..... (17.18)}$$

Since [M] = 1, Eq. 17.18 can be utilised to write the equations for the two half-cell reactions for the Daniell cell shown below :

$$Zn\,(s) \mid ZnSO_4\,(c_1) \parallel CuSO_4\,(c_2) \mid Cu\,(s)$$

$$E_{cell} = E_{anode} + E_{cathode} \qquad \text{..... (17.19)}$$

$$= (-\,E_{Zn^{2+}/Zn}) + E_{Cu^{2+}/Cu} \qquad \text{..... (17.20)}$$

Note that zinc is oxidised in the anode. But $E_{Zn^{2+}/Zn}$ represents the reduction potential of zinc.

Hence,

$E_{anode} = -\,E_{Zn^{2+}/Zn}$

Using Eq. 17.18

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{2.303\ RT}{2F} \log \frac{1}{[\,Zn^{2+}\,]} \qquad \text{..... (17.21)}$$

$$E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} - \frac{2.303\ RT}{2F} \log \frac{1}{[\,Cu^{2+}\,]} \qquad \text{..... (17.22)}$$

Using Eqs. 17.20, 17.21 and 17.22,

$$E_{cell} = (E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn}) - \frac{2.303\ RT}{2F} \left(\log \frac{1}{[\,Cu^{2+}\,]} - \log \frac{1}{[\,Zn^{2+}\,]} \right)$$

$$E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{2F} \log \frac{[\,Zn^{2+}\,]}{[\,Cu^{2+}\,]} \qquad \text{..... (17.23)}$$

Note that $E^\circ_{cell} = -\,E^\circ_{Zn^{2+}/Zn} + E^\circ_{Cu^{2+}/Cu}$ ..... (17.24)

Eq. 17.24 could be used to indicate whether a given cell can function as a galvanic cell when the substances are in their standard states; that is, when the concentrations of the electrolytes are equal to 1 M.

Eq. 17.23 is useful in predicting whether a given cell can function as a galvanic cell when the concentrations of the substances are not equal to 1 M.

Example 5

Calculate the cell potential of a Daniell cell at 298 K when the concentrations of Zn^{2+} and Cu^{2+} are 1.5 M and 0.5 M, respectively.

Solution

For Daniell cell, $E^\circ_{cell} = 1.1$ V and $n = 2$

Also at 298 K, $\dfrac{2.303\ RT}{2} = 0.059$ V

Hence Eq. 17.23 becomes,

$$E_{cell} = (1.1 - \frac{0.059}{2} \log \frac{1.5}{0.5})\ V$$

$$= (1.1 - \frac{0.059}{2} \times 0.4771)\ V$$

$E_{cell} = 1.09$ V.

The cell reaction for Daniell cell is as follows:

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$$

The substances in the l.h.s. are Zn and Cu^{2+}; the substances in the r.h.s. are Zn^{2+} and Cu.

We have derived Eqs. 17.23 and 17.24 for Daniell cell. We can write generalised expressions for any electrochemical as follows:

$$E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{nF} \log_{10} \frac{\text{Product of concentrations of substances in the r.h.s. raised to suitable powers}}{\text{Product of concentrations of substances in the l.h.s. raised to suitable powers}} \qquad \text{..... (17.25)}$$

In the above expression, $E^\circ_{\text{cell}} = E^\circ_{\text{anode}} + E^\circ_{\text{cathode}}$

n = Number of electrons required to balance the oxidation and the reduction reactions

Substances in the r.h.s. = Substances in the right hand side of the cell reaction.
Substances in the l.h.s. = Substances in the left hand side of the cell reaction.

The term 'suitable powers' refers to stoichiometric coefficients in the cell reaction.

Thermodynamic Quantities from emf Values

We shall now study how ΔH, ΔS, and ΔG for the cell reaction can be calculated using modified forms of Nernst equation. Eq. 17.6 gives the relationship between ΔG and E values. Hence, if E_{cell} value is known, ΔG, for the cell reaction can be calculated.

$$-\Delta G = nFE \qquad \text{..... (17.6)}$$

Similarly, the change in entropy accompanying the cell-reaction can also be determined. In Unit 9, we have derived Eq. 9.42 which relates the temperature coefficient of the free energy change at constant pressure, $\left[\dfrac{\partial(\Delta G)}{\partial T}\right]_p$, to the decrease in entropy $(-\Delta S)$.

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = -\Delta S \qquad \text{..... (9.42)}$$

By differentiating ΔG and E_{cell} appearing in Eq. 17.6 with respect to temperature at constant pressure, we can write

$$-\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = nF\left(\frac{\partial E}{\partial T}\right)_p \qquad \text{..... (17.26)}$$

since n and F are constants.

Using Eqs. 9.42 and 17.26, we get,

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_p \qquad \text{..... (17.27)}$$

$$\text{i.e., } \Delta S = nF\left[\frac{(E_2 - E_1)}{(T_2 - T_1)}\right]_p \qquad \text{..... (17.28)}$$

In case E_2 and E_1 (the emf's of the cell at temperatures T_2 and T_1) are known, ΔS can be calculated. $\left(\dfrac{\partial E}{\partial T}\right)_p$ is known as the temperature coefficient of emf at constant pressure.

Again Eq. 9.15 states,

$$\Delta G = \Delta H - T\Delta S$$

$$\text{or } \Delta H = \Delta G + T\Delta S \qquad \text{..... (17.29)}$$

Using Eqs. 17.6, 17.27 and 17.29,

$$\Delta H = -nFE + TnF\left(\frac{\partial E}{\partial T}\right)_p \qquad \text{.... (17.30)}$$

Hence if E, T and $\left(\dfrac{\partial E}{\partial T}\right)_p$ are known, then the enthalpy change accompanying the cell reaction can be calculated.

In the light of above discussion, answer the following SAQs.

SAQ 4

Calculate the equilibrium constant at 298 K for the following reaction :

$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$

Use the standard potentials given below:

$Zn^{2+} + 2e \longrightarrow Zn \qquad E^\circ = -0.76\ \text{V}$
$[Zn(NH_3)_4]^{2+} + 2e \longrightarrow Zn + 4NH_3 \qquad E^\circ = -1.03\ \text{V}$

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SAQ 5

Write down the equations relating ΔH°, ΔS° and ΔG° to E° and $\left(\frac{\partial E^\circ}{\partial T}\right)_p$

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17.8 TYPES OF ELECTRODES

A large number of electrodes are known and these can be conveniently divided into several categories depending upon the nature of the half-cell reactions. We shall now look at some of the commonly used electrodes.

Metal-metal ion electrode : This is the most common type of electrode where a metal is in equilibrium with a solution containing its ions. The half-cell reaction is represented by

$$M^{n+} + ne \longrightarrow M$$

and the potential is given by Eq. 17.18

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{2.303\,RT}{nF} \log \frac{1}{[M^{n+}]} \qquad ..... (17.18)$$

Cu^{2+}/Cu, Zn^{2+}/Zn, Ag^+/Ag, Pb^{2+}/Pb etc. are common examples of metal-metal ion electrodes.

Gas Electrodes : Hydrogen electrode (Fig. 17.4) is a typical example of this type of electrode where a gas is in equilibrium with its ions in solution. The gas/electrolyte equilibrium takes place on the surface of an inert metal or any other inert conductor. The commonly used inert electrode materials are platinum and carbon.

The electrode potential for the reaction is given below:

$$2H^+ + 2e^- \longrightarrow H_2$$

$$E = E^\circ - \frac{0.059}{n} \log Q \qquad ..... (17.13)$$

Applying Eq. 17.9 to the reduction of H^+ ions,

$$Q = \frac{a_{H_2}}{a^2_{H^+}} \qquad ..... (17.31)$$

In case of a solution, the activity can be replaced by concentration, while for a gas, activity can be substituted by its partial pressure.

Thus, $a_{H^+} = [\,H^+\,]$ and $a_{H_2} = p_{H_2}$

Using these in Eq. 17.13, we get at 298 K,

$$E_{H^+/H_2} = E^\circ_{H^+/H_2} - \frac{0.059}{2} \log \frac{p_{H_2}}{[\,H^+\,]^2} \qquad ..... (17.32)$$

(since $n = 2$)

i.e., $E_{H^+/H_2} = E^\circ_{H^+/H_2} + 0.059 \log [\,H^+\,] - \frac{0.059}{2} \log p_{H_2}$

$$E_{H^+/H_2} = -\,0.059\ \text{pH} - \frac{0.059}{2} \log p_{H_2} \qquad ..... (17.33)$$

[since $E^\circ_{H^+/H_2} = 0$ and $-\log [\,H^+\,] = \text{pH}$]

If $p_{H_2} = 1$ atm, then $E_{H^+/H_2} = -\,0.059$ pH ..... (17.34)

Hence pH of the solution will decide the electrode potential of a hydrogen electrode, when hydrogen gas pressure is 1 atm. This principle is made use of in Sec. 17.11 for determining the pH of a solution using hydrogen electrode.

Amalgam Electrode : Active metals of Group IA and IIA which react with water can be used in amalgam form. The reaction can be represented as :

$M^{n+} + ne^- \longrightarrow M(Hg)$

and the electrode potential is written as

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{0.059}{n} \log \frac{[\,M(Hg)\,]}{[\,M^{n+}\,]} \qquad \text{..... (17.35)}$$

where [M(Hg)] indicates the concentration of the metal M dissolved in Hg.

Metal-Insoluble Salt Electrode : The typical examples of such electrodes are calomel electrode and silver-silver chloride electrode. These are represented as :

$Hg/Hg_2Cl_2\,(s)$, KCl (*c*) and

$Ag/AgCl\,(s)$, KCl (*c*)

It can be seen from the above half-cells that a metal (Hg or Ag) is in contact with a saturated solution of its sparingly soluble salt (Hg_2Cl_2 or AgCl) and another soluble salt (KCl) having common anion (Cl^-).

In this connection we discuss the functioning of saturated calomel electrode. The saturated calomel electrode is often used as a reference electrode in place of hydrogen electrode which is inconvenient and difficult to prepare. As a reference electrode, saturated calomel electrode is reversible and has a fixed potential. It can be represented as

$Hg \mid Hg_2Cl_2(s) \mid$ KCl (saturated)

Fig. 17.6 shows a simple construction of saturated calomel electrode (SCE). It consists of mercury in contact with mercurous chloride (calomel) and chloride ions (from saturated KCl). Mercurous chloride is reduced to mercury, when saturated calomel electrode is used as cathode, according to the equation:

$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$

The half-cell potential for saturated calomel electrode is 0.2682 V.

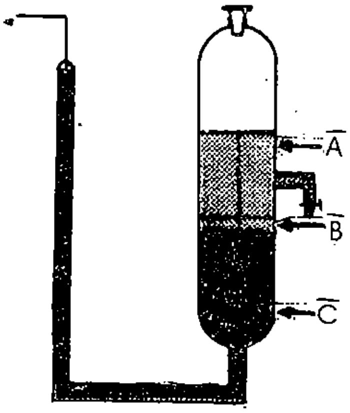

Fig. 17.6 : Saturated calomel electrode : A) KCl (saturated); B) Hg_2Cl_2; C) Hg.

In the silver-silver chloride electrode, Ag is in equilibrium with Ag ion in solution:

$Ag^+ + e^- \rightleftharpoons Ag$

As the solution is saturated with AgCl, silver ion produced will combine with Cl^- ions to give insoluble AgCl and the electron is transferred to the electrode.

$AgCl + e^- \longrightarrow Ag + Cl^-$

The standard half-cell potential is 0.2223 V.

In silver-silver chloride electrode, half-cell reaction can be considered to be one of the following two types. Care must be evinced in choosing proper E° values and expression for E calculation:

i) $Ag^+ + e^- \longrightarrow Ag$

$E^\circ_{Ag^+/Ag} = 0.80$ V and

$E_{Ag^+/Ag} =$

$$\left(0.80 - \frac{2.303\,RT}{F} \log \frac{1}{[\,Ag^+\,]}\right) V \qquad \text{..... (17.36)}$$

ii) $AgCl + e^- \longrightarrow Ag + Cl^-$

$E^\circ_{AgCl/Cl^-} = 0.2223$ V and

$E_{AgCl/Cl^-} =$

$$\left(0.2223 - \frac{2.303\,RT}{F} \log [\,Cl^-\,]\right) V \qquad \text{..... (17.37)}$$

Membrane Electrode : In this type of electrode (Fig. 17.7), a semipermeable membrane (X) separates two solutions containing different concentrations of the salt, MA and is permeable to one of the ions say, M^+. This ion will have a tendency to diffuse into a more dilute solution, but the anion, A^-, cannot follow and therefore, a difference of potential is set up. This will retard the migration of M^+ and after sometime equilibrium will be established. Under these conditions, the standard potential difference is given by

$$E^\circ = \frac{RT}{F} \ln \frac{[\,M^+\,]_\alpha}{[\,M^+\,]_\beta} \qquad \text{..... (17.38)}$$

Fig. 17.7 : Membrane electrode.

where $[M^+]_\alpha$ and $[M^+]_\beta$ represent $[M^+]$ in the two halves of the cell across the membrane. The most useful and common electrode of this kind is a **glass electrode**. This is used for measuring the H^+ ion concentration of solutions. Other ion selective electrodes have been developed for measurement of concentrations of Na^+, K^+ etc.

Glass electrode and quinhydrone electrode (a redox electrode) are discussed in Sec. 17.11.

Redox Electrodes : It is usually referred to as a system in which a species exists in solution in two different oxidation states. The electrodes are nonreactive with solution and are just carriers of electrons. A typical example is $Pt/Fe^{3+}, Fe^{2+}$, where platinum electrode is immersed into a solution containing Fe^{3+} and Fe^{2+} ions. The half-cell reaction can be represented by

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$

with a potential given by

$$E = E^\circ - \frac{0.059}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \qquad \text{..... (17.39)}$$

SAQ 6

The chlorine gas electrode is represented as $Pt(s) \mid Cl_2(p) \mid Cl^-(c)$. Write an expression for its half-cell potential.

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17.9 TYPES OF GALVANIC CELLS

As seen in the previous section, there are many kinds of electrodes. All these electrodes may combine in many different ways to give a large number of galvanic cells. Hence, it would be desirable and useful to classify them into two broad groups: (1) chemical cells (2) concentration cells.

Chemical Cells

Any cell in which the two half-cell reactions use different reactants is called a chemical cell. A typical example is Daniell cell.

Concentration Cells

If the chemical reactions in two half-cells are the same, but the concentrations of the electrolyte solutions or electrode materials are different, then the net reaction is the transfer of species from higher concentration to lower concentration. There is no net chemical reaction in the cell. Such cells are known as concentration cells.

Two examples for electrode concentration cells are given below:

i) A cell having amalgams of different concentrations of the same metal as the electrodes.
ii) A cell having hydrogen electrodes, the gas pressures being different.

For example, consider a cell consisting of two half-cells at different Zn^{2+} concentrations (c_1 and c_2).

$$Zn(s) \mid ZnSO_4\,(c_1) \parallel ZnSO_4(c_2) \mid Zn(s)$$

The overall reaction involves the passage of Zn^{2+} from a solution of higher concentration (c_2) to that of lower concentration (c_1).

At the anode

$$Zn \longrightarrow Zn^{2+}(c_2) + 2e^-$$

At the cathode

$$Zn^{2+}(c_2) + 2e^- \longrightarrow Zn$$

Cell reaction : $Zn^{2+}(c_2) \longrightarrow Zn^{2+}(c_1)$

You must remember that, E°_{cell} for a concentration cell is zero. This can be shown as follows :

$$E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$$

$$= -(E^\circ_{Zn^{2+}/Zn}) + (E^\circ_{Zn^{2+}/Zn})$$

Hence, $E^\circ_{cell} = 0$

The emf of the above concentration cell can be calculated using Eq. 17.14.

$$E_{cell} = -\frac{2.303\,RT}{2F}\log\frac{c_1}{c_2} \qquad \text{..... (17.40)}$$

At 298 K, this expression becomes,

$$E_{cell} = \frac{0.059}{2}\log\frac{c_2}{c_1} \qquad \text{..... (17.41)}$$

Although chemical cells and concentration cells can be further classified based on transfer of matter across the two half-cells, we do not discuss these types.

SAQ 7

Calculate the emf of the following concentration cell at 298 K :

$Zn(s) \mid ZnSO_4\,(1\ M) \parallel ZnSO_4\,(2\ M) \mid Zn(s)$

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17.10 PRACTICAL CELLS

Most of the galvanic cells described above are primary cells. In such cases, where the cell reaction reaches an equilibrium state, there is no further flow of current and the cell ceases to function. It is then called a 'dead' cell. For the purposes of practical applications, the chemical cells are usually sealed into a container. The more common types are zinc-carbon, silver oxide-zinc, zinc-mercury etc. and they are commonly called dry cells.

There are other kinds of cells which are known as secondary cells or storage batteries. These batteries require initial charging from some other energy source to generate a non-equilibrium state of the reactants. When they are in use to produce electricity, they slowly return to equilibrium state. Such batteries can be recharged and the cycle repeated a number of times. Lead storage and nickel-cadmium cells fall under this category of secondary cells.

Finally, there is the third kind of practical cells known as 'fuel cells' which have found applications in space-crafts etc. Let us now study some of these practical cells. Except the fuel cells, others are used by us in every day life and are available in the market.

Leclanche Cell : It is also called zinc-carbon dry cell. This type of cell is commonly used in toys, flash lights etc. It contains a zinc cup which acts as an anode and is filled with a moist paste of ammonium chloride, manganese dioxide, zinc chloride in starch and finely divided carbon. A central carbon rod immersed in the paste acts as a cathode. The whole cell is enclosed in either card board or metal which seals it against the atmosphere as shown in Fig. 17.8. The actual reactions which take place in the cell are quite complicated and not completely understood. However, simplified version of the reactions is given below:

At the anode

$Zn \longrightarrow Zn^{2+} + 2e^-$

$Zn^{2+} + 4NH_3 \longrightarrow [\,Zn(NH_3)_4\,]^{2+}$

At the cathode

$2MnO_2 + 2NH_4^+ + 2e^- \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$

Fig. 17.8 : Leclanche cell :
I) Graphite cathode;
II) Zinc cup anode;
III) Moist paste of NH_4Cl, MnO_2, $ZnCl_2$ and carbon

This cell produces about 1.5 V but drops to about 0.8 V as the reaction proceeds. This drop is because the reaction products cannot diffuse away from the electrolyte. If such a cell is left unused for a short time, the voltage may rise back again to about 1.3 V. The cell appears to be dead, because large excess of $[\,(Zn(NH_3)_4)\,]Cl_2$ formed crystallises out around the anode. The electrolyte becomes unable to conduct electricity effectively. A little warming of the cell may restore the voltage again due to the diffusion of the complex.

Alkaline Cells : These are similar to Leclanche cell except that the electrolyte, ammonium chloride, is replaced by potassium or sodium hydroxide. They can withstand under heavy use, have longer shelf-life and deliver more current. Main reasons for the better performance of alkaline cells are: (i) larger effective area since the anode is made porous and (ii) absence of acid atmosphere; due to the acid atmosphere caused by the presence of NH_4^+ ions in Leclanche cell, the electrodes in it get corroded easily.

Due to prolonged storage, these cells slowly get discharged even without putting them to any usage. The period for which a particular cell can retain its voltage is called its shelf-life.

The basic reactions that take place in alkaline cells are given below :

At the anode

$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2$

At the cathode

$2MnO_2 + 2H_2O + 2e^- \longrightarrow 2MnO(OH) + 2OH^-$

The cell produces approximately 1.5 V.

Button-Cells : These are small button like cells which are used in watches, calculators, cameras etc. The main advantage is the small size and stable voltage of about 1.3 to 1.5 V. Some cells use a mixture of HgO, $Zn(OH)_2$ and KOH while others use Ag_2O, $Zn(OH)_2$ and KOH. In the mercury cell, the cathode is steel, while in the other cell, it is silver oxide (Fig. 17.9). The anode in both the cases is zinc.

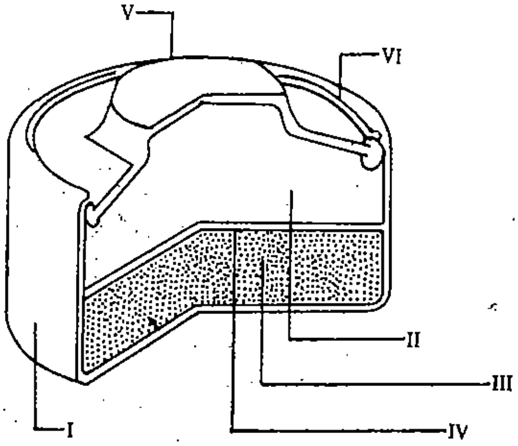

Fig. 17.9 : Button cell : I) metal cup; II) zinc anode; III) Ag_2O cathode; IV) separator; V) cap over anode; VI) gasket.

The reactions are given below:

At the anode

$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e^-$

At the cathode

$$\left.\begin{array}{l} Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^- \\ \text{or } HgO + H_2O + 2e^- \longrightarrow Hg + 2OH^- \end{array}\right\}$$

Emergency Cells : These batteries are used in life-vests. Initially there is no electrolyte solution present, but when sea water fills in, the reaction starts and lights up a bulb connected to the battery.

For example, for one such battery, the electrode reactions are given below :

At the anode

$Mg \longrightarrow Mg^{2+} + 2e^-$

At the cathode

$CuCl + e^- \longrightarrow Cu + Cl^-$

Secondary Cells : The most common example of this type is the lead storage battery (Fig. 17.10) used in cars etc. It consists of a series of lead plates or preferably lead-antimony alloy plates which are harder than lead plates. These plates are covered with a paste of lead sulphate and are dipped in a solution of dilute H_2SO_4 which acts as the electrolyte. They are connected in series, so that the emf of the battery becomes the sum of emfs of all the galvanic cells. The battery is first connected to an outside source of electricity and charged. During charging, reduction takes place on one of the electrodes and $PbSO_4$ is converted into lead and sulphate ions. At the other electrode, oxidation takes place and PbO_2 deposits on the plate.

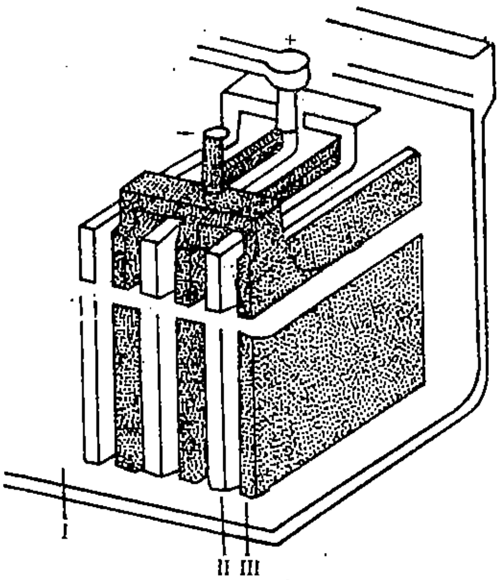

Fig. 17.10 : One cell of a storage battery showing alternating plates of Pb and PbO_2. I) H_2SO_4 (electrolyte); II) PbO_2 (cathode); III) Pb (anode).

During the use or the discharge of the battery, following reactions occur :

At the anode

$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

At the cathode

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$

The batteries can be charged repeatedly a number of times. If it is left unused for a long time a slow discharging may take place.

Fuel Cells : These cells are ordinary galvanic cells with a difference that reactants are continually supplied from outside and not sealed inside the cell. The reactants are easily available fuels such as hydrogen, methane, oxygen etc. Let us consider one practically useful hydrogen/oxygen fuel cell. The basic reactions at the electrodes are given below :

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH$ and $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

The overall reaction can be written as, $2H_2 + O_2 \longrightarrow 2H_2O$
with an emf of 1.2 V.

Figure 17.11 shows the basic features of H_2/O_2 fuel cell. It consists of two electrodes (usually platinum/carbon) which are porous. Hydrogen and oxygen gases are passed over the

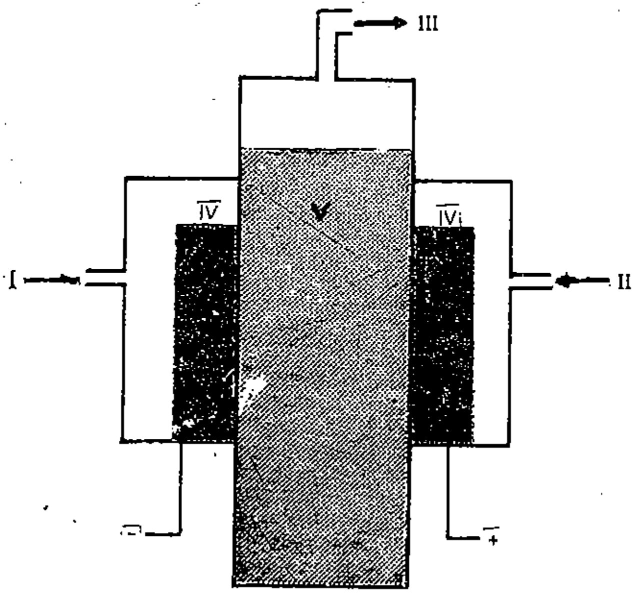

Fig. 17.11 : Fuel Cell : I) inlet for H_2; II) inlet for O_2; III) outlet for steam; IV) porous carbon electrodes; V) KOH solution.

electrodes through which they diffuse into a central compartment. The latter contains KOH at high temperature (473 K) and pressure (30 − 40 atm). The water formed during the reaction evaporates and can be condensed to be used as drinking water. Instead of H_2, other anodic materials like CH_4, N_2H_4 etc., have also been used. It is not advisable to burn H_2 and O_2 to produce heat which may then be converted into electricity. The reason is that the thermodynamic efficiency of fuel cells is much more than the burning process.

The following SAQ is based on the above information.

SAQ 8
Explain why :

a) a dry cell comes back to life if left idle for a while.

b) fuel cells are considered better than an electrical power plant using the same fuel.

c) alkaline cells are considered better than Leclanche cell.

....

....

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17.11 APPLICATIONS OF EMF MEASUREMENTS

The emf measurements on redox reactions can lead to a large amount of useful data. For instance, with the help of emf measurements, we can obtain the overall equilibrium constant of a reaction, solubility product constant for a sparingly soluble salt, pH of a solution, thermodynamic quantities for a reaction or can even perform a redox titration. In each case, we have to devise a suitable cell for the potential measurements. We shall discuss a few common examples to see how it is actually done.

Determination of Equilibrium Constant
As we have already studied in Sec. 17.7, if we measure the standard cell potential for a system, we can calculate the equilibrium constant. We know that

$$\log K = \frac{nFE^\circ}{2.303\,RT} = \frac{nE^\circ}{0.059}\ \text{(at 298 K)} \qquad \text{..... (17.42)}$$

Determination of Solubility Product Constant
Suppose that we want to find the solubility product constant for a sparingly soluble salt, $PbSO_4$. We can set up a cell consisting of Pb/Pb^{2+} as one of the electrodes and Cu^{2+}/Cu as the other. The electrolytes contains SO_4^{2-} ions at 1 M concentration in the two compartments and the concentration of Cu^{2+} ions is also kept at 1 M. The two half-cells are connected through a salt bridge. The cell can be represented as :

$$Pb(s) \mid PbSO_4(s) \mid K_2SO_4\ (1\ M) \mid\mid CuSO_4\ (1\ M) \mid Cu(s)$$

and the overall reaction can be represented as :

$$Pb + Cu^{2+} \longrightarrow Pb^{2} + Cu$$

In the above cell, since the Pb^{2+} ions are in equilibrium with solid $PbSO_4$, it is a saturated solution. The standard cell potential for the given cell calculated from the standard reduction potentials (Table 17.1) comes out to be 0.47 V. In an experiment, the cell potential for the above cell was found to be 0.70 V. Substituting these values in Eq. 17.45, we get

$$0.70\ V = \left(0.47 - \frac{0.059}{2}\log\frac{[Pb^{2+}]}{(1)}\right)V, \text{ since } [Cu^{2+}] = 1\ M$$

or $[Pb^{2+}] = 1.6 \times 10^{-8}$ M
Since, $K_{sp} = [Pb^{2+}][SO_4^{2-}]$,
K_{sp} for $PbSO_4 = (1.6 \times 10^{-8}) \times 1$ [since $[SO_4^{2-}] = 1M$]
$= 1.6 \times 10^{-8}$

Note that similar to Ag-AgCl electrode discussed in Sec. 17.8, the half-cell reaction for $Pb-PbSO_4$ electrode can be considered to be one of the following two types :

i) $Pb^{2} + 2e^- \longrightarrow Pb$

$$E_{Pb^{2+}/Pb} = E^\circ_{Pb^{2+}/Pb} - \frac{2.303\,RT}{2F}\log\frac{1}{[Pb^{2+}]} \qquad \text{..... (17.43)}$$

ii) $PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$

$$E_{PbSO_4/SO_4^{2-}} = E^\circ_{PbSO_4/SO_4^{2-}} - \frac{2.303\,RT}{2F}\log[SO_4^{2-}] \qquad \text{..... (17.44)}$$

For the present calculation, first type shown above is used as the anode and Cu^{2+}/Cu is used as the cathode.

Hence, $E_{cell} =$

$$E^\circ_{cell} - \frac{0.059}{2}\log^{10}\frac{[Pb^{2+}]}{[Cu^{2+}]} \qquad \text{...... (17.45)}$$

Note that $E^\circ_{cell} = -E^\circ_{Pb^{2+}/Pb} + E^\circ_{Cu^{2+}/Cu}$

$= (-(-0.13) + 0.34)$ V
$= 0.47$ V

Potentiometric Titrations : A large variety of titrations can be performed with the help of emf measurements. Let us consider one such titration where the concentration of an unknown amount of Fe^{2+} ions is to be determined by titrating against a solution of Ce^{4+} ions of known concentration. We shall construct a cell where a known volume of ferrous salt solution is kept in one compartment with an inert Pt electrode and the other half-cell contains calomel electrode as reference. The two are connected as usual by a salt bridge. We keep on measuring the emf of the cell after each addition of small quantities of Ce^{4+} ions from a burette. At any instant during the titration, we shall have a mixture of Fe^{2+}/Fe^{3+} and emf will be guided by the ratio of the concentrations of Fe^{2+} and Fe^{3+} ions.

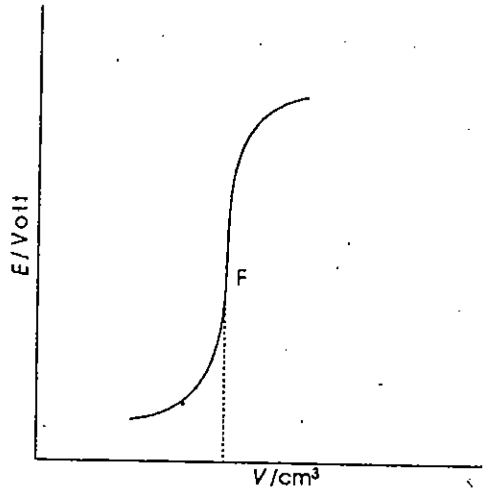

Fig. 17.12 : A plot of the cell potential (*E*) against the volume (*V*) of Ce^{4+} solution added.

As more and more of Ce^{4+} is added, more and more Fe^{3+} ion will be produced and lesser will be the concentration of Fe^{2+} ions. The net result will be a gradual increase in the emf till the equivalence point where the greatest change in emf will occur. After the equivalence point, the emf will, however, be governed by the ratio $(Ce^{4+})/(Ce^{3+})$. If we plot a graph of emf (E) against volume (V) of Ce^{4+} solution, we shall get a curve as shown in Fig. 17.12 from which we can determine the equivalence point (F).

Determination of pH

While determining pH of a solution, one of the electrodes must be hydrogen electrode or quinhydrone electrode or glass electrode while the other electrode can be calomel or any other electrode.

Using Hydrogen Electrode

Consider a cell in which a Cu^{2+}/Cu electrode is connected with a H_2/H^+ electrode through a salt bridge. The concentration of Cu^{2+} ion is kept at 1 M, the pressure of hydrogen gas at 1 atm and temperature at 298 K.

The cell can be represented as

$Pt(s) \mid H_2(g, 1\ atm) \mid H^+(c) \parallel CuSO_4\ (1\ M) \mid Cu\ (s)$

The overall reaction will be

$$Cu^{2+} + H_2 \longrightarrow Cu + 2H^+$$

We substitute the given values in Eq. 17.14.

$$E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{2F} \log \frac{[\,H^+\,]^2}{[\,Cu^{2+}\,]\,.\,p_{H_2}} \qquad \text{..... (17.46)}$$

$$E_{cell} = (0.34 - \frac{0.059}{2}.\log [\,H^+\,]^2)\ V \quad [\text{ since } [\,Cu^{2+}\,] = 1\ M \text{ and } p_{H2} = 1\ atm\ ]$$

$$E_{cell} = (0.34 + 0.059\ pH)\ V$$

Generally calomel electrode is used along with hydrogen electrode for determining the pH of a solution.

$$E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$$
$$= -E^\circ_{H^+/H_2} + E^\circ_{Cu^{2+}/Cu}$$
$$= -[-(-0) + 0.34]\ V$$
$$= 0.34\ V$$

Thus, by measuring the emf of the cell, we can calculate the hydrogen ion concentration or the pH of the solution.

Using Quinhydrone Electrode

In Sec. 17.8, we mentioned that an inert metal dipped in a solution containing a mixture of oxidised and reduced forms of a substance constitutes an oxidation-reduction electrode. One such example is 'quinone-hydroquinone electrode', which is commonly-used in analytical chemistry. It is also called quinhydrone electrode. The reaction involves transfer of electrons between the reduced and the oxidised forms as shown by the following equation :

We commonly use the symbol H_2Q for hydroquinone [$C_6H_4(OH)_2$] and Q for quinone [$C_6H_4O_2$].

$$\underset{(Q)}{C_6H_4O_2} + 2H^+ + 2e^- \rightleftharpoons \underset{(H_2Q)}{C_6H_4(OH)_2}$$

Using Eq. 17.14, we can write emf of the electrode as

1 : 1 mixture of quinone and hydroquinone is called quinhydrone.

$$E_{Q/H_2Q} = E^\circ_{Q/H_2Q} - \frac{RT}{2F}\ln\frac{[\,H_2Q\,]}{[\,Q\,][\,H^+\,]^2}$$ (Where E_{Q/H_2Q} is the potential of quinhydrone electrode) ..... (17.47)

At 298 K, $E^\circ = +\,0.6990$; if we take equal amounts of quinone and hydroquinone (i.e., $[\,Q\,] = [\,H_2Q\,]$ at 298 K, we can write the above equation as

$$E_{Q/H_2Q} = (0.6990 + \frac{0.059}{2}\log[\,H^+\,]^2)\ \text{V}$$

$$= (0.6990 - 0.059\ \text{pH})\ \text{V} \qquad \text{..... (17.48)}$$

This electrode can be used in conjunction with a saturated calomel electrode to measure the pH of a solution. Let us represent such a cell as follows:

Hg (l) | Hg_2Cl_2 (s) | KCl (saturated) || H^+ (c) | Q, H_2Q | Pt (s)

To measure the pH of a solution, first the emf of the cell (E_{cell}) is measured :

E_{SCE} = Potential of the saturated calomel electrode = 0.2682 V

$$\text{But } E_{cell} = E_{anode} + E_{cathode}$$
$$E_{cell} = -\,E_{SCE} + E_{Q/H_2Q}$$
$$\text{i.e. } E_{cell} = (-\,E_{SCE} + 0.6990 - 0.059\ \text{pH})\ \text{V}$$
$$= (-\,0.2682 + 0.6990 - 0.059\ \text{pH})\ \text{V}$$
$$= (0.4308 - 0.059\ \text{pH})\ \text{V}$$

$$\text{Hence, pH} = \frac{(0.4308 - E_{cell})}{0.059} \qquad \text{..... (17.49)}$$

If E_{cell} is known, pH of the solution can be calculated.

The quinone-hydroquinone electrode is easier to make than a hydrogen electrode and the former attains equilibrium quickly. The main limitation with this electrode is that it cannot be used in alkaline medium.

Using Glass Electrode

It has been observed that when a thin membrane of soft glass separates two solutions, a potential is developed across the membrane and the potential depends mainly on the pH of the two solutions. The emf of the electrode is given by

$$E = E^\circ_{glass} - \frac{RT}{nF}\ln[\,H^+\,] \qquad \text{..... (17.50)}$$

It is prepared by dipping an Ag − AgCl electrode in a solution of 0.1 M HCl contained in a thin glass bulb as shown in Fig. 17.13.

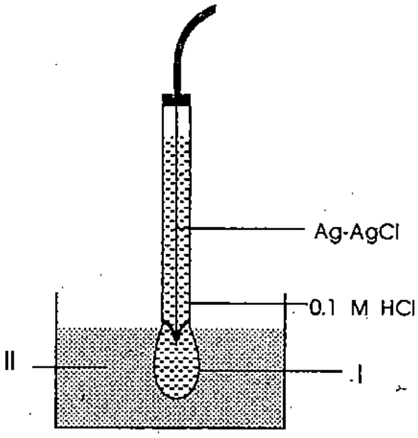

Fig. 17.13 : Glass electrode: I) thin glass membrane; II) H^+ Ion

Just like quinone-hydroquinone electrode, this is used in conjunction with a saturated calomel electrode and can be represented as

Ag(s) | AgCl(s) | HCl (0.1 M) | glass | H^+(c) | | KCl (saturated) | Hg_2Cl_2(s) | Hg(l)

The pH of the solution can be calculated, once we know the cell potential and the saturated calomel potential as in the case of quinone-hydroquinone electrode..Since we do not know the E°_{glass} value, we first find the cell potential for a solution of known hydrogen ion concentration. Then we measure the emf with the solution of unknown pH using the same set-up. The difference in potential between the solutions of known and unknown pH can be written as,

$$E_{known} - E_{unknown} = 2.303 \frac{RT}{F} (pH_{known} - pH_{unknown}) \quad \text{..... (17.51)}$$

17.12 ELECTROLYTIC CELLS

Although we have learnt the laws of electrolysis in Unit 16, we have not studied the electrode reactions in different systems and their practial applications. We shall now discuss some of these points in this section.

When electricity is passed through a fused electrolyte, it causes a change which is otherwise non-spontaneous. As an example, molten sodium chloride on electrolysis leads to the following electrode reactions:

$Na^+ + e^- \longrightarrow Na$

$2Cl^- \longrightarrow Cl_2 + 2e^-$

Thus sodium metal could be collected at the cathode whereas evolution of chlorine gas takes place at the anode. The extent of electrolysis is determined on the basis of Faraday's laws. The situation becomes different if instead of molten sodium chloride, we take an aqueous solution of sodium chloride for electrolysis.

Overvoltage
In an electrolytic cell, evolution of gases at the electrodes occurs in sufficient amounts only when the applied potential is much higher than the calculated potential for the cell. The difference between the reversible potential and the applied potential is called the overvoltage.

Electrolysis of Aqueous Sodium Chloride Solution

In this case, the prediction of electrode reaction may not be that easy and straightforward, since there is more than one possibility of electrode reactions. For instance, the following anodic reactions can occur :

$2Cl^- \longrightarrow Cl_2 + 2e^-$

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Similarly, the possible reactions at the cathode are :

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$Na^+ + e^- \longrightarrow Na$

$2H^+ + 2e^- \longrightarrow H_2$

It can be shown on the basis of electrode potentials that the following reactions take place at the two electrodes:

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$2Cl^- \longrightarrow Cl_2 + 2e^-$

As per experimental results also, it is found that Cl_2 is evolved at the anode and H_2 at the cathode and the overall reaction can be written as :

$2Cl^- + 2H_2O \longrightarrow Cl_2 + H_2 + 2OH^-$

It gives us the information that the oxidation of Cl^- is easier than that of water, whereas water can be reduced much more easily than sodium or hydrogen ions.

Electrolysis of Aqueous Sodium Sulphate Solution

In this case, the cathodic reaction is the same as above. The evolution of hydrogen gas takes place. However, at the anode, SO_4^{2-} ions are much more difficult to oxidise than water. Hence, at the anode, evolution of O_2 gas takes place. The electrode reactions are :

$4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^-$ (at the cathode)

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ (at the anode)

and the overall reaction can be written as

$2H_2O \longrightarrow 2H_2 + O_2$

Corrosion
The loss of material due to chemical attack is known as corrosion. For example, when a wet surface of iron is exposed to air, rusting or corrosion takes place. Metallic iron gets oxidised and oxygen gets reduced (to OH^- ions).

Passivity
In some cases like aluminium metal, aluminium oxide forms a thin surface coating on the metal. Such formation of oxide on the surface stops further reactivity of some metals. In such cases, the metals are said to have become passive.

An experimental observation is that in order to produce appreciable amounts of products, one has to apply much higher cell potential than the calculated value. The additional voltage that must be applied beyond the cell potential is called the overvoltage. It is mainly due to slow attainment of equilibrium at the electrode and depends on the nature and physical state of the electrode, physical state of the substance deposited and number of other factors. We do not intend considering at length some of the irreversible phenomena like overvoltage, corrosion and passivity in this course. Let us now look at some of the applications of electrolysis.

17.13 APPLICATIONS OF ELECTROLYSIS

A large number of chemical industries use electrolytic processes to give products in rather pure state. It is used in metallurgy and refining of many metals. Production of many non-metals like halogens etc., as well as a large number of compounds is based on electrolysis. Electroplating is yet another application.

Metallurgy

Many a times after performing basic processes of concentrating the ore and roasting it, we end up with the oxides of metal. These have to be reduced to get the metal. In some cases, the reduction of metal oxides is not possible with common reducing agents like carbon etc., which instead of reducing metal oxide to metal, react with carbon to give metal carbides. Active metals like Na, Mg etc., which are usually found in common salt as their ions, are manufactured by electrolysis of molten salt. In the metallurgy of aluminium from bauxite ore, the ore is refined and treated to obtain pure Al_2O_3, which is then subjected to electrolysis in molten cryolite to yield aluminium metal.

Production of Other Chemicals

Chlorine, which has antibacterial and pesticidal properties and is used in the production of many useful compounds such as polyvinyl chloride etc., is not found free in nature. It is produced electrolytically. Similarly, fluorine is obtained by oxidising fluoride ion electrolytically since the oxidizing power can be increased with the increase in the applied voltage. Production of commercially useful compounds like caustic soda, bleaching powder etc., is also done electrolytically. Many organic compounds are also being synthesised by this process.

Electroplating

Electroplating is defined generally as the process of depositing a layer of any metal on an object by electrolysis. The object to be electroplated (either a metal or even plastic) is made the cathode after it is first coated with graphite or some metal (e.g. palladium). Electrolyte is a solution of a salt of the metal to be plated. Usually but not necessarily, the anode is an impure metal to be plated. As an example, consider a solution of copper sulphate in which cathode is a thin strip of pure metal and the anode is a rod of impure copper. As the current is passed and electrolysis progresses, impure copper dissolves and pure copper is deposited on the cathode. Impurities which do not dissolve, such as silver, gold etc., simply fall off to the bottom of the cell. Electroplating besides being decorative, can be very useful in preventing corrosion. Chromium electroplated over steel prevents rusting of iron.

17.14 SUMMARY

We began our study with an elementary account of production of electricity with the help of chemical reactions. Then we looked at how the cell potential is measured under standard conditions. We explained the setting up of standard hydrogen electrode, with reference to which, all other potentials are measured. Then we discussed the importance of the table of standard reduction potentials for some selected half-cell reactions. Measurement of cell potential and its relation with the concentrations of the oxidised and the reduced species was developed in the form of Nernst equation. The different applications of Nernst equation were then discussed. Next we briefly looked at different kinds of galvanic cells and some of the commercial cells. We finally discussed some of the applications of emf measurements.

17.15 TERMINAL QUESTIONS

1) Explain why copper does not dissolve in hydrochloric acid but dissolves in dilute nitric acid.
Hints : Look at the $E°$ values of Cu^{2+}/Cu and H^+/H_2. Also $E°_{NO_3^-/NO}$ is 0.96 V; assume that copper dissolves in an acid to form Cu^{2+} ion.

2) With the help of standard reduction potential values, decide
   a) which is a better oxidising agent—MnO_4^- or $Cr_2O_7^{2-}$ and
   b) which is a better reducing agent—Cl^- or Br^-?

3) Calculate the cell potential at 298 K for the reaction

   $Al^{3+} + Fe \longrightarrow Al + Fe^{3+}$

   The concentrations of Al^{3+} and Fe^{3+} are 1.2 and 2.5 M.

4) Calculate $E°$ for the cell

   $Zn(s) \mid Zn^{2+}\ (1.0\ M) \parallel H^+\ (1.0\ M) \mid H_2(g,\ 1\ atm) \mid Pt(s)$

   and then calculate the equilibrium constant for the reaction,

   $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

5) Write an expression for the half-cell potential for the following redox system:

   $Pt(s) \mid Cr_2O_7^{2-}\ (c_1),\ Cr^{3+}\ (c_2),\ H^+\ (c_3)$

6) For the following concentration cell, calculate the H^+ ion concentration and pH of the solution in the cathodic compartment at 298 K.

   $Pt\ (s) \mid H_2\ (g,\ 1\ atm) \mid H^+\ (2 \times 10^{-4}\ M) \parallel H^+\ (c) \mid H_2\ (g,\ 1\ atm) \mid Pt\ (s)$

   For this cell, emf is 0.150 V.

7) For Weston cell, emf is 1.018 V at 293 K. Its temperature coefficient $\left(\frac{\partial E}{\partial T}\right)_p$ $= -4.00 \times 10^{-5}\ V\ K^{-1}$. Calculate ΔG, ΔS and ΔH for the cell reaction of this cell.

17.16 ANSWERS

Self Assessment Questions

1) The electrode, at which oxidation occurs, is called anode, whereas the electrode where reduction takes place, is called cathode.
   a) In galvanic cell, the cathode is given a positive sign and the anode, a negative sign.
   b) In electrolytic cell, the two signs are reversed. The anode is given a positive sign and the cathode is given a negative sign.

2) As explained in Sec. 17.4, if any reaction leads to negative cell potential, that particular reaction will be non-spontaneous. Hence, we have to calculate the cell potentials in each case to know whether a particular reaction is spontaneous or not.

   i) $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$

   $E°_{cell} = E°_{anode} + E°_{cathode}$

   $= [-(-0.44) + 0]$ V (since standard potential for Fe^{2+}/Fe is − 0.44 V)

   $= 0.44$ V.

   This reaction is spontaneous.

   ii) $Cu + 2H^+ \longrightarrow Cu^{2+} + H_2$

   $E°_{cell} = E°_{anode} + E°_{cathode}$

   $= [-(0.34) + 0]$ V (since for Cu^{2+}/Cu, $E° = +0.34$ V)

   $= -0.34$ V.

   This reaction is non-spontaneous.

   iii) $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

   $E°_{cell} = E°_{anode} + E°_{cathode}$

   $= [-(0.54) + 0.77]$ V

   $= 0.23$ V. This reaction is spontaneous.

3) Remember in a galvanic cell, the l.h.s. compartment is the one where oxidation takes place, and in the r.h.s. compartment, the reduction takes place. The flow of electrons in the wire is from anode to cathode. The two compartments are separated by a salt bridge. Following these conventions, we can draw the diagram as given in Fig. 17.14.

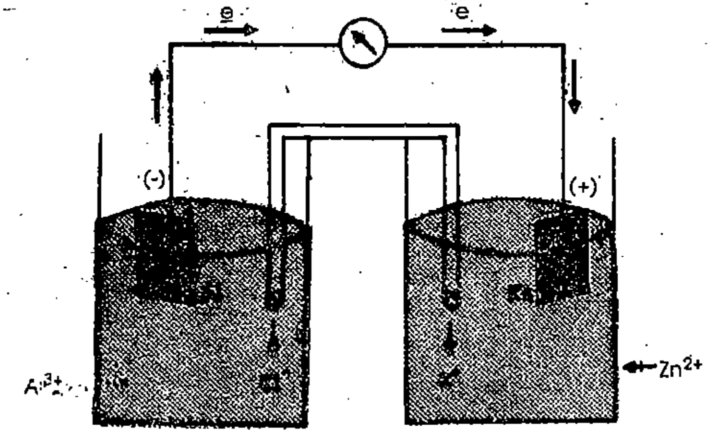

Fig. 17.14 : Galvanic cell.

Following the steps given in Sec. 17.5, it is represented as

$Al(s) \mid Al_2(SO_4)_3(c_1) \parallel ZnSO_4(c_2) \mid Zn(s)$

4) From the given values, we can calculate the $E°$ value for the overall reaction as follows :

$Zn^{2+} + 2e^- \longrightarrow Zn$ $\qquad E°_{cathode} = -0.76\ V$

$Zn + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+} + 2e^-$ $\qquad E°_{anode} = -(-1.03)\ V = 1.03\ V$

Combining the two we get,

$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$; $E° = (1.03 - 0.76)\ V = 0.27\ V$

Note that $n = 2$ for this reaction.

Substituting the values in Eq. 17.42, we get,

$$\log K = n\left(\frac{F}{2.303\,RT}\right)E°$$

$$= 2 \times \frac{1}{0.059\ V} \times 0.27\ V$$

$$= 9.2$$

$$K = 10^{9.2} = 1.6 \times 10^{9}$$

5) Similar to Eqs. 17.6, 17.28 and 17.30, we can write

$$-\Delta G° = nFE°$$

$$\Delta S° = nF\left[\frac{(E_2° - E_1°)}{(T_2 - T_1)}\right]_p$$

$$\Delta H° = -nFE° + TnF\left(\frac{\partial E°}{\partial T}\right)_p$$

6) The half-cell reaction is

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$

The half-cell potential can be written as :

$$E_{Cl_2/Cl^-} = E°_{Cl_2/Cl^-} - \frac{0.059}{2}\log\frac{c^2}{p_{Cl_2}}$$

7) Using Eq. 17.41, $E_{cell} = (0.0295 \log 2)\ V$

$= 0.0295 \times 0.3010\ V$

$= 8.88 \times 10^{-3}\ V$

8) a) As the reaction products accumulate near the electrodes, the electrode reactions become slow and may finally stop. After leaving it idle for a while, the products diffuse away and the cell starts functioning again.

b) The fuel cells are considered better since the reactions take place under nearly reversible conditions and the efficiency is higher in producing more useful work.

c) Alkaline dry cell lasts longer because zinc electrode does not corrode easily (due to absence of acidic conditions).

Terminal Questions

1) The standard reduction potential for

$Cu^{2+} + 2e^- \longrightarrow Cu$

is + 0.34 V as compared to standard hydrogen electrode for which potential is 0.0 V. This indicates that copper is a poorer reducing agent than hydrogen. Thus copper would not dissolve in acids unless these contain oxidising anions like NO_3^-. Since $E^\circ_{NO_3^-/NO}$ is larger than $E^\circ_{Cu^{2+}/Cu}$, NO_3^- can be reduced by Cu.

2) a) The electrode potentials for the two systems are :

$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V

and $E^\circ_{MnO_4^-/Mn^{2+}} = 1.49$ V

Hence, MnO_4^- is a better oxidising agent than $Cr_2O_7^{2-}$.

b) $E^\circ_{Cl_2/Cl^-} = 1.36$ V and $E^\circ_{Br_2/Br^-} = 1.09$ V

Hence, Br^- is a better reducing agent than Cl^-.

3) For the reaction

$Al^{3+} + Fe \longrightarrow Al + Fe^{3+}$

We can write.

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[Fe^{3+}]}{[Al^{3+}]}$$

$$= -1.62 - \frac{0.059}{3} \log \frac{2.5}{1.2}$$

$$= -1.63 \text{ V}$$

4) $E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$

$$= (-(-0.76) + 0) \text{ V} = 0.76 \text{ V}$$

Using Eq. 17.42, $\log K = \frac{0.76 \times 2}{0.059} = 25.76$

$$K = 5.8 \times 10^{25}$$

5) The half-cell reaction can be represented by :

$Cr_2O_7^{2-} + 14\,H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

The half-cell potential is given by

$$E_{Cr_2O_7^{2-}/Cr^{3+}} = E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} - \frac{0.059}{6} \log \frac{c_2^2}{c_1 c_3^{14}}$$

6) Following Sec. 17.9, the cell reaction is

$2H^+ (c) \longrightarrow 2H^+ (2 \times 10^{-4}$ M)

Using Eq. 17.40, $E_{cell} = 0.150 \text{ V} = \left[-\frac{0.059}{2} \log \left(\frac{2 \times 10^{-4}}{c} \right)^2 \right]$ V

$0.150 = 0.059 \log c - 0.059 \log (2 \times 10^{-4})$

$= 0.059 \log c + 0.2182$

$0.059 \log c = -0.0682$

$\log c = -1.16$ and pH = 1.16.

$[H^+]$ in the cathode $= c = 6.92 \times 10^{-2}$ M

7) Substituting the given values in Eq. 17.6 we get

$\Delta G = -2 \times 96{,}500 \text{ C} \times 1.018 \text{ V}$

$= -2 \times 96{,}500 \times 1.018 \text{ J}$

$= -1.964 \times 10^5 \text{ J}$

Using Eq. 17.28 we get,

$\Delta S = 2 \times 96{,}500 \text{ C} \times (-4.00 \times 10^{-5} \text{ V K}^{-1})$

$= -7.72 \text{ J K}^{-1}$

Also, substitution in Eq. 17.30 gives,

$\Delta H = -2 \times 96{,}500 \text{ C} \times 1.018 \text{ V} + [293 \text{ K} \times 2 \times 96{,}500 \text{ C} \times (-4.00 \times 10^{-5} \text{ V K}^{-1})$

$= -1.99 \times 10^5$ J.

Uttar Pradesh Rajarshi Tandon
Open University

UGCHE-04
Physical Chemistry

Block

5

DYNAMICS AND MACROMOLECULES

UGCHE-04(13A)

DYNAMICS AND MACROMOLECULES

Dynamics, in chemical sense, refers to reaction dynamics. Reaction dynamics is the study of the effect of concentration, temperature, catalyst, etc. on the speed (or rate) of chemical reactions. Units 18,19 and 21 deal with some of the aspects of reaction dynamics. In Unit 18, we shall explain the effect of concentration of the reactants and temperature on the speed of chemical reactions. In Unit 19, we shall discuss the light-induced reactions. In Unit 21, we shall study the role of catalysts on chemical reactions.

In Unit 20, we shall discuss some of the aspects of colloids and macromolecules. In colloids, the size of the solute particles is much larger than that of the solvent particles. Macromolecules have large molar masses and many of them yield colloidal solutions. Hence the studies of colloids and macromolecules are combined in Unit 20.

In Unit 14 of Block 4, we discussed the effect of pressure, concentration and temperature on the amounts of products formed. Time required for a particular fraction of a reactant to react was not considered in that Unit. This aspect is covered in detail in Block 5.

Objectives

After studying this block, you should be able to

- explain the effect of concentration and temperature on the rates of chemical reactions,
- discuss the importance of light-induced reactions,
- describe the role of catalyts in chemical reactions, and
- explain the properties of colloids.

UNIT 18 CHEMICAL KINETICS

Structure

18.1 INTRODUCTION

Chemical kinetics is the study of rates and mechanisms of chemical reactions. The rate of a reaction depends on many factors such as the concentration of the reactants, temperature, catalyst, etc. Some of these factors shall be examined in this unit. We shall study thermal reactions in this unit. In thermal reactions, the reactants gain the energy required for the reaction through molecular collisions. In Unit 19, we shall study reactions induced by light.

We shall start the unit explaining the dependence of rate of reaction on the concentrations of the reactants. In this process, we shall be defining the terms such as rate equation, rate law and order of a reaction. We shall then derive first order, second order and zeroth order equations. These equations will be used for calculating the rate constants of the reactions. We shall then explain the methods of determining the order of reaction.

We shall discuss the mechanism of simple reactions. We shall illustrate the significance of rate-determining step in explaining the rate law. We shall study the effect of temperature on reaction rates. We shall state the theories of reaction rates. Finally, the methods of studying fast reactions will be dealt with.

Objectives

After studying this unit, you should be able to:

- define rate law, rate constant and order of reaction,
- differentiate between order of reaction and stoichiometry,
- state the experimental methods for studying the reaction rates,
- derive integrated rate laws for first order, second order and zeroth order reactions and use them for calculating rate constants,
- state the methods for determining the order of reaction,
- define elementary reaction and molecularity,

- propose mechanism for simple reactions using the experimental rate law,
- discuss the theory of unimolecular reactions,
- explain Arrhenius equation, collision theory and activated complex theory, and
- describe the methods of studying fast reactions.

18.2 SOME FUNDAMENTAL CONCEPTS

Throughout this unit, the phrase 'rate of reaction' means instantaneous reaction rate.

In this section, we shall define some terms such as rate of reaction, rate law, rate constant, order of a reaction and stoichiometry.

Rate of Reaction

We shall shortly study the method of arriving at the reaction rates from the values of concentrations of a component at different time intervals.

The symbol 'Δ' is to be read as delta. It denotes change in a property.

The rate of reaction or the velocity of reaction at a specified time is defined as the decrease in the concentration of a reactant or the increase in the concentration of a product per unit time. The rate of reaction at a specified time is also known as instantaneous rate of reaction; it can be generally defined as the rate of change of concentration of a specified species at a particular instant. While specifying the reaction rate, we must mention the component with respect to which it is stated. Let us consider a simple reaction,

$$A \rightarrow B$$

As per the reaction stoichiometry, one molecule of B is formed for every molecule of A consumed. The reaction rate can be specified in the following ways:

Convention For Expressing Reaction Rates

In order to obtain a single value for the reaction rate, it is necessary to divide the rate of consumption of a reactant or the rate of formation of a product by the stoichiometric coefficient of the respective species. To illustrate this, let us consider the reaction:

$$aA + bB \longrightarrow cC + dD$$

In this reaction, A and B are reactants, and C and D are products; *a*, *b*, *c* and *d* are the stoichiometric coefficients. The reaction rate is related to the rates of consumption of the reactants and the rates of formation of the products as follows:

Reaction rate

$$= \frac{1}{a}\left(\frac{-\mathrm{d}[A]}{\mathrm{dt}}\right) = \frac{1}{b}\left(\frac{-\mathrm{d}[B]}{\mathrm{dt}}\right)$$

$$= \frac{1}{c}\left(\frac{\mathrm{d}[C]}{\mathrm{dt}}\right) = \frac{1}{d}\left(\frac{\mathrm{d}[D]}{\mathrm{dt}}\right) \quad \ldots (18.2)$$

Using this general equation, you examine Eq. 18.1

The number preceding the formula of a substance in the balanced equation is its stoichiometric coefficient.

- We can measure the concentration of the reactant A at various time intervals. From these values, we can specify the decrease in concentration of A with respect to time at any particular instant. The reaction rate thus obtained is the rate of consumption of A.

$$\text{Rate of consumption of A} = \frac{\text{Decrease in the concentration of A}}{\text{Change in time}}$$

$$= \frac{-\Delta[A]}{\Delta t}$$

- $\Delta[A]$ means change in the concentration of A and $-\Delta[A]$ means the decrease in the concentration of A. While writing a rate expression with respect to a reactant, there is a preceding negative sign (since it is customary to express the rate of a reaction as a positive quantity).

- We can measure the concentration of the product B at various time intervals. From these values, we can arrive at the rate of formation of B at any particular instant.

$$\text{Rate of formation of B} = \frac{\text{Increase in the concentration of B}}{\text{Change in time}}$$

$$= \frac{\Delta[B]}{\Delta t}$$

The rates of consumption of reactants and the rates of formation of products are related through their stoichiometric coefficients. For example, consider the decomposition of NO_2.

$$2\,NO_2(g) \rightarrow 2\,NO(g) + O_2(g)$$

We can write the relationship between the rates of consumption of NO_2 and the rates of formation of NO and O_2 as follows:

$$\left.\begin{aligned}\frac{1}{2}\,(\text{Rate of consumption of } NO_2) &= \frac{1}{2}\,(\text{Rate of formation of NO})\\ &= \text{Rate of formation of } O_2\end{aligned}\right] \ldots (18.1)$$

Using the convention as expressed by Eq. 18.2, we can write as shown below:

$$\text{Reaction rate} = \frac{1}{2}\left(\frac{-\mathrm{d}[NO_2]}{dt}\right) = \frac{1}{2}\left(\frac{\mathrm{d}[NO]}{dt}\right) = \left(\frac{\mathrm{d}[O_2]}{dt}\right)$$

You can understand the above relationship if you bear in mind that if two molecules of NO_2 are consumed, two molecules of NO and one molecule of O_2 are formed. In other words, the reaction rate is equal to :

- half the rate of consumption of NO_2
- half the rate of formation of NO, and
- the rate of formation of O_2

Calculation of Reaction Rate

You may be curious to know as to how the reaction rates are calculated. Take for instance the following reaction:

$$2\,NO_2(g) \rightarrow 2\,NO(g) + O_2(g)$$

In Figs. 18.1 a, b and c, you can see concentration (c) against time (t) plots for NO_2, NO and O_2 as per the values given in Table 18.1. In these figures, the graphical method of calculation of the reaction rates for the consumption of NO_2 and for the formation of NO and O_2 are illustrated. The reaction rate at any particular instant is obtained by calculating the slope of a line tangent to the curve at that point.

From the slope of the tangent line drawn (corresponding to a particular time) to the concentration (c) against time (t) curve for a component , we can obtain the rate of the reaction.

Rate of reaction

$$= \frac{-\text{(Slope of tangent to the } c \text{ against } t \text{ curve for the reactant)}}{\text{Stoichiometric coefficient of the reactant}}$$

$$= \frac{\text{Slope of tangent to the } c \text{ against } t \text{ curve for the product}}{\text{Stoichiometric coefficient of the product}}$$

The concentrations of components are given in molarity (M) unit.

1 M = 1 mol dm^{-3}

Table 18.1: Concentrations of NO_2, NO and O_2 at Different Time Intervals at 673 K.

Time/s	$[NO_2]$/M	[NO]/M	$[O_2]$/M
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033

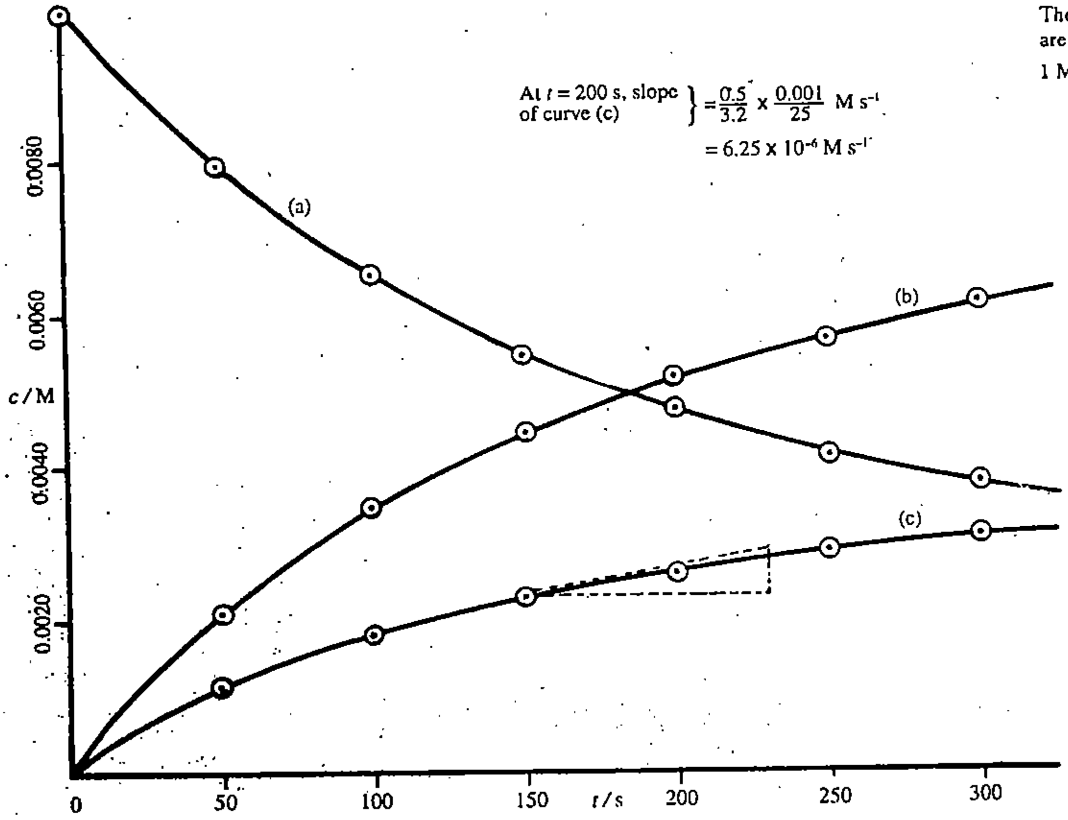

Fig: 18.1: a) Concentration against time plot for NO_2; note the falling nature of the curve which is characteristic of concentration against time plot for a reactant.

Rate of consumption of NO_2 at t = 200 s = – Slope of the tangent line at t = 200 s

$$= -(-1.31 \times 10^{-5})\ \text{M s}^{-1}$$
$$= 1.31 \times 10^{-5}\ \text{M s}^{-1}$$

Reaction rate $= \frac{1}{2}$ (Rate of consumption of NO_2) $= \frac{1}{2} \times 1.31 \times 10^{-5}\ \text{M s}^{-1}$

$$= 6.55 \times 10^{-6}\ \text{M s}^{-1}$$

b) **concentration against time plot for NO; note the rising nature of the curve which is characteristic of concentration against time plot for a product.**

Rate of formation of NO at t = 200 s = Slope of the tangent line at t = 200 s

$$= 1.30 \times 10^{-5}\ \text{M s}^{-1}$$

Reaction rate $= \frac{1}{2}$(Rate of formation of NO)

$$= 1/2 \times 1.30 \times 10^{-5}\ \text{M s}^{-1}$$
$$= 6.50 \times 10^{-6}\ \text{M s}^{-1}$$

c) **concentration against time plot for O_2; note again the rising curve. Compared to the curve for NO, the curve for O_2 rises slowly.**

Rate of formation of O_2 at t = 200 s = Slope of the tangent line at t = 200 s

$$= 6.25 \times 10^{-6}\ \text{M s}^{-1}$$

Reaction rate = Rate of formation of O_2

$$= 6.25 \times 10^{-6}\ \text{M s}^{-1}$$

For the curves (a) and (b), the tangents are not indicated.
From the slope values at t = 200 s, you can see that the following relationship is nearly correct.

Reaction rate $= \frac{1}{2}$ (Rate of consumption of NO_2) $= \frac{1}{2}$ (Rate of formation of NO)

= Rate of formation of O_2

In our discussion, we are mainly interested in the concentration against time plots for the reactants. In other words, we want to study the reactions under conditions where the rate of the forward reaction is significant but the reverse reaction rate is low. This is made possible, if we study the reaction upto a point where the product amounts are not high. For example, in the decomposition of NO_2, there could be a decrease in the concentration of NO_2 upto a particular time. Afterwards, enough nitric oxide and oxygen are formed and the reverse reaction also could take place leading to the formation of NO_2. In order to simplify the situation, it is better to study the reaction rates before significant amounts of products are formed. In general, the rates of reactions are complex functions of the concentrations of the reactants and the products at a given temperature. However, there are some reactions in which the rates are proportional to the simple powers of the concentrations of the reactants. We shall be mostly concerned with this class of reactions.

Decomposition of N_2O_5

The decomposition of N_2O_5 in the gas phase was studied at 323 K.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

The instantaneous rates of this reaction calculated from $[N_2O_5]$ against time plot (similar to Fig. 18.1) are given in Table 18.2.

Table 18.2 : Rates for the Decomposition of N_2O_5 at 323 K

$[N_2O_5]$/M (i)	Rate/M s^{-1} (ii)	$\frac{\text{Rate}}{[N_2O_5]}$. s (iii)
0.300	2.73×10^{-4}	9.1×10^{-4}
0.150	1.37×10^{-4}	9.1×10^{-4}
0.100	9.10×10^{-5}	9.1×10^{-4}

From columns (i) and (ii), you can see that the rate for the decomposition of N_2O_5 decreases with the decrease in the concentration of N_2O_5. Further, column (iii) gives the ratio of the rate to the concentration of N_2O_5. In all the three cases, it is a constant. This shows that the rate is directly proportional to the concentration of N_2O_5

$$\text{i.e.,}\quad \frac{\text{Rate}}{[N_2O_5]} = k \qquad \ldots (18.3)$$

$$\text{Hence, rate} = k\,[N_2O_5] \qquad \ldots (18.4)$$

where k is proportionality constant.

Decomposition of Hydrogen Iodide

The decomposition of hydrogen iodide was followed at a constant temperature:

$$2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)$$

The instantaneous rates of this reaction were calculated using the [HI] against time plot like that of Fig.18.1. These values are given in Table 18.3.

Table 18.3: Rates for the Decomposition of HI

[HI]/M (i)	Rate/M s^{-1} (ii)	$\frac{\text{Rate}}{[HI]}$, s (iii)	$\frac{\text{Rate}}{[HI]^2}$, M s (iv)
3.00×10^{-2}	3.60×10^{-5}	1.2×10^{-3}	4.00×10^{-2}
2.00×10^{-2}	1.60×10^{-5}	8.0×10^{-4}	4.00×10^{-2}
1.50×10^{-2}	9.01×10^{-6}	6.0×10^{-4}	4.00×10^{-2}

From Table 18.3, you can see that the rate of decomposition of HI decreases with decrease in the concentration of HI, as in the case of the decomposition of N_2O_5. Further, it is evident from column (iii) that rate/[HI] is not a constant. But, as per column (iv), rate/$[HI]^2$ is a constant.

From Table 18.3, it is evident that

$$\text{Rate} / [HI]^2 = k \qquad \ldots (18.5)$$

$$\text{Hence, rate} = k\,[HI]^2 \qquad \ldots (18.6)$$

where k is a proportionality constant.

For many chemical reactions, the relationship between the reaction rate and the concentration can be expressed in a simple way as in Eq.18.4 or 18.6. We shall first consider these simple cases. Later we shall discuss those reactions for which the rate – concentration relationship is more complex.

Rate Law and Rate Constant

The relationship expressed as in Eq.18.4 or Eq.18.6 is called the **rate law.** **A rate law is an equation expressing the relationship between the instantaneous reaction rate and the concentrations of the reactants in a reaction.**

The rate law for a simple reaction with one reactant may be of the following type:

$$\text{Reaction rate} = k\,[\text{Reactant}]^n \qquad \ldots (18.7)$$

From Eq. 18.7, it can be seen that if [reactant] = 1, then k = rate. For this reason, k is called the specific rate

where k is called the rate constant or rate coefficient or the specific rate of the reaction. Thus by definition, the rate constant is independent of concentration, but it may depend on other factors. In this equation, n refers to the order of the reaction. The **order** with respect to a component is the power to which the concentration of that component is raised in the rate law. Comparing Eq.18.7 with Eqs.18.4 and 18.6, we conclude that

i) $n = 1$ in Eq.18.4; i.e., decomposition of N_2O_5 is a **first order** reaction. The significance of this statement is that the reaction rate is proportional to the first power of concentration of N_2O_5.

$$\text{i.e., Rate} = k\,[N_2O_5]^1 \qquad \ldots (18.8)$$

where k is the first order rate constant.

ii) $n = 2$ for the decomposition of HI; i.e., the decomposition of HI is a **second order reaction.** Again this means that the decomposition rate of HI is proportional to the second power or square of the concentration of HI.

$$\text{i.e., Rate} = k[\text{HI}]^2 \quad \dots (18.9)$$

where k is the second order rate constant.

Order of Reaction and Stoichiometry

The rate laws as well as the order of the reaction must be determined experimentally; these cannot be predicted from the stoichiometry of the reaction. The stoichiometry of reaction gives the relationship between the amounts of the reactants and the amounts of the products. The stoichiometry of a reaction must be differentiated from the order of a reaction. Let us consider the following examples.

Example 1

The gas-phase decomposition of N_2O_5 yields NO_2 and O_2 at a particular temperature.

$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$$

The experimentally observed rate law for the reaction rate $= k[N_2O_5]$

Comment on the order and the stoichiometry of the reaction.

Solution

It can be seen that the stoichiometric coefficient of N_2O_5 is 2 whereas the order of reaction is 1.

Example 2

The balanced equation for the decomposition of nitrous oxide is given below:

$$2\,N_2O(g) \rightarrow 2\,N_2(g) + O_2(g)$$

The rate law is,

$$\text{rate} = k[N_2O]$$

Comment on the order of the reaction and the stoichiometry.

Solution

Again the stoichiometric coefficient of N_2O is 2 whereas the order of reaction is 1.

In the above two examples, the order of reaction and the stoichiometry are not identical. But there are cases where the order and stoichiometric coefficient are identical. One of the examples can be seen in the following reaction:

$$2\,HI(g) \rightarrow H_2(g) + I_2(g)$$

$$\text{Rate} = k[\text{HI}]^2$$

In the decomposition of HI, the order of reaction is two. The stoichiometric coefficient of HI is also 2.

From the above examples, you can see that the stoichiometric coefficient and the order of the reaction need not be the same always. You must bear in mind the following points while arriving at a rate law:

i) In the case of simple reactions, the concentrations of the reactants appear in rate law; but the concentrations of the products do not appear in the rate law. It is so since the rate measurements are done under the conditions where the reverse reaction rate is negligibly low.

ii) The order of the reaction must be determined experimentally; the experimental methods will be discussed in the next section.

iii) The order of a reaction need not be identical with the stoichiometric coefficient of the reactant.

So far we considered the reactions involving only one reactant. In case of reactions involving many reactants, the rate of a reaction may depend on the concentrations of more than one reactant. In such cases, we can calculate the order of the reaction with respect to the individual reactant and also the **overall order**. The overall order is the sum of the powers to which the individual concentrations are raised in the rate law.

In general, for a reaction,

$$A + B + C \rightarrow \text{products}$$

if the rate law is experimentally found to be,

$$\text{rate} = k\,[A]^m\,[B]^n\,[C]^p \qquad \ldots (18.10)$$

then, the overall order of the reaction $= m + n + p$.

For example in the following reaction,

$$BrO_3^-(aq) + 5\,Br^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O\,(l)$$

$$\text{Rate} = k\,[BrO_3^-]\,[Br^-]\,[H^+]^2 \qquad \ldots (18.11)$$

The overall rate of the reaction is four, being first order in BrO_3^-, first order in Br^- and second order in H^+

The rate laws discussed so far are called **differential rate laws.** Such rate laws describe the dependence of reaction rate on concentration. From these differential rate laws, we can obtain the **integrated rate laws** through integration. The integrated rate laws help us in relating the concentration of a substance to time. In other words, using the integrated rate laws, we can calculate the concentration of a substance at any specified time. In Secs. 18.4 and 18.5, we shall discuss the derivation of the integrated forms of rate laws. In the next section, we shall discuss some experimental methods of studying the reaction rates.

For the $BrO_3^- - Br^- - H^+$ reaction let us compare the order of reaction and the stoichiometric coefficient for each reactant.

	BrO_3^-	Br^-	H^+
Order	1	1	2
Stoichiometric coefficient	1	5	6

It may be noticed that the stoichiometric coefficients and the respective orders of reaction are not identical throughout.

SAQ 1

At 323 K, the rate of reaction for the decomposition of N_2O_5 at a particular instant is $2.74 \times 10^{-4}\ M\,s^{-1}$. Calculate the rate of formation of O_2. The reaction is represented below:

$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$$

....

....

....

SAQ 2

In the decomposition of hydrogen iodide, what is the relationship between the rate of decomposition of HI and the rate of formation of H_2 ?

....

....

....

18.3 EXPERIMENTAL METHODS OF RATE STUDIES

Many physical and chemical methods are available for studying the reaction rates. Some of them are listed below:

i) **Volume or Pressure Measurement**

When one or more of the components are gases, the reaction rate can be followed by measuring the volume or pressure change. The partial pressures of the species are to be calculated using the reaction stoichiometry.

ii) **Titrimetry**

Using acid-base or oxidation-reduction titrations, the reaction course can be followed if atleast one of the components in the reaction is an acid or a base or an oxidising agent or a reducing agent.

iii) **Conductometry or Potentiometry**

If one or more of the ions are present or produced in the reaction, suitable methods can be designed based on conductivity or potentiometric measurements.

Spectrophotometers have arrangements for generation of nearly monochromatic radiation in visible and ultraviolet regions and also for the measurement of radiation transmitted by the absorbing substance.

iv) **Spectrophotometry**

When a component of the reaction has a strong absorption band at a particular wavelength region, spectrophotometers could be used for measuring the reaction rate.
- Photoelectric colorimeters are cheaper instruments and are mainly useful for reaction rate studies in visible region.

Nowadays many sophisticated instruments such as nuclear magnetic resonance spectrometer, mass spectrometer etc, are used in reaction kinetics. We shall not discuss these aspects.

v) **Polarimetry**

When atleast one of the components of a reaction is optically active, the reaction rate can be studied from the measurements of optical rotation.

Depending on the reaction under study, the concentration of a reactant or a product is followed at various time intervals using any of the methods mentioned above. These values are then used for calculating the rate constant. Examples are worked out in the next section to illustrate the rate constant calculation. Before studying these examples, we shall discuss the method of arriving at the integrated forms of rate laws.

SAQ 3

State the name of a suitable experimental method that can be followed to monitor the reaction rate in each of the following cases:

i) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

Hint : Bromine absorbs strongly in the visible region , while hydrogen and hydrogen bromide do not.

ii) $CH_3COOC_2H_5(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + C_2H_5OH(aq)$

iii) $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ (at constant volume conditions)

....

....

....

18.4 FIRST ORDER AND SECOND ORDER REACTIONS

In this section, we shall derive integrated rate laws for first and second order reactions.

Integrated Rate Law for First Order Reactions

Let us consider the following reaction, which is experimentally found to be first order.

$$A \rightarrow \text{Products} \quad \ldots (18.12)$$

Applying Eq. 18.7 , we can write

$$\text{rate} = \frac{-d[A]}{dt} = k[A]^1 \quad \ldots (18.13)$$

where k is the first order rate constant and $n = 1$. This means that the rate of consumption of A at any given time is directly proportional to the first power of the concentration of A at that time.

In order to obtain the integrated rate for first order reaction, we have to know the concentrations of A at the start of the reaction and at a time t as mentioned below:

At time = 0 (i.e., at the start), the concentration of A = $[A]_0$

At time = t, the concentration of A = $[A]_t$

Using these limits of concentration and time, we can integrate Eq.18.13 after rearranging it as follows:

$$\int_{[A]_0}^{[A]_t} -\frac{d[A]}{[A]} = \int_0^t k\,dt \qquad \ldots(18.14)$$

In order to understand the transformation of Eq. 18.14 into Eq. 18.16, refer to Sec. 6.6 of Unit 6 of this course.

$$\text{i.e.,} -\left\{\ln[A]\right\}_{[A]_0}^{[A]_t} = k[t]_0^t \qquad \ldots(18.15)$$

$$-\left\{\ln[A]_t - \ln[A]_0\right\} = k(t-0) \qquad \ldots(18.16)$$

$$\ln[A]_0 - \ln[A]_t = kt \qquad \ldots(18.17)$$

$$\text{Hence, } \ln\frac{[A]_0}{[A]_t} = kt \qquad \ldots(18.18)$$

Eq. 18.18 can be written in the exponential form as follows:

$$[A]_t = [A]_0\, e^{-kt} \qquad \ldots(18.19)$$

The transformation of Eq. 18.18 into Eq. 18.19 could be explained as follows:

$$\ln\frac{[A]_0}{[A]_t} = kt \qquad \ldots(18.18)$$

$$-\ln\frac{[A]_t}{[A]_0} = kt$$

$$\ln\frac{[A]_t}{[A]_0} = -kt$$

Taking antilogarithms,

$$\frac{[A]_t}{[A]_0} = e^{-kt}$$

$$[A]_t = [A]_0\, e^{-kt} \qquad \ldots(18.19)$$

Corresponding to Eq. 18.19, we can draw the concentration vs. time plot for a first order reaction. This curve is of the type shown in Fig.18.2. Such a curve is called an exponential decay curve. In an exponential decay curve, there is a steep decrease in concentration initially. It is followed by a slow decrease in concentration subsequently. Note that the decay curve goes parallel to x - axis after longer time intervals indicating that the reaction will take infinite time for completion.

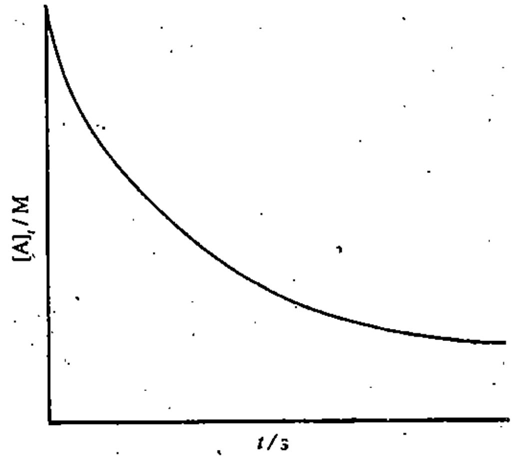

Fig. 18.2 : Exponential decay of A.

Radioactive decay is a good example of first order reaction. A detailed discussion on radioactive decay has been given in Unit 9 of "Atoms and Molecules" course.

Let us come back to Eq. 18.18. It is more convenient to work with logarithms to the base 10 (known as common logarithms). Hence we can rewrite Eq.18.18 as follows:

$$2.303 \log\frac{[A]_0}{[A]_t} = kt$$

$$\text{or} \qquad k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t} \qquad \ldots(18.20)$$

Remember the following formula: $\ln x = 2.303 \log x$

Eq.18.20 is useful in calculating the concentration of the reactant at a time t (i.e., $[A]_t$ provided, its initial concentration (i.e., $[A]_0$), k and t are known. Also, k can be calculated, if $[A]_0$, $[A]_t$ and t are known. Using the graphical method, we can test whether a reaction follows first order or not.

Graphical Method of Calculating First Order Rate Constant

In order to facilitate graphical representation, Eq.18.20 is modified as follows:

$$\log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = \frac{kt}{2.303} \qquad \ldots(18.21)$$

Hence
$$\log\,[\mathrm{A}]_0 - \log\,[\mathrm{A}]_t = \frac{kt}{2.303} \qquad \ldots(18.22)$$

i.e.,
$$-\log\,[\mathrm{A}]_t = \frac{kt}{2.303} - \log\,[A]_0 \qquad \ldots(18.23)$$

$$\log\,[\mathrm{A}]_t = \frac{-k}{2.303}t + \log\,[A]_0 \qquad \ldots(18.24)$$

By comparing Eq. 18.24 with the equation for a straight line,

$$y = mx + c,$$

we can infer that by plotting log $[\mathrm{A}]_t$ against time, a straight line must be obtained for a first order reaction. Such plots are shown in Figs. 18.3-18.5. The rate constant can be calculated from the slope as follows :

$$k = -2.303 \times \text{slope} \qquad \ldots(18.25)$$

From Eq. 18.21, we can derive Eq.18.27 by substituting the concentrations of A at time intervals t_1 and t_2 as follows :

At time $= t_1$,

concentration of A $= [\mathrm{A}]_1$

At time $= t_2$,

concentration of A $= [\mathrm{A}]_2$

$$\log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_1} = \frac{kt_1}{2.303}$$

$$\log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_2} = \frac{kt_2}{2.303}$$

Hence,

$$\log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_2} - \log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_1} = \frac{k}{2.303}(t_2 - t_1) \qquad \ldots(18.26)$$

i.e., $\log \dfrac{[A]_1}{[A]_2} = \dfrac{k}{2.303}(t_2 - t_1)$ ...(18.27)

Knowing the concentration of a reactant undergoing first order reaction at a particular time, it is possible to calculate its concentration at another time interval using Eq.18.27.

$$\log \frac{[\mathrm{A}]_1}{[\mathrm{A}]_2} = \frac{k}{2.303}(t_2 - t_1) \qquad \ldots(18.27)$$

The following hints may be useful while calculating the rate constants using the integrated rate law:

i) If the concentrations of the reactant are given at various time intervals, the concentration at $t = 0$ is equal to $[\mathrm{A}]_0$ and the concentration at any given time is $[\mathrm{A}]_t$; log $[\mathrm{A}]_t$ against t plot is made as described earlier. This principle is followed in Example 3.

ii) Instead of giving the concentrations of a reactant at various time intervals, parameters such as partial pressures, absorbances, volumes, titre values etc. which are proportional to the concentration of the reactant may be given. In these cases, the measurements made at zero time and at any given time t may be used instead of $[\mathrm{A}]_0$ and $[\mathrm{A}]_t$. For example, we can substitute the partial pressure of the reactant instead of its concentration in Eq.18.21 and obtain Eq. 18.28.

$$\log \frac{(p_\mathrm{A})_0}{(p_\mathrm{A})_t} = \frac{kt}{2.303} \qquad \ldots(18.28)$$

where $(p_\mathrm{A})_0$ and $(p_\mathrm{A})_t$ are the partial pressures of the reactant at the start and, after a time, t. In Example 4, we use this method.

iii) Sometimes the rate measurements are made in terms of the concentrations of the product formed. If the stoichiometry of the reaction is such that one molecule of the product is formed when one molecule of the reactant is consumed, then the concentration of the product at $t = \infty$ must be equal to initial concentration of the reactant. Let us assume that the concentration of the product at any given time is x. Then x also represents the decrease in the concentration of the reactant after a time, t. Thus, $[\mathrm{A}]_0$ = concentration of the product at $t = \infty$ and $[\mathrm{A}]_t = [\mathrm{A}]_0 - x$. Using these relationships, Eq.18.21 could be written as,

$$\log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_0 - x} = \frac{kt}{2.303} \qquad \ldots(18.29)$$

Calculation of this type is illustrated in Example 5.

Let us work out some examples to illustrate the calculation of k by graphical method.

Example 3

On heating cyclopropane to 770 K, it is converted into propene. In one experiment, the following data were obtained:

t/ s	0	300	600	900
$\frac{[\text{Cyclopropane}]}{\text{M}}$	1.50×10^{-3}	1.24×10^{-3}	1.00×10^{-3}	8.3×10^{-4}

Using graphical method, test whether the above data satisfy first order rate equation. Calculate the rate constant.

Solution

Using the data, log [cyclopropane]/M values are calculated and tabulated alongwith t values.

log [cyclopropane]/M	−2.82	−2.91	−3.00	−3.08
t/s	0	300	600	900

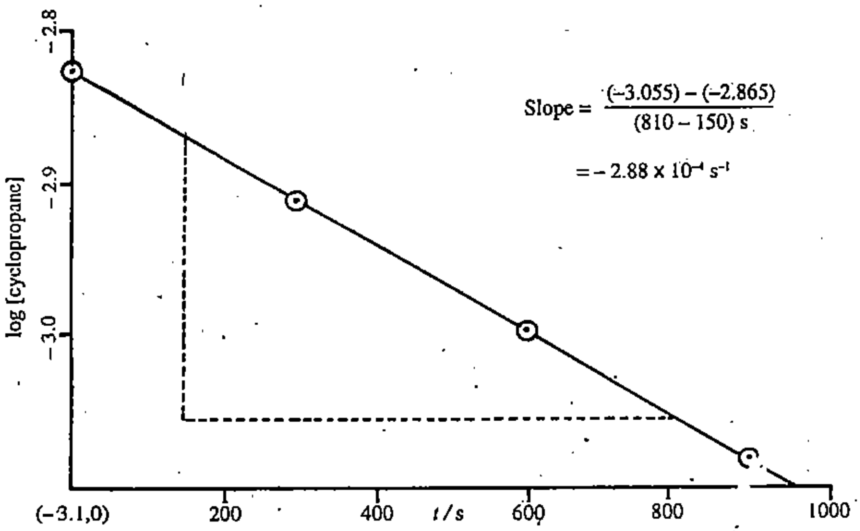

Fig. 18.3: log [cyclopropane] against t plot.

log [cyclopropane] vs. t plot is shown in Fig.18.3.

The graph is a straight line, confirming that the reaction is first order.

$$k = -2.303 \times \text{slope} = -2.303 \times (-2.88 \times 10^{-4})\ \text{s}^{-1}$$

$$= 6.63 \times 10^{-4}\ \text{s}^{-1}$$

Example 4

Azomethane ($CH_3-N = N-CH_3$) decomposes at 600 K as per the equation:

$$CH_3-N = N-CH_3\,(g) \rightarrow C_2H_6\,(g) + N_2\,(g)$$

The reaction rate was followed by measuring the partial pressure of azomethane (p_A) at different time intervals and the data are given below:

p_A /Pa	10.9	7.6	5.3	3.7	2.6
t / s	0	1000	2000	3000	4000

Using the data, test whether the reaction follows first order kinetics and calculate the rate constant.

Solution

Using Eq.2.41 of Unit 2 of this course, the concentration of azomethane (c_A) can be related to its partial pressure (p_A) as follows:

$$p_A = c_A RT \text{ or } p_A \propto c_A$$

So we can use partial pressure of azomethane in Eq.18.21 instead of concentration as shown in Eq.18.28. Rearranging Eq.18.28, we get,

$$\log\ (p_A)_t = \log\ (p_A)_0 - \frac{kt}{2.303}$$

where $(p_A)_0$ and $(p_A)_t$ are the partial pressures of azomethane at the start, and after a time, t. We tabulate the data accordingly:

$\log(p_A)_t$/Pa	1.04	0.88	0.72	0.57	0.41
t/s	0	1000	2000	3000	4000

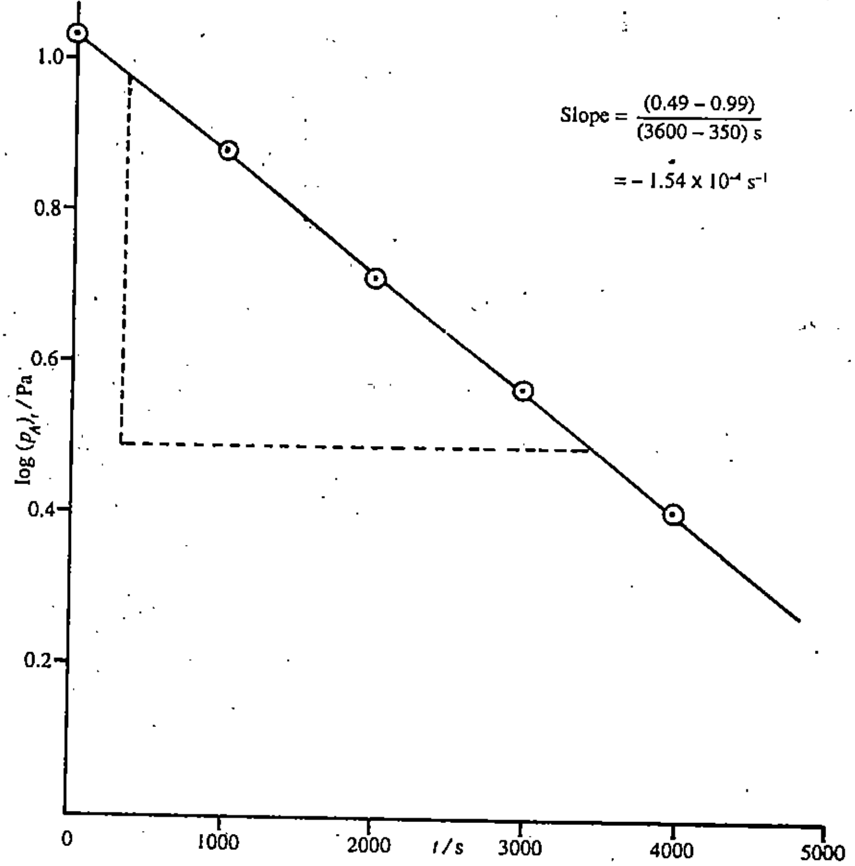

Fig.18.4 : log $(p_A)_t$ against t plot for the decomposition of azomethane.

log $(p_A)_t$ is plotted against t as shown in Fig.18.4.

From Fig.18.4, we see that the graph is a straight line. Hence, the decomposition of azomethane is a first order reaction.

$$\text{Slope} = -1.54 \times 10^{-4}\,\text{s}^{-1}$$

$$k = -2.303 \times \text{slope} = -2.303 \times (-1.54 \times 10^{-4}\,\text{s}^{-1})$$

$$= 3.55 \times 10^{-4}\,\text{s}^{-1}$$

Example 5

The hydrolysis rate of benzene diazonium chloride ($C_6H_5N = NCl$) in its aqueous solution was followed by measuring the volume of nitrogen evolved at different time intervals. The reaction was found to be first order. Using the data given below, calculate the first order rate constant.

Time / s	0	1500	3000	4500	∞
Volume of N_2 / cm^3	0	6.4	12.1	17.6	81

Solution

In this example, the rate measurement is done in terms of the product. The volume (V_t) of nitrogen produced at any given time, t, is proportional to the concentration of benzene diazonium chloride reacted (x). The volume at $t = \infty$ (i.e. ,V_∞) indicates the volume of nitrogen produced by the complete hydrolysis of benzene diazonium chloride and, it is proportional to the initial concentration of benzene diazonium chloride.

So, $[A]_0 \propto V_\infty$

$x \propto V_t$

and $[\mathrm{A}]_0 - x \propto V_\infty - V_t$

Hence $$\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0 - x} = \frac{V_\infty}{V_\infty - V_t}$$

Using this relationship in Eq.18.29,

$$\log \frac{V_\infty}{V_\infty - V_t} = \frac{kt}{2.303}$$

i.e., $$\log(V_\infty - V_t) = \log V_\infty - \frac{kt}{2.303}$$

Using the data given above, ($V_\infty - V_t$) and log ($V_\infty - V_t$) values are tabulated for different t values.

Time / s	0	1500	3000	4500
$(V_\infty - V_t)/\mathrm{cm}^3$	81	74.6	68.9	63.4
$\log(V_\infty - V_t)/\mathrm{cm}^3$	1.908	1.873	1.838	1.802

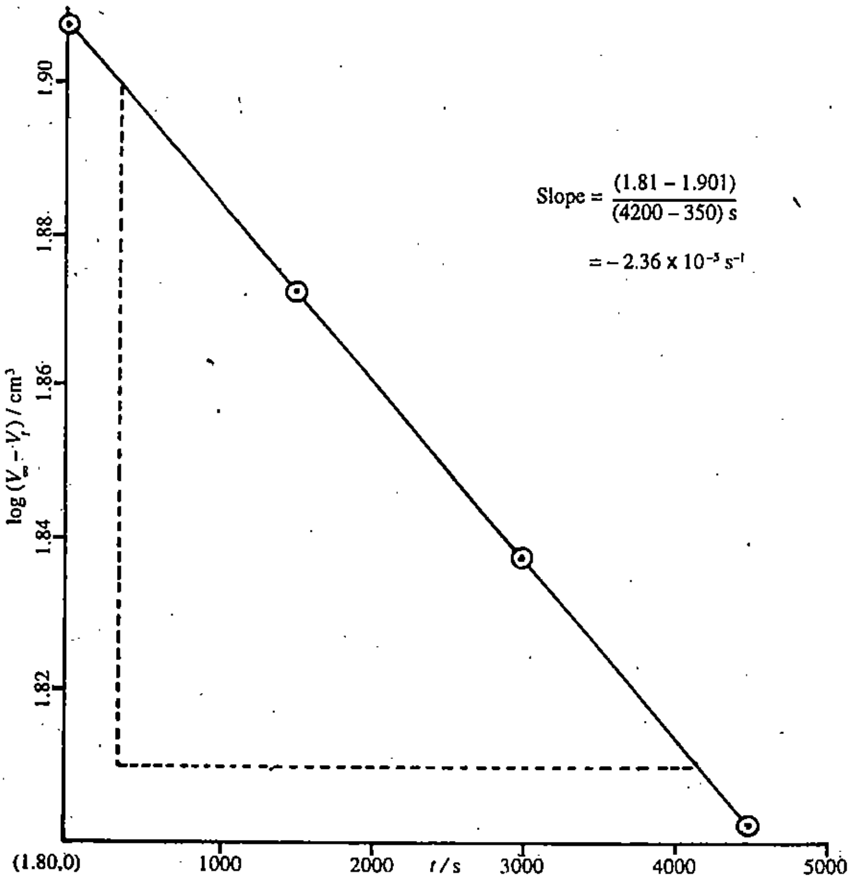

Fig.18.4. log ($V_\infty - V_t$) against t plot for the hydrolysis of benzene diazonium chloride.

$\log(V_\infty - V_t)$ is plotted against t as shown in Fig.18.5.

From Fig. 18.5,

$$\therefore \text{slope} = -2.36 \times 10^{-5}\ \text{s}^{-1}$$

$$k = -2.303 \times \text{slope}$$

$$= -2.303 \times (-2.36 \times 10^{-5}\ \text{s}^{-1})$$

$$= 5.44 \times 10^{-5}\ \text{s}^{-1}$$

Half-Life of First Order Reactions

The time taken for the concentration of a reactant to fall to half its initial value is called the half-life of a reaction. It is denoted by the symbol, $t_{½}$. We can derive an expression useful in calculating the half-life of a substance undergoing first order reaction using Eq.18.21.

$$\log \frac{[\text{A}]_0}{[\text{A}]_t} = \frac{kt}{2.303} \qquad \ldots(18.21)$$

We must bear in mind that when

$$t = t_{½},\ [\text{A}]_t = [\text{A}]_0/2$$

Using these relationships in Eq. 18.21, we get,

$$\log \frac{[\text{A}]_0}{[\text{A}]_0/2} = \frac{kt_{½}}{2.303}$$

i.e.,

$$\log 2 = \frac{kt_{½}}{2.303}$$

or

$$t_{½} = \frac{2.303 \log 2}{k} = \frac{0.693}{k} \qquad \ldots(18.30)$$

In a first order reaction, the amount of the reactant remaining after n half-life periods is given by the formula :

$$\begin{Bmatrix}\text{Concentration}\\ \text{of the reactant}\\ \text{remaining after}\\ n \text{ half-lives}\end{Bmatrix} = \left(\frac{1}{2}\right)^n \times \begin{Bmatrix}\text{Initial}\\ \text{concentration}\\ \text{of the}\\ \text{reactant}\end{Bmatrix} \qquad \ldots(18.31)$$

From Eq.18.30, we understand that $t_{½}$ does not depend on initial concentration of the substance in the case of a first order reaction. This means that for a given first order reaction, half-life period is the same, whatever be the initial concentration. This leads to an interesting result that the time taken for the changes in the concentrations of the reactant such as,

$$[\text{A}]_0 \rightarrow [\text{A}]_0/2$$

or

$$[\text{A}]_0/2 \rightarrow [\text{A}]_0/4$$

or

$$[\text{A}]_0/4 \rightarrow [\text{A}]_0/8$$

is the same. The half-life periods required to bring about decrease in concentration of a reactant upto 12.5% of its initial concentration can be represented as in Fig.18.6.

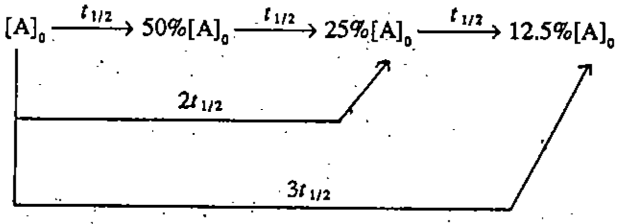

Fig.18.6: Change in % [A]$_0$ over the first three half-life periods of a first order reaction; $t_{½}$ is the half-life period for the conversion, [A]$_0$ → 50% [A]$_0$.

Example 6

The first-order rate constant for the decomposition of N_2O_5 at 340 K is $5.20 \times 10^{-3}\ s^{-1}$. Calculate the time required for the concentration of N_2O_5 to fall to (a) one-half and (b) one-fourth of its initial value.

Solution

a) Using Eq. 18.30, $t_{1/2} = \frac{0.693}{k}$

$$= \frac{0.693}{5.20 \times 10^{-3}\ s^{-1}}$$

$$= 133\ s$$

Hence, time taken for the concentration of N_2O_5 to decrease by 50% is 133 s.

b) The time required for the decrease in the concentration of N_2O_5 to 25% of its initial value is twice the half-life period, i.e., 266 s.

Having studied the equations useful in calculating the first order rate constant and the half-life period of the reactant, let us derive similar equations for second order reactions.

Integrated Rate Laws for Second Order Reactions

There are two types of second order reactions.

i) A single reactant could give rise to products through a second order reaction.

$$A \rightarrow \text{Products} \qquad \ldots(18.32)$$

The rate equation is

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^2 \qquad \ldots(18.33)$$

where k is the second order rate constant.

Two examples of this type are given below:

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

ii) Two different reactant molecules could react to give products through a second order reaction.

$$A + B \rightarrow \text{Products} \qquad \ldots(18.34)$$

The rate equation is,

$$\text{reaction rate} = k[A][B] \qquad \ldots(18.35)$$

Examples of this type are given below. Note that the stoichiometric ratio of the reactants is 1:1.

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

$$CH_3Br(aq) + OH^-(aq) \rightarrow CH_3OH(aq) + Br^-(aq)$$

$$CH_3COOC_2H_5(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + C_2H_5OH(aq)$$

Again the study of these reactions could be simplified if the initial concentrations of both the reactants ($[A]_0$ and $[B]_0$) are the same. i.e.,

i.e. $\quad [A]_0 = [B]_0$ and so $[A] = [B]$

where $[A]$ and $[B]$ are concentrations of the reactants at any given time, t.

Then, Eq.18.35 takes the same form as Eq.18.33.

$$\text{Rate} = \frac{-d[\mathrm{A}]}{dt} = k[\mathrm{A}][\mathrm{B}] = k[\mathrm{A}][\mathrm{A}]$$

$$= k[\mathrm{A}]^2 \qquad \ldots (18.33)$$

Thus, we could see that the rate equation takes the same form for a second order reaction, if the reaction is

i) second order in a single reactant or

ii) first order in each of the two reactants such that the concentrations of the two are same throughout the reaction.

We use Eq.18.33 as the rate law for both these two types. We derive the integrated rate law for these two under case (i).

Case (i): Integrated Rate Law for a Reaction that Follows Differential Rate Law as per Eq.18.33

We start with the differential rate law,

$$-\frac{d[A]}{dt} = k[\mathrm{A}]^2 \qquad \ldots (18.33)$$

The integrated form of this equation can be obtained using the following limiting conditions:

At time = 0 (i.e., at the start), the concentration of A = $[\mathrm{A}]_0$. At time = t, the concentration of A = $[\mathrm{A}]_t$.

Applying these limits on the rearranged form of Eq.18.33, we get,

$$-\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = \int_0^t k\,dt \qquad \ldots (18.36)$$

i.e.,

$$-\left[-\frac{1}{[\mathrm{A}]}\right]_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} = k(t-0) \qquad \ldots (18.37)$$

$$-\left[\frac{-1}{[\mathrm{A}]_t} + \frac{1}{[\mathrm{A}]_0}\right] = kt \qquad \ldots (18.38)$$

$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = kt \qquad \ldots (18.39)$$

or

$$\frac{1}{[\mathrm{A}]_t} = \frac{1}{[\mathrm{A}]_0} + kt \qquad \ldots (18.40)$$

The second order rate constant can be calculated by plotting $1/[\mathrm{A}]_t$ against t. A straight line curve must be obtained, if the reaction is second order in the reactant. The slope of the straight line gives the second order rate constant.

$$k = \text{Slope} \qquad \ldots (18.41)$$

We shall later illustrate this method in Example 8.

Each successive half-life is double the preceding half-life in a second order reaction. In a first order reaction, all successive half-life periods are same.

Half-Life of a Second Order Reaction

For reactions following second order rate as per Eq.18.33, an equation could be derived which is useful in calculating the half-life period.

At the half-life period ($t = t_{1/2}$), $[\mathrm{A}]_t = [\mathrm{A}_0]/2$. Using this in Eq.18.40,

$$\frac{1}{[\mathrm{A}]_0/2} = \frac{1}{[\mathrm{A}]_0} + kt_{1/2}$$

i.e.,

$$\frac{2}{[\mathrm{A}]_0} = \frac{1}{[\mathrm{A}]_0} + kt_{1/2}$$

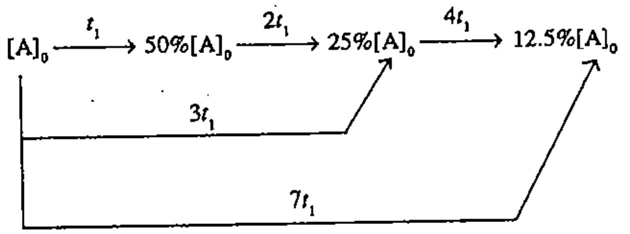

Fig.18.7: Change in %[A]$_0$ over three successive half-lives in a second order reaction; t_1 refers to half-life for the change in concentration from [A]$_0$ to 50%[A]$_0$

$$t_{1/2} = \frac{1}{k[\,A\,]_0} \qquad \ldots(18.42)$$

From Eq.18.42, we understand that $t_{1/2}$ is inversely proportional to initial concentration for a second order reaction. As initial concentration of the reactant decreases, $t_{1/2}$ increases. If for the decrease in concentration of A to 50% of its initial value, time required is 100 s, then for the change from 50% A to 25% A, it will require 200 s.

Three successive half-lives for a second order reaction can be represented by Fig.18.7.

Example 7

At 700 K, the second order rate constant for the reaction,

$$2\,HI(g) \rightarrow H_2(g) + I_2(g)$$

is $1.83 \times 10^{-3}\ M^{-1}\,s^{-1}$. Calculate the time taken for 1.00×10^{-2} M HI to fall to (a) one-half and (b) one-eighth of its initial concentration.

Solution

a) Using Eq. 18.42, $t_{1/2} = \dfrac{1}{k[\,A\,]_0} = \dfrac{1}{1.83 \times 10^{-3} \times 1.00 \times 10^{-2}}$ s

$= 5.46 \times 10^4$ s.

Time needed for the decrease in concentration of HI to one-eighth of its initial value is seven times the value calculated above as shown in Fig.18.7; i.e., time needed is 3.82×10^5 s.

Now we derive the integrated rate law for a reaction that is second order overall and is first order in each of the two reactants having different initial concentrations.

Case (ii): Integrated Rate Law for a Reaction that Follows Rate Law as per Eq.18.35

Let us start the reaction between A and B with different initial concentrations, [A]$_0$ and [B]$_0$. Let these two react to give products as per the rate law given in Eq.18.35.

$$A + B \rightarrow \text{Products} \qquad \ldots(18.34)$$

$$\text{Reaction rate} = k[\,A\,][\,B\,] \qquad \ldots(18.35)$$

For simplicity we have taken the reaction in which the stoichiometric coefficients of the reactants are same. But similar methods can be followed for reactions with different stoichiometric coefficients.

As per the reaction stoichiometry, A and B react in the ratio 1:1. After t seconds, let the concentrations of A and B be $[\,A\,]_0 - x$ and $[\,B\,]_0 - x$.

Hence, the reaction rate $= \dfrac{-d[\,A\,]}{dt} = \dfrac{-d[\,B\,]}{dt} = k[\,A\,][\,B\,]$

i.e. $$\frac{-d\{[\,A\,]_0 - x\}}{dt} = k\{[\,A\,]_0 - x\}\{[\,B\,]_0 - x\}$$

i.e., $$\frac{-d[\,A\,]_0}{dt} + \frac{dx}{dt} = k\{[\,A\,]_0 - x\}\{[\,B\,]_0 - x\}$$

So
$$\frac{dx}{dt} = k\left\{[A]_0 - x\right\}\left\{[B]_0 - x\right\} \qquad \ldots(18.43)$$

$$\frac{d[A]_0}{dt} = 0 \text{ since } [A]_0 \text{ is a constant.}$$

In order to get the integrated form, we have to transform Eq.18.43 as shown below:

$$\frac{dx}{\left\{[A]_0 - x\right\}\left\{[B]_0 - x\right\}} = kdt \qquad \ldots(18.44)$$

Let us write the expression, $\frac{1}{\left\{[A]_0 - x\right\}\left\{[B]_0 - x\right\}}$ as follows:

$$\frac{1}{\left\{[A]_0 - x\right\}\left\{[B]_0 - x\right\}} = \frac{p}{\left\{[A]_0 - x\right\}} + \frac{q}{\left\{[B]_0 - x\right\}} \qquad \ldots(18.45)$$

i.e.,
$$\frac{1}{\left\{[A]_0 - x\right\}\left\{[B]_0 - x\right\}} = \frac{p\left\{[B]_0 - x\right\} + q\left\{[A]_0 - x\right\}}{\left\{[A]_0 - x\right\}\left\{[B]_0 - x\right\}}$$

In other words, $p\left\{[B]_0 - x\right\} + q\left\{[A]_0 - x\right\} = 1$ ...(18.46)

Put $x = [A]_0$, then $p\left\{[B]_0 - [A]_0\right\} = 1$

or
$$p = \frac{1}{[B]_0 - [A]_0} \qquad \ldots(18.47)$$

Hence,
$$p = -\frac{1}{[A]_0 - [B]_0} \qquad \ldots(18.48)$$

Put $x = [B]_0$ in Eq.18.46.

Hence $q\left\{[A]_0 - [B]_0\right\} = 1$

or
$$q = \frac{1}{[A]_0 - [B]_0} \qquad \ldots(18.49)$$

From Eqs. 18.45, 18.48 and 18.49,

$$\frac{1}{\left\{[A]_0 - x\right\}\left\{[B]_0 - x\right\}} = -\frac{1}{\left\{[A]_0 - [B]_0\right\}\left\{[A]_0 - x\right\}} + \frac{1}{\left\{[A]_0 - [B]_0\right\}\left\{[B]_0 - x\right\}} \qquad \ldots(18.50)$$

We have adopted the **partial fraction procedure** in the above steps.

Using Eq.18.50 in Eq.18.44,

$$-\frac{dx}{\left\{[A]_0 - [B]_0\right\}\left\{[A]_0 - x\right\}} + \frac{dx}{\left\{[A]_0 - [B]_0\right\}\left\{[B]_0 - x\right\}} = kdt \qquad \ldots(18.51)$$

You can see that the two terms in the L.H.S. of Eq.18.51 contain either $\left\{[A]_0 - x\right\}$ or $\left\{[B_0] - x\right\}$ in the denominator. The splitting of the expression in L.H.S of Eq.18.44 through partial fraction method facilitates usage of Formula 2 of Sec.6.6 of Unit 6 for integration.

At time = 0, $x = 0$ ("x" denotes the change in concentration of A or B due to reaction)

At time = t, $x = x_t$

$$\int_0^{x_t} \frac{dx}{\left\{[A]_0 - [B]_0\right\}\left\{[B]_0 - x\right\}} - \int_0^{x_t} \frac{dx}{\left\{[A]_0 - [B]_0\right\}\left\{[A]_0 - x\right\}} = k\int_0^t dt \qquad \ldots(18.52)$$

$$\frac{1}{[A]_0 - [B]_0}\Big[-\ln([B]_0 - x)\Big]_0^{x_t} - \frac{1}{[A]_0 - [B]_0}\Big[-\ln([A]_0 - x)\Big]_0^{x_t} = kt \qquad \ldots(18.53)$$

$$\frac{-1}{[A]_0 - [B]_0}\left\{\ln([B]_0 - x_t) - \ln[B]_0\right\} + \frac{1}{[A]_0 - [B]_0}\left\{\ln([A]_0 - x_t) - \ln[A]_0\right\}$$

$$= kt$$

$$\frac{1}{[\mathrm{A}]_0-[\mathrm{B}]_0}\ln\frac{([\mathrm{A}]_0-x_t)[\mathrm{B}]_0}{([\mathrm{B}]_0-x_t)[\mathrm{A}]_0}=kt \qquad \ldots(18.54)$$

$$\log\frac{([\mathrm{A}]_0-x_t)[\mathrm{B}]_0}{([\mathrm{B}]_0-x_t)[\mathrm{A}]_0}=\frac{k\{[\mathrm{A}]_0-[\mathrm{B}]_0\}}{2.303}\,t \qquad \ldots(18.55)$$

$$\log\frac{[\mathrm{A}]_0-x_t}{[\mathrm{B}]_0-x_t}=\log\frac{[\mathrm{A}]_0}{[\mathrm{B}]_0}+\frac{k([\mathrm{A}]_0-[\mathrm{B}]_0)}{2.303}\,t \qquad \ldots(18.56)$$

By plotting $\log\frac{[\mathrm{A}]_0-x_t}{[\mathrm{B}]_0-x_t}$ against t, a straight line is obtained. The slope of the straight line is equal to $\frac{k([\mathrm{A}]_0-[\mathrm{B}]_0)}{2.303}$.

$$k=\frac{2.303\times \text{slope}}{([\mathrm{A}]_0-[\mathrm{B}]_0)} \qquad \ldots(18.57)$$

The name saponification is derived from the fact that soaps are produced by the hydrolysis of esters of long-chain fatty acids using alkalies.

Let us discuss the saponification of ester as an example for the calculation of second order rate constant. The hydrolysis of ester by an alkali is called saponification. For example, the saponification of methyl acetate can be represented by the following equation:

$$CH_3COOCH_3+OH^- \rightarrow CH_3COO^-+CH_3OH$$

The saponification rate is studied as follows. A reaction mixture is prepared with known concentrations of alkali and ester. At regular intervals, certain volume of the solution is withdrawn and titrated against standard HCl. From the titre values, the concentrations of the unreacted alkali and the unreacted ester could be determined at various time intervals.

The rate constant can be determined using,

i) Eqs.18.40 and 18.41, if the initial concentrations of ester and alkali are same;

ii) Eqs.18.56 and 18.57, if their initial concentrations are different.

Now study the following example.

Example 8

The saponification of methyl acetate using sodium hydroxide was studied at 298 K. The initial concentrations of the alkali and ester in the reaction mixture were both 1.00×10^{-2} M. The reaction rate was followed by titration of a definite volume of the reaction mixture with standard HCl. The concentrations of unreacted alkali, $[\mathrm{A}]_t$, at various time intervals are given below:

Time / s	240	550	720	1000	1550
$10^3[\mathrm{A}]_t/\mathrm{M}$	6.85	4.81	4.17	3.38	2.49

Calculate the second order rate constant.

Solution

Since the initial concentrations of the alkali and the ester are same, we can use Eqs.18.40 and 18.41 for solving this problem. We tabulate $\frac{1}{[\mathrm{A}]_t}$ values against various time intervals as follows:

$\frac{1}{[\mathrm{A}]_t}\mathrm{M}$	146	208	240	296	402
t / s	240	550	720	1000	1550

$1/[\mathrm{A}]_t$ is calculated in each case as shown in the following example:

$10^3[\mathrm{A}]_t/\mathrm{M}=6.85$;

$[\mathrm{A}]_t/\mathrm{M}=6.85\times10^{-3}$

$$\frac{1}{[\mathrm{A}]_t}\mathrm{M}=\frac{1}{6.85\times10^{-3}}=\frac{1000}{6.85}=146$$

Note the unit for the slope of the curve in Fig. 18.8.

$$\text{Unit of slope}=\frac{\text{Unit of }1/[\mathrm{A}]_t}{\text{Unit of }t}$$

$$=\mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

As suggested by Eq.18.40, $1/[\mathrm{A}]_t$ against t plot is a straight line (Fig.18.8) showing that the saponification of methyl acetate follows second order kinetics.

$$\text{Using Eq.18.41, } k = \text{Slope}$$
$$= 0.194\ \mathrm{M^{-1}\,s^{-1}}.$$

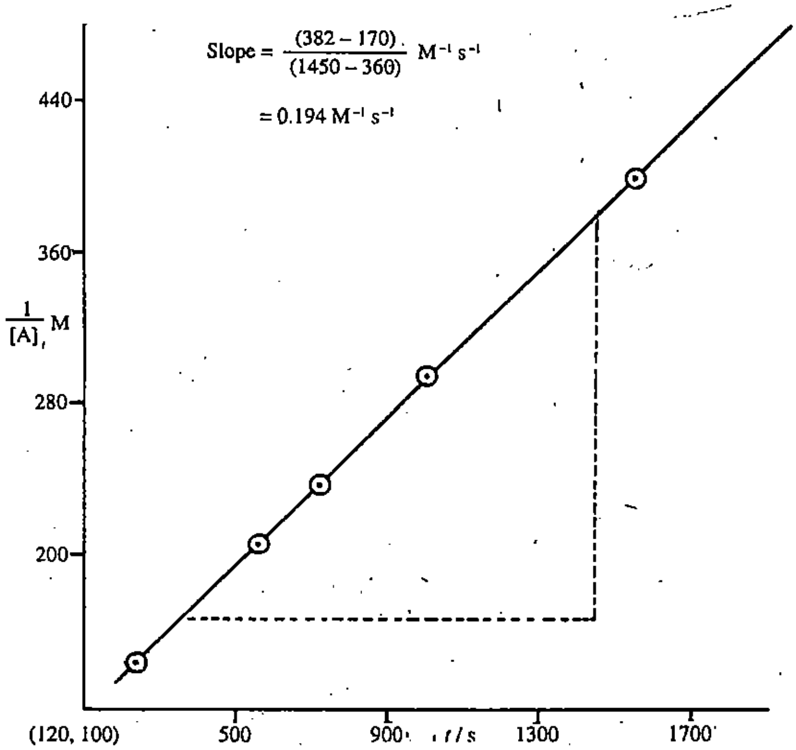

Fig. 18.8: $1/[A]_t$ against t plot for the saponification of methyl acetate.

Having some experience with the differential and the integrated forms of rate laws for first order and second order reactions, we shall discuss zeroth order reactions in the next section. Also, we shall give some examples of third order reactions.

SAQ 4

State the units of the rate constants for zeroth order, first order and second order reactions. The rate of reaction is measured in M s^{-1} units.

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SAQ 5

The decomposition of HI is a second order reaction. At 700 K, the rate constant for the reaction is $1.83 \times 10^{-3}\ \mathrm{M^{-1}\ s^{-1}}$. If the initial concentration of HI is 1.00×10^{-2} M, calculate its concentration after 1.68×10^{5} s.

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18.5 ZEROTH ORDER AND THIRD ORDER REACTIONS

Let us study zeroth order reactions.

Zeroth order reaction is generally a heterogeneous reaction.

Zeroth Order Reactions

The rate law for a zeroth order reaction is of the following form,

$$-\frac{d[A]}{dt} = k[A]^0 = k \qquad \ldots(18.58)$$

since $[A]^0 = 1$

In a zeroth order reaction, the reaction rate is independent of the concentrations of the reactant.

Some examples of zeroth order reactions are given below:

i) Decomposition of ammonia on a hot platinum surface.

$$2\,NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$$

ii) Decomposition of nitrous oxide on a hot platinum surface.

$$2\,N_2O(g) \xrightarrow{Pt} 2N_2(g) + O_2(g)$$

iii) Decomposition of hydrogen iodide on finely divided gold at 320 K.

$$2\,HI(g) \xrightarrow{Au} H_2(g) + I_2(g)$$

Let us derive the integrated rate law for a zeroth order reaction.

Integrated Rate Law for Zeroth Order Reaction

Let us consider the zeroth order reaction:

$$A \rightarrow \text{Products}$$

Let the concentration of A at the start be $[A]_0$ and its concentration at the time t be $[A]_t$. The integrated form of Eq.18.58 can be derived as follows:

$$\int_{[A]_0}^{[A]_t} -d[A] = \int_0^t k\,dt \qquad \ldots(18.59)$$

$$-\Big\{[A]\Big\}_{[A]_0}^{[A]_t} = k(t-0)$$

$$-[A]_t + [A]_0 = kt$$

i.e., $[A]_0 - [A]_t = kt$

or $[A]_t = [A]_0 - kt \qquad \ldots(18.60)$

On plotting $[A]_t$ against t, a straight line is obtained for a zeroth order reaction. The slope is equal to $-k$.

$$k = -\text{Slope} \qquad \ldots(18.61)$$

Example 9

The decomposition of hydrogen iodide on gold at 323 K is zeroth order reaction and the rate constant is 1.20×10^{-4} M s^{-1}.

a) If the initial concentration of hydrogen iodide is 0.500 M, calculate its concentration after 3.00×10^3 s.

b) How long will it take for all of the hydrogen iodide to decompose?

Solution

(a) Using Eq.18.60, $[A]_t = [A]_0 - kt$

$$= (0.500 - (1.20 \times 10^{-4} \times 3.00 \times 10^3))\ \text{M}$$

$$= 0.140\ \text{M}$$

(b) If hydrogen iodide completely decomposes, then $[\mathrm{A}]_t = 0$

or
$$t = \frac{[\mathrm{A}]_0}{k} = \frac{0.500\ \mathrm{M}}{1.20 \times 10^{-4}\ \mathrm{M\ s^{-1}}}$$
$$= 4.17 \times 10^{3}\ \mathrm{s}$$

Hence, the reaction will be complete after 4.17×10^{3}s.

Half-Life of a Zeroth Order Reaction

As discussed for first and second order reactions,
$$[\mathrm{A}]_t = [\mathrm{A}]_0/2 \text{ when } t = t_{½}$$

Hence, Eq.18.60 becomes,
$$[\mathrm{A}]_0/2 = [\mathrm{A}]_0 - kt_{½}$$

or
$$kt_{½} = [\mathrm{A}]_0/2$$
$$t_{½} = \frac{[\mathrm{A}]_0}{2k} \qquad \ldots (18.62)$$

This means that the half-life of a zeroth order reaction is directly proportional to the initial concentration of the reactant.

Example 10

Calculate the half-life for the decomposition of hydrogen iodide on gold at 323 K. Use the data from Example 9.

Solution

Using the data from Example 9 in Eq.18.62,
$$t_{½} = \frac{[\mathrm{A}]_0}{2k} = \frac{0.500\ \mathrm{M}}{2 \times 1.20 \times 10^{-4}\ \mathrm{M\ s^{-1}}} = 2.08 \times 10^{3}\ \mathrm{s}$$

From Examples 9 and 10, you can understand that the zeroth order reaction is complete in two half-lives as shown in Fig.18.9.

$$\begin{tikzcd}
[\mathrm{A}]_0 \arrow[r, "t_1"] \arrow[rr, bend right, "2t_1"'] & 50\%[\mathrm{A}]_0 \arrow[r, "t_1"] & 0\%[\mathrm{A}]_0
\end{tikzcd}$$

Fig.18.9: Completion of a zeroth order reaction; t_1 is the time taken for both the conversions, $[\mathrm{A}]_0 \rightarrow 50\%[\mathrm{A}]_0$ and $50\%[\mathrm{A}]_0 \rightarrow 0\%[\mathrm{A}]_0$.

Third Order Reactions

There are a few third order reactions. Two examples are given below:
$$2\mathrm{NO}(g) + \mathrm{O_2}(g) \rightarrow 2\mathrm{NO_2}(g)$$
$$2\mathrm{NO}(g) + \mathrm{Br_2}(g) \rightarrow 2\mathrm{NOBr}(g)$$

The methods of arriving at differential and integrated rate laws for third order reactions are similar to those of first and second order reactions. We are not going to discuss the same.

SAQ 6

Using the data in Example 9, calculate the time required for the decomposition of HI on gold at 323 K to proceed to 75%.

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18.6 PSEUDO FIRST ORDER REACTIONS

One of the ways of simplifying the study of reactions involving more than one reactant is to study under pseudo first order conditions. For example, consider the reaction:

$$CH_3Br\,(aq) + OH^-\,(aq) \rightarrow CH_3OH\,(aq) + Br^-\,(aq) \qquad \ldots (18.63)$$

$$\text{Reaction rate} = k\,[CH_3Br]\,[OH^-] \qquad \ldots (18.64)$$

If the concentrations of CH_3Br and OH^- are comparable, then the reaction is second order overall as indicated by Eq.18.64. Suppose that the concentration of OH^- is much larger (say, 10 times or more) than the concentration of CH_3Br. In such cases the concentration of OH^- does not change much during the reaction and can be considered constant. Hence, the reaction rate depends on the concentration of CH_3Br only .

$$\text{Reaction rate} = k'\,[CH_3Br]$$

where $k' = k\,[OH^-]$; k' is the pseudo first order rate constant. The reaction can be treated as first order for calculation purposes. Hence, the integrated rate law is similar to Eq.18.21. .

$$\log \frac{[CH_3Br]_0}{[CH_3Br]_t} = \frac{k't}{2.303}$$

In general, the reactions like the above which are effectively first order due to large excess of one of the reactants are called pseudo first order reactions.

Let us discuss the following two reactions which are studied under pseudo first order conditions.

i) **Acid Hydrolysis of Ester**

The hydrolysis of ethyl acetate in presence of a mineral acid (say, HCl) can be represented by the following equation:

$$CH_3COOC_2H_5 + H_2O + H_3O^+ \rightarrow CH_3COOH + C_2H_5OH + H_3O^+$$

The reaction rate depends on [ester], [water] and $[H_3O^+]$. Here H_3O^+ ion is a catalyst. Since the concentration of the catalyst does not change during the reaction, and water is present in large amount, the reaction becomes pseudo first order in ester.

$$\text{Rate} = k'\,[\text{ester}]$$

where k' includes concentrations of water and H_3O^+. If the reaction is carried out in a solvent other than water, the first order dependence on [water] also could be seen.

The pseudo first order rate constant is determined by titrating a definite volume of the reaction mixture containing ester and to HCl with standard alkali. Let V_0, V_t and V_∞ be the volumes of standard alkali at the start, after a time t and after the completion of the reaction.

Infinite reading (V_∞) is usually taken after heating the reaction mixture for a few minutes or after keeping the reaction mixture at the experimental temperature for a long time.

V_∞ = Volume of alkali equivalent to i) acetic acid liberated after the completion of the reaction and ii) HCl present.

V_t = Volume of alkali equivalent to i) acetic acid produced at the time t and ii) HCl present.

V_0 = Volume of alkali equivalent to HCl only.

Since the concentration of HCl is constant throughout the experiments,

$[A]_0$ (i.e, Initial concentration of ester) $\propto (V_\infty - V_0)$

and $[A]_t$ (i.e, Concentration of ester remaining unreacted at t) $\propto (V_\infty - V_t)$

We can calculate pseudo first order rate constant for the acid hydrolysis of ethyl acetate by using the following modified form of Eq.18.21.

$$\frac{k't}{2.303} = \log \frac{[A]_0}{[A]_t} = \log \frac{V_\infty - V_0}{V_\infty - V_t} \qquad \ldots (18.65)$$

where k' is the pseudo first order rate constant.

ii) Inversion of Sucrose

The hydrolysis of sucrose to form glucose and fructose in presence of mineral acid is similar to the acid hydrolysis of ester as far as the reaction kinetics is concerned.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O + H_3O^+ \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} + H_3O^+$$

Sucrose turns the plane-polarised light to the right, (i.e., it is dextro rotatory). Glucose also turns the plane-polarised light to the right, while fructose turns it to the left (i.e., it is laevo rotatory). On completion of the reaction, the reaction mixture is laevo rotatory, since the angle of rotation is more for fructose than for glucose. To start with, the reaction mixture is dextrorotatory due to sucrose. Thus, the completion of reaction (infinite reading) is marked by the change in the sign of rotation. Due to this reason, the reaction is called inversion of sucrose.

If r_0, r_t and r_∞ are the angles of rotation at the beginning, after time t and after completion of the reaction, then the pseudo first order rate constant (k') for the inversion of sucrose is given by,

$$k' = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty} \qquad \ldots (18.66)$$

Eq. 18.66 is a modified form of Eq. 18.21, where $[\,A\,]_0$ is proportional to $(\, r_0 - r_\infty \,)$ and $[\,A\,]_t$ and is proportional to $(\, r_t - r_\infty \,)$.

SAQ 7

Give the details of the graphical method of obtaining the pseudo first order rate constant for

i) acid hydrolysis of ethyl acetate

ii) inversion of sucrose.

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18.7 DETERMINING THE ORDER OF REACTION

In order to write the rate law, we must know the order of reaction with respect to each reactant. In this section, we discuss some methods for determining the order of reaction.

1) Method of Initial Rates

The instantaneous rate of reaction extrapolated to the instant when the reagents were just mixed is called the initial rate of the reaction. Let us consider the reaction,

$$A + B \rightarrow \text{Products}$$

Let the rate of reaction be represented as,

$$v = k[\,A\,]^m[\,B\,]^n$$

Extrapolation is the process of extending a curve upto a desired x or y coordinate to obtain the corresponding y or x value.

where the reaction is m^{th} order in A and n^{th} oder in B. The rate constant for the reaction is k. We have to obtain the initial rates from atleast two experiments in which the initial concentrations of A (a_1 and a_2) are different while the initial concentration of B (b_1) is constant.

$$\text{Rate in Experiment I} = v_1 = k\, a_1^m\, b_1^n$$

$$\text{Rate in Experiment II} = v_2 = k\, a_2^m\, b_1^n$$

Initial reaction rate, could be graphically arrived at by plotting the concentration of a reactant against time. The tangent to the concentration curve is drawn at the very start of the reaction and its slope is calculated. The negative of the slope value is the initial rate.

From the ratio $\frac{v_1}{v_2}$, we can calculate m, since a_1 and a_2 are known.

$$\frac{\text{Rate in Experiment I}}{\text{Rate in Experiment II}} = \frac{v_1}{v_2} = \frac{k\, a_1^m\, b_1^n}{k\, a_2^m\, b_1^n} = \left(\frac{a_1}{a_2}\right)^m \qquad \ldots (18.67)$$

Taking logarithms we can write,

$$\log \frac{v_1}{v_2} = m \log \frac{a_1}{a_2} \qquad \ldots (18.68)$$

Similarly, the rate is measured for one more experiment in which the initial concentration of A is a_2 and the initial concentration of B is b_2.

So, rate in Experiment III = $v_3 = k\, a_2^m\, b_2^n$

$$\frac{\text{Rate in Experiment II}}{\text{Rate in Experiment III}} = \frac{v_2}{v_3} = \frac{k\, a_2^m\, b_1^n}{k\, a_2^m\, b_2^n} = \left(\frac{b_1}{b_2}\right)^n \qquad \ldots (18.69)$$

$$\text{i.e., } \log \frac{v_2}{v_3} = n \log \frac{b_1}{b_2} \qquad \ldots (18.70)$$

Since v_2, v_3, b_1 and b_2 are known, n can be calculated. The overall reaction order = $m + n$. You can understand this method from the following example.

Example 11

For the reaction, $Cl_2\,(g) + 2\,NO\,(g) \rightarrow 2\,NOCl\,(g)$, the initial concentrations, $[\,Cl_2\,]_0$ and $[\,NO\,]_0$ are given along with initial rates.

$$\text{Rate} = \frac{-d[\,Cl_2\,]}{dt}$$

$[\,Cl_2\,]_0$/M	$[\,NO\,]_0$/M	Initial rate / M s^{-1}
0.10	0.10	3.0×10^{-3}
0.20	0.10	6.0×10^{-3}
0.20	0.20	2.4×10^{-2}

Calculate (i) order of the reaction with respect to each of the reactants and the overall order; (ii) what is the rate law? (iii) calculate the rate constant.

Solution

i) We can write the rate law as, $k\,[\,Cl_2]^m\,[\,NO\,]^n$.

Similar to Eqs. 18.68 and 18.70, we can write the logarithmic ratios and, calculate m and n as follows:

$$v_1 = k\,(0.10)^m\,(0.10)^n = 3.0 \times 10^{-3}\ \text{M s}^{-1}$$

$$v_2 = k\,(0.20)^m\,(0.10)^n = 6.0 \times 10^{-3}\ \text{M s}^{-1}$$

$$v_3 = k\,(0.20)^m\,(0.20)^n = 2.4 \times 10^{-2}\ \text{M s}^{-1}$$

Using Eq. 18.68,
$$m = \frac{\log \dfrac{3.0 \times 10^{-3}}{6.0 \times 10^{-3}}}{\log \dfrac{0.10}{0.20}} = \frac{\log \dfrac{6.0}{3.0}}{\log \dfrac{0.20}{0.10}} = 1$$

Using Eq. 18.70,
$$n = \frac{\log \dfrac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}}}{\log \dfrac{0.10}{0.20}} = \frac{\log \dfrac{24}{6.0}}{\log \dfrac{0.20}{0.10}} = 2$$

Hence, the reaction is second order in NO and first order in Cl_2. The overall order is $2 + 1 = 3$.

ii) The rate law is given below:

$$\text{Rate} = k\,[\,Cl_2\,]\,[\,NO\,]^2$$

iii) The rate constant can be calculated using any one of the three rates given above.

$$v_1 = 3.0 \times 10^{-3}\ \mathrm{M\ s^{-1}} = k\,(0.10\ \mathrm{M})\,(0.10\ \mathrm{M})^2$$

$$k = \frac{3.0 \times 10^{-3}}{(0.10)^3}\ \mathrm{M^{-2}\,s^{-1}} = 3.0\ \mathrm{M^{-2}\,s^{-1}}$$

Care must be taken in applying the method of initial rates. For complex reactions like the formation of HBr (discussed in the next section) the product also affects the rate. The method of initial rates is applicable to simple reactions only.

Clock Reactions

Only those reactions in which the reaction mixture undergoes a colour change can be used as clock reactions. The colour change may be due to a reactant or a product or an added indicator.

In the case of some reactions, the time taken for the colour change of the reaction mixture can be used for measuring the initial rate. Such self-indicating reactions are known as clock reactions. For example, the kinetics of the reaction,

$$2\,\mathrm{KI} + \underset{\text{Potassium perdisulphate}}{\mathrm{K_2S_2O_8}} \rightarrow 2\,\mathrm{K_2SO_4} + \mathrm{I_2}$$

can be monitored as a clock reaction. A reaction mixture is prepared using potassium perdisulphate and potassium iodide in a higher concentration and sodium thiosulphate in much lower concentration. A drop of starch is also present in the reaction mixture. The reaction mixture is colourless in the beginning and it turns blue after some time.

$1/\Delta t$ is a measure of the initial rate.

The time, Δt, between the mixing of the reactants and the appearance of blue colour is noted. The blue colour develops due to the liberation of free iodine, after sodium thiosulphate (present in less concentration) is consumed completely as per the reaction:

$$2\,\mathrm{Na_2S_2O_3} + \mathrm{I_2} \rightarrow 2\,\mathrm{NaI} + \underset{\text{Sodium tetrathionate}}{\mathrm{Na_2S_4O_6}}$$

The order of the reaction with respect to KI (m) and the order of the reaction with respect to $\mathrm{K_2S_2O_8}$ (n) can be calculated by using the following formula:

$$\log(1/\Delta t) = m \log[\mathrm{KI}] + n \log[\mathrm{K_2S_2O_8}] + \text{constant}$$

A plot of $\log(1/\Delta t)$ against $\log[\mathrm{KI}]$ is made using Δt values obtained by varying [KI] and keeping $[\mathrm{K_2S_2O_8}]$ constant. The slope of the straight line gives m. Similarly n is obtained from the slope of the straight line got by plotting $\log(1/\Delta t)$ against $\log[\mathrm{K_2S_2O_8}]$. For the second plot, Δt is obtained by varying $[\mathrm{K_2S_2O_8}]$ and keeping [KI] constant. Experimentally it has been found that $m = 1$ and $n = 1$.

$$\text{Hence, } \frac{-d[\mathrm{K_2S_2O_8}]}{dt} = k[\mathrm{KI}][\mathrm{K_2S_2O_8}]$$

For clock reactions, two more examples are given below:

1) Acid catalysed iodination of acetone

2) Saponification of ester (using phenolphthalein indicator).

Some methods of studying fast reactions will be discussed in Sec. 18.12.

2) Trial and Error Method

We can determine the order of reaction

i) by substitution of experimental data into Eqs. 18.21, 18.40 and 18.60, or

ii) by graphical method using plots such as log [A] against t, 1/[A] against t and [A] against t. The order of the reaction is one, two or zero depending on

   i) which of the equations gives rise to a constant value for k or

   ii) which of the plots gives a straight line.

3) Half-Life Method

The half-lives are determined using different initial concentrations of the reactant. If the half-life is independent of initial concentration, the reaction is first order. If the half-life is inversely proportional to the first power of initial concentration, the reaction is second order. If the half-life is directly proportional to the first power of initial concentration, the reaction is zeroth order.

In general, half-life period (t) is proportional to $[A]_0^{1-n}$ where $[A]_0$ is the initial concentration of the reactant and n is the order of the reaction.

If the half-life periods are t_1 and t_2 corresponding to the initial concentrations $[A]_1$ and $[A]_2$ of a reactant, then

$$\frac{t_2}{t_1} = \left(\frac{[A]_2}{[A]_1}\right)^{1-n} = \left(\frac{[A]_1}{[A]_2}\right)^{n-1}$$

$$n-1 = \frac{\log t_2/t_1}{\log [A]_1/[A]_2}$$

or

$$n = 1+\frac{\log t_2/t_1}{\log [A]_1/[A]_2} \qquad \text{...(18.71)}$$

Example 12

For the decomposition of acetaldehyde in gas-phase at 791 K, the half-life periods are 328 s and 572 s corresponding to the initial concentrations 9.72×10^{-3} M and 4.56×10^{-3} M. What is the order of the reaction?

Solution

Using Eq. 18.71,

$$n = 1+\frac{\log 572/328}{\log 9.72\times10^{-3}/4.56\times10^{-3}} = 1+\frac{0.2415}{0.3287} = 1.735$$

The order of the reaction is 1.735. Note that the order of the reaction is fractional.

4. Isolation Method

In the case of reactions having more than one reactant, the rate law can be simplified if the concentrations of all reactants except one are taken in excess. The reaction rate then depends on the reactant present in lesser quantity. The order of the reaction is determined by one of the methods given above. It is equal to the order in the reactant present in lesser quantity. This procedure is repeated in turn with each of the reactants being in lesser amount while others are in excess. This procedure is called van't Hoff's isolation method.

For example, consider the reaction,

$$A + B \rightarrow \text{Products}$$

for which the rate law is,

$$\text{rate} = k[A]^m[B]^n \qquad \text{...(18.72)}$$

In the first set of experiments B is in excess as compared to A, such that the rate depends on A only.

Hence, the rate $= k_1[A]^m$ ...(18.73)

where $k_1 = k(\text{Initial concentration of B})^n$ ...(18.74)

Since B is in excess as compared to A, the concentration of B almost remains a constant throughout the experiment. From the rate measurements, m can be found out using graphical method.

In the second set of experiments, [A] is much large as compared to [B]. The rate measurements are made and using the rate law stated below, n is calculated.

$$\text{rate} = k_2[B]^n \qquad \text{...(18.75)}$$

Where $k_2 = k(\text{Initial concentration of A})^m$ ...(18.76)

The overall order of the reaction is $m + n$.

SAQ 8

For the alkaline hydrolysis of ethyl nitrobenzoate, the half-life periods and the initial concentrations are given below:

$[A]_0/10^{-}$ M	5.00	4.00
$t_{1/2}$/s	240	300

Calculate the order of reaction.

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18.8 SOME REACTION MECHANISMS

Many chemical reactions take place through a series of steps. Each step is known as an **elementary reaction.** A **reaction mechanism** is a series of elementary reactions proposed for explaining the rate law for the overall reaction. The elementary reactions are written as chemical equations. Such chemical equations give a possible explanation for the reaction path.

For an elementary reaction, the molecularity is the same as the order of reaction.

The rate law for each elementary reaction can be written using **molecularity.** The molecularity is the number of reactant molecules or atoms in an elementary reaction. If there is only one reactant molecule (or atom) in an elementary reaction, the reaction is said to be unimolecular. An elementary reaction in which two molecules (or atoms) react is called a bimolecular reaction. Most reaction mechanisms consider mainly unimolecular and bimolecular reactions. The chance of termolecular reactions (where three species are to combine) occurring is much less, because the probability of three species colliding simultaneously is quite low. An example each for unimolecular and bimolecular reactions is given below:

Unimolecular Reaction

$$O_3\,(g) \rightarrow O_2\,(g) + O\,(g) \qquad \ldots(18.77)$$

A unimolecular reaction has a first order rate law, hence, the rate of decomposition of O_3 could be represented as follows:

$$\text{Rate} = k\,[\,O_3\,] \qquad \ldots(18.78)$$

Bimolecular Reaction

$$O_3\,(g) + O\,(g) \rightarrow 2O_2\,(g) \qquad \ldots(18.79)$$

A bimolecular reaction has an overall second order rate law, being first order in each reactant. Hence, for the elementary reaction given in Eq.18.79, rate can be expressed as follows:

$$\text{Rate} = k\,[\,O\,]\,[\,O_3\,] \qquad \ldots(18.80)$$

Some of the guidelines followed in suggesting a reaction mechanism are given below:

1) The elementary reactions when added must be equal to the overall balanced chemical equation for the reaction.

   For example, the overall reaction in the decomposition of O_3 in the upper atmosphere is,

   $$2O_3\,(g) \rightarrow 3O_2(g) \qquad \ldots(18.81)$$

   This reaction could be taken as the result of the following two elementary reactions:

   Step (i) : $O_3\,(g) \rightarrow O_2\,(g) + O\,(g)$ ...(18.77)

   Step (ii) : $O_3\,(g) + O\,(g) \rightarrow 2O_2\,(g)$ ...(18.79)

   Overall reaction: $2O_3\,(g) \rightarrow 3O_2\,(g)$ (same as in Eq. 18.81)

2) While writing such a mechanism, one possible support is proving the presence of **intermediates.** For example, in the mechanism suggested above, atomic oxygen is an intermediate. Such intermediates can be detected by physical or chemical methods. They are generally reactive species. Further an intermediate is produced and ultimately used up.

3) The mechanism must agree with the overall rate law determined experimentally. In other words, the rate laws for the elementary reactions must be combined in such a

way that the overall rate law is explained. In order to accomplish this, we must be able to decide the **rate determining step**. Out of the elementary reactions suggested, the slowest one is called the rate determining step. The overall reaction rate cannot be faster than the slowest step in a mechanism. The rate determining step decides the rate of the overall reaction.

For example, in the mechanism suggested for the decomposition of ozone, step ii (i.e., Eq.18.79) is possibly the rate determining step. We shall explain this shortly.

4) The possibilities of both forward and reverse reactions occurring fast must also be considered. That is, the possibility of a dynamic equilibrium must also be examined. This is one of the ways to

   - find a suitable relationship for expressing the concentration of an intermediate and
   - eliminate the term denoting the concentration of the intermediate from the rate expression for the overall reaction.

5) Kinetic information can only support a proposed mechanism; it should not be taken as a proof since a mechanism cannot be proved absolutely.

Only a few guidelines are given here for proposing a reaction mechanism. However, these are sufficient for studying the reaction mechanisms of simple reactions.

The studies on organic and inorganic reaction mechanisms have led to the growth of separate branches of chemistry. You are advised to take up the course on Organic Reaction Mechanisms, if you desire to study theories of organic reactions.

Now, we shall discuss the reaction mechanisms involving

- a fast equilibrium followed by a slow step,
- a slow step followed by a fast step, and
- a chain reaction.

We shall also state the following types with an example in each case without discussing the reaction mechanisms.

- Consecutive reactions,
- Opposing reactions, and
- Parallel reactions

Example 13

For the decomposition of O_3,

$$2O_3\,(g) \rightarrow 3O_2\,(g) \qquad \text{...(18.81)}$$

the overall rate law is given below:

$$\text{Overall rate} = k\frac{[O_3]^2}{[O_2]} \qquad \text{...(18.82)}$$

Suggest a possible mechanism to explain the observed rate law.

Solution

You can see that the overall rate contains the term for the concentration of oxygen which is a product. This indicates that the mechanism consists of more than one step. A possible mechanism is suggested through Eqs.18.83 and 18.79.

$$\text{Step i): } O_3\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2\,(g) + O\,(g) \qquad \text{(fast)} \qquad \text{...(18.83)}$$

$$\text{Step ii): } O_3\,(g) + O\,(g) \xrightarrow{k_2} 2O_2\,(g) \qquad \text{(slow)} \qquad \text{...(18.79)}$$

Note that the addition of Eq.18.79 and the forward reaction of Eq.18.83 gives the overall balanced equation as per Eq.18.81. In the mechanism suggested above, k_1 and k_{-1} are the rate constants for the forward and the reverse reactions as per Eq.18.83; k_2 is the rate constant for the reaction as per Eq.18.79.

As per the mechanism suggested above,

$$\text{Overall rate} = k_2 [\,O_3\,][\,O\,] \qquad \text{...(18.80)}$$

Now we shall eliminate [O] in Eq. 18.80. For this purpose, we shall assume the following:

$$\text{Rate of formation of O} = \text{Rate of Consumption of O} \qquad \text{...(18.84)}$$

i.e.,

$$k_1 [\,O_3\,] = k_{-1} [\,O_2\,][\,O\,] + k_2 [\,O_3\,][\,O\,] \qquad \text{...(18.85)}$$

This assumption is valid because [O] is extremely small at any given time. Its variation with time (d [O]/dt) is still small and it may be taken to be zero. This type of assumption is called steady-state approximation and we shall discuss it in Sec. 18.9.

The above equation is written on the basis of the proposed mechanism which implies that oxygen atom is formed in the forward reaction of step (i) and is consumed in the reverse reaction of step (i) and, in step (ii). The forward and reverse reactions as per step (i) are much faster than the reaction as per step (ii). In other words, $k_2 [\,O_3\,][\,O\,]$ is negligibly smaller than $k_{-1} [\,O\,][\,O\,]$.

Hence, Eq.18.85 becomes,

$$k_1 [\,O_3\,] = k_{-1} [\,O_2\,][\,O\,] \qquad \text{...(18.86)}$$

or

$$[\,O\,] = \frac{k_1 [\,O_3\,]}{k_{-1} [\,O_2\,]} \qquad \text{...(18.87)}$$

Using Eq.18.87 in Eq.18.80,

$$\text{Overall rate} = k_2 [\,O_3\,][\,O\,]$$

$$= \frac{k_1 k_2}{k_{-1}} \frac{[\,O_3\,][\,O_3\,]}{[\,O_2\,]} \qquad \text{...(18.88)}$$

i.e., overall rate

$$= k \frac{[\,O_3\,]^2}{[\,O_2\,]} \qquad \text{...(18.89)}$$

where k is the composite rate constant since it combines the rate constants, k_1, k_2 and k_{-1} as per the equation,

$$k = \frac{k_1 k_2}{k_{-1}} \qquad \text{...(18.90)}$$

You can see that Eq.18.89 is the same as Eq.18.82.

Example 14

The rate expression for the reaction,

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g) \qquad \text{...(18.91)}$$

is given below:

$$\text{Overall rate} = k [\,NO_2\,]^2 \qquad \text{...(18.92)}$$

Spectroscopically NO_3 radical has been detected. Suggest a mechanism in keeping with these facts.

Solution

While suggesting the mechanism, the following facts must be borne in mind:

i) The stoichiometry for the overall reaction must be as per Eq.18.91.

ii) As per Eq.18.92, the rate does not depend on [CO] but depends on $[\,NO_2\,]^2$. This means that the reaction consists of more than one step and CO does not take part in the rate determining step.

iii) NO_3 is a probable intermediate in the reaction. Keeping in view the above features, the following mechanism is proposed:

Step i): $NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$ (slow) ...(18.93)

Step ii): $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ (fast) ...(18.94)

Overall reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

The stoichiometry is as per Eq.18.91. Since [CO] does not appear in the rate expression, step (i) is assumed to be slower than step (ii). It is also assumed that the intermediate, NO_3, is consumed at a faster rate than it is formed. In other words,

i.e., Overall rate = Rate of formation of NO_3

$$\left.\begin{matrix}\text{But rate of formation of} \\ NO_3\text{ (as per Eq. 18.93)}\end{matrix}\right] = k[NO_2]^2$$

Hence, the overall rate $= k[NO_2]^2$

which is same as Eq.18.92.

Example 15

The rate law for the reaction between hydrogen and bromine is quite complex as given by Eq.18.96.

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g) \qquad ...(18.95)$$

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + \frac{k'[HBr]}{[Br_2]}} \qquad ...(18.96)$$

Suggest a mechanism which could explain the above rate law.

Solution

To explain the rate law, a reaction sequence is proposed as follows:

$Br_2 \xrightarrow{k_1} 2Br$ Chain initiation ...(18.97)

$Br + H_2 \xrightarrow{k_2} HBr + H$ ...(18.98)

$H + Br_2 \xrightarrow{k_3} HBr + Br$ Chain propagation ...(18.99)

$H + HBr \xrightarrow{k_4} H_2 + Br$ ...(18.100)

$2Br \xrightarrow{k_5} Br_2$ Chain termination ...(18.101)

The rate of reaction can be represented by Eq.18.102, noting that HBr is formed as per Eqs.18.98 and 18.99 and consumed as per Eq.18.100.

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \qquad ...(18.102)$$

The negative sign preceding $k_4[H][HBr]$ in Eq.18.102 is due to the consumption of HBr as per Eq.18.100. The reaction sequence given above is an example of a chain reaction. In a chain reaction, an intermediate reacts to produce another intermediate. For example, Br, a radical intermediate produced as per Eq.18.97 reacts with H_2 to produce another radical intermediate, H. Again H reacts with Br_2 as per Eq.18.99 to give Br and so on. Reaction represented by Eq.18.97 is the **chain initiation** reaction, since it is the start of the chain reaction. Reactions such as Eqs.18.98-18.100 are known as **chain propagation** reactions. Although Eq.18.100 represents a propagation reaction in producing Br, it also results in the consumption of HBr. For the latter reason, Eq.18.100 represents an **inhibiting reaction.** Eq.18.101 is a **chain terminating reaction** since the intermediates combine to give a molecule.

Often an intermediate in a chain reaction is a free radical. A free radical is an atom or a fragment of a molecule and has an unpaired electron.

To simplify Eq.18.102, we must express [H] and [Br] in terms of [Br_2], [H_2] and [HBr]. Such a step is required since the concentrations of the intermediates are not easy to measure whereas the concentrations of the reactants and products could be measured. Such a simplification is possible assuming that the net rates of formations of intermediates are equal to zero.

i.e.,
$$\frac{d[\mathrm{Br}]}{dt} = 0 \qquad \text{...(18.103)}$$

and
$$\frac{d[\mathrm{H}]}{dt} = 0 \qquad \text{...(18.104)}$$

As per the elementary reactions given above, Br is formed as per Eqs.18.97, 18.99 and 18.100; Br is consumed as per Eqs.18.98 and 18.101. Also two bromine atoms are formed as per Eq.18.97 for every bromine molecule dissociated and two bromine atoms are consumed as per Eq.18.101 for every bromine molecule formed. Using these ideas and Eq.18.103, we can write,

$$\frac{d[\mathrm{Br}]}{dt} = 0 = 2k_1[\mathrm{Br_2}] - k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] + k_4[\mathrm{H}][\mathrm{HBr}] - 2k_5[\mathrm{Br}]^2 \qquad \text{...(18.105)}$$

Similarly, H is formed as per Eq.18.98 and consumed as per Eqs.18.99 and 18.100. Using these ideas and Eq.18.104, we can write,

$$\frac{d[\mathrm{H}]}{dt} = 0 = k_2[\mathrm{Br}][\mathrm{H_2}] - k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{H}][\mathrm{HBr}] \qquad \text{...(18.106)}$$

By adding Eqs.18.105 and 18.106, we get,

$$2k_1[\mathrm{Br_2}] = 2k_5[\mathrm{Br}]^2$$

or
$$[\mathrm{Br}] = \left(\frac{k_1}{k_5}\right)^{1/2}[\mathrm{Br_2}]^{1/2} \qquad \text{...(18.107)}$$

From Eq.18.106, we can write,

$$[\mathrm{H}] = \frac{k_2[\mathrm{H_2}][\mathrm{Br}]}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]} \qquad \text{...(18.108)}$$

Using Eqs.18.107 and 18.108, we get,

$$[\mathrm{H}] = \frac{k_2\left(\frac{k_1}{k_5}\right)^{1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]} \qquad \text{...(18.109)}$$

Rearranging Eq.18.102, we get,

$$\frac{d[\mathrm{HBr}]}{dt} = k_2[\mathrm{H_2}][\mathrm{Br}] + [\mathrm{H}](k_3[\mathrm{Br_2}] - k_4[\mathrm{HBr}]) \qquad \text{..(18.110)}$$

Using Eqs.18.107, 18.109 and 18.110, we get,

$$\frac{d[\mathrm{HBr}]}{dt} = k_2\left(\frac{k_1}{k_5}\right)^{1/2}[\mathrm{Br_2}]^{1/2}[\mathrm{H_2}] + \frac{(k_3[\mathrm{Br_2}] - k_4[\mathrm{HBr}])(k_2(k_1/k_5)^{1/2}[\mathrm{H_2}[\mathrm{Br_2}]^{1/2}}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]}$$

$$= \frac{2k_2k_3(k_1/k_5)^{1/2}[\mathrm{Br_2}]^{3/2}[\mathrm{H_2}]}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]} \qquad \text{...(18.111)}$$

Dividing the numerator and denominator of R.H.S. by k_3 [Br_2],

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + \dfrac{k_4[\mathrm{HBr}]}{k_3[\mathrm{Br_2}]}} \qquad \text{...(18.112)}$$

By comparison you can see that Eqs.18.96 and 18.112 are same, where

$$k = 2k_2\left(\frac{k_1}{k_5}\right)^{1/2} \quad \text{and} \quad k' = \frac{k_4}{k_3}$$

The presence of the term [HBr]/[Br_2] in the denominator of Eq.18.96 or Eq.18.112, has the following significance:

- HBr formed inhibits the rate of the reaction,
- At high [Br_2], the inhibition is less.

Both these predictions have been verified experimentally.

In the H_2–Br_2 reaction, inhibition takes place due to the product formed. Sometimes, impurities are deliberately added to some materials to inhibit undesirable reactions. For example, food products generally get spoiled due to chain reactions involving oxidation. To preserve the food products, it is customary to use the preservatives which inhibit oxidation by removing chain-propagating radicals. Such "antioxidants" are also added to plastics and rubber to prevent their degradation.

Free-Radical Reactions

In H_2–Br_2 reaction, H and Br atoms have unpaired electrons and these are monoatomic free-radicals. In 1929, Paneth and Hofeditz reported the formation of polyatomic free-radicals (CH_3 radicals) by the thermal decomposition of lead tetramethyl. It was found that lead was deposited as a mirror, in the hot portion of a tube through which hydrogen gas carrying lead tetramethyl vapour was passed.

$$Pb\,(CH_3)_4 \longrightarrow Pb + 4CH_3 \qquad ...(18.113)$$

After the discovery of this reaction, many free radical reactions were studied and chain mechanisms were proposed to explain their reaction rates. An example is the thermal decomposition of ethane for which the mechanism proposed is given below:

$$C_2H_6 \xrightarrow{k_1} 2CH_3$$

$$CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5$$

$$C_2H_5 \xrightarrow{k_3} C_2H_4 + H$$

$$H + C_2H_6 \xrightarrow{k_4} H_2 + C_2H_5$$

$$H + C_2H_5 \xrightarrow{k_5} C_2H_6$$

The free-radicals such as CH_3 and C_2H_5 are detected by direct experimental methods or from the products they give. Experimentally obtained rate law is given by the equation,

$$\text{rate} = k\,[C_2H_6] \qquad ...(18.114)$$

where k is the overall rate constant; k is the complex combination of the rate constants of the individual elementary reactions.

The radical intermediates can be removed by using substances like NO. Since NO molecule has an unpaired electron, it combines with a radical intermediate which also has an unpaired electron. This could result in chain termination. Here NO molecule is called the radical scavenger and it is said to quench the chain reaction. To prove the chain mechanism, such radical scavengers are used.

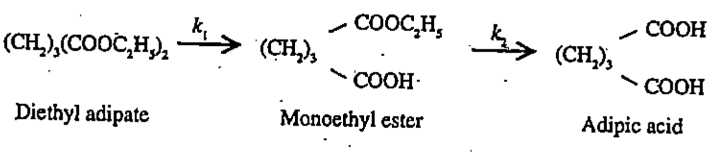
Just as we can terminate a chain reaction using radical scavengers, we can start a chain reaction using free radical sensitizers such as $Pb(CH_3)_4$ or $Hg\,(CH_3)_2$. To increase the decomposition rate of an organic compound, $Pb\,(CH_3)_4$ or $Hg\,(CH_3)_2$ is added. These substances decompose, and introduce CH_3 radicals into the system. This starts the decomposition of the organic compounds through a chain reaction. $Pb\,(CH_3)_4$ and $Hg\,(CH_3)_2$ are said to sensitize the decomposition of organic compounds.

Consecutive Reactions

We have postulated the existence of intermediates. In many cases, the intermediate in one step is the reactant in the next step. Such reactions are called consecutive reactions. The rates of consecutive reactions could be stated in terms of the concentrations of the reactant taken initially and the products formed in each stage.

Example

Acid hydrolysis of diethyl adipate.



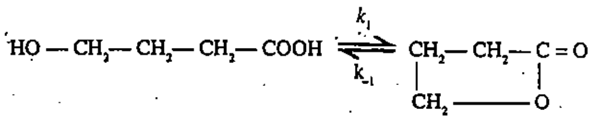
$$(CH_2)_4(COOC_2H_5)_2 \xrightarrow{k_1} (CH_2)_4\begin{matrix}\diagup COOC_2H_5\\ \diagdown COOH\end{matrix} \xrightarrow{k_2} (CH_2)_4\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix}$$

Opposing Reactions

In opposing reactions, rates of forward and reverse reactions are both appreciable. While proposing a mechanism both the reaction rates must be considered.

Example

Formation of butyrolactone from γ-hydroxybutyric acid.



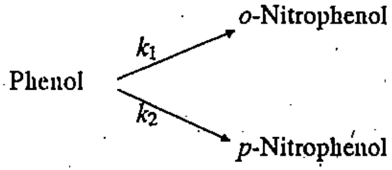
$$HO-CH_2-CH_2-CH_2-COOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{array}{l} CH_2-CH_2-C=O \\ |\qquad\qquad\quad | \\ CH_2 \text{———} O \end{array}$$

Parallel Reactions

If a reactant can undergo more than one reaction, the resulting reactions are called parallel reactions. The rates of a set of parallel reactions can be measured in terms of the concentrations of the products formed in each case.

Example

Nitration of phenol yielding *o*-nitrophenol and *p*-nitrophenol,



In the next section we shall explain the theory of unimolecular reaction rates.

SAQ 9

For the following elementary reactions, write the rate laws:

i) $O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$

ii) $CH_3NC(g) \rightarrow CH_3CN(g)$

iii) $Cl_2(g) \rightarrow 2Cl(g)$

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SAQ 10

For the reaction,

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

the rate law is given below:

$$\text{Rate.} = k[NO]^2[O_2]$$

Is the following mechanism consistent with the rate law?

Step i) $NO + O_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} NO_3$ Both rates fast and equal

Step ii) $NO_3 + NO \xrightarrow{k_3} 2NO_2$ Slow

Hint: Consider NO_3 as an intermediate.

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18.9 THEORY OF UNIMOLECULAR REACTIONS

A unimolecular reaction is an elementary reaction in which only one molecule or a radical reacts. The unimolecular reaction follows first order kinetics. A number of gas phase reactions follow first order kinetics. These reactions are assumed to proceed through unimolecular rate-determining step. But how does the reactant molecule attain the activation energy? The activation energy is the minimum energy needed for the reactant molecules to react and yield products. If the molecules obtain their activation energy through collisions, it is difficult to explain first order kinetics. A collision process needs atleast two molecules and hence, second order kinetics could be expected but not first order kinetics. In 1922, Lindemann and Hinshelwood proposed a mechanism which could explain the unimolecular reactions in which molecules attain their activation energy through collisions.

Let two molecules of the reactant gas (X) collide yielding an activated molecule (X^*) and a normal molecule (X). Such a collision is called an activating collision.

$$X + X \xrightarrow{k_a} X^* + X \quad \text{...(18.115)}$$

$$\text{Rate of activation of } X = k_a[X][X] \quad \text{...(18.116)}$$

The activated molecule, X^*, can undergo either of the following reactions:

i) X^* can undergo collision with another molecule X and lose its excess energy. Such a collision is called a deactivating collision.

$$X^* + X \xrightarrow{k'_a} X + X \quad \text{...(18.117)}$$

$$\text{Rate of deactivation of } X^* = k'_a[X^*][X] \quad \text{...(18.118)}$$

ii) Alternatively, X^* can decay to yield the product, Y.

$$X^* \xrightarrow{k_b} Y \quad \text{...(18.119)}$$

$$\text{Rate of decay of } X^* = \text{Rate of product formation} = \frac{d[Y]}{dt} = k_b[X^*] \quad \text{...(18.120)}$$

Note that decay of X^* is a unimolecular reaction.

If the decay of X^* yielding products is the rate-determining step, then the overall rate of the reaction is given by the following expression.

$$\text{Rate} = k_b[X^*] \quad \text{...(18.121)}$$

In order to express the concentration of X^*, an active species, in terms of concentrations of reactants (or products) in the ground state, **steady-state approximation** is used. According to this procedure, it is assumed that a steady-state is reached after a reaction starts such that the concentration of the activated species is more or less a constant and does not change with time.

According to steady-state approximation, the concentrations of all reactive intermediates are constant and small during the major part of the reaction.

i.e.,
$$\frac{d[X^*]}{dt} = 0 \quad \text{...(18.122)}$$

This means that the activated species, X^*, is consumed as soon as it is formed. Since X^* is formed as per Eq.18.115 and is consumed as per Eqs.18.117 and 18.119,

$$\frac{d[X^*]}{dt} = 0 = k_a[X]^2 - k'_a[X][X^*] - k_b[X^*] \quad \text{...(18.123)}$$

i.e.,
$$[X^*](k'_a[X] + k_b) = k_a[X]^2$$

or
$$[X^*] = \frac{k_a[X]^2}{(k'_a[X] + k_b)} \quad \text{...(18.124)}$$

Using Eqs.18.121 and 18.124,

$$\text{rate} = \frac{k_a k_b [X]^2}{(k_a' [X] + k_b)} \qquad \text{...(18.125)}$$

From Eq. 2.41 of this course, $p = cRT$ or $p \propto c$. Hence, when the pressure of a gas is high, its concentration is high. When the concentration is high, there will be large number of collisions.

At High Pressures

At high pressures, the number of collisions is large and the probability of deactivating collisions occurring is high. That is, the rate of deactivation is larger than the rate of product formation (through decay); the unimolecular decay of X^* is the rate-determining step at high pressures; i.e.,

$$k_a' [X^*][X] \gg k_b [X^*]$$

or
$$k_a' [X] \gg k_b \qquad \text{...(18.126)}$$

In other words, $k_a' [X] + k_b \simeq k_a' [X]$ ...(18.127)

Using this in Eq. 18.125, we get

$$\text{rate} = \frac{k_a k_b [X]^2}{k_a' [X]} = \frac{k_a k_b}{k_a'} [X] \qquad \text{...(18.128)}$$

In other words, the rate is first order at high pressures.

At Low Pressures

Eqs. such as 18.127 or 18.130 are instances of **limiting conditions.** Using such approximation procedure, it is possible to simplify a complicated equation as Eq. 18.125.

At low pressures, the number of collisions decreases. This means that the activated molecule yields the product as soon it is formed and there is not much time left for deactivating collision to occur. In other words, the bimolecular formation of X^* is the rate-determining step. Further, the rate of deactivating collisions is much small as compared to the rate of product formation.

$$k_b [X^*] \gg k_a' [X^*][X]$$

or
$$k_b \gg k_a' [X] \qquad \text{...(18.129)}$$

or
$$k_a' [X] + k_b \simeq k_b \qquad \text{...(18.130)}$$

Using this in Eq. 18.125,

$$\text{rate} = \frac{k_a k_b [X]^2}{k_b} = k_a [X]^2 \qquad \text{...(18.131)}$$

Hence the reaction follows second order kinetics at low pressures.

The variation of the order of reaction with pressure as predicted by Lindemann - Hinshelwood theory could be observed in reactions such as the decomposition of N_2O_5. Using this theory, we could explain the unimolecular decomposition of N_2O_5 at high pressures.

18.10 THEORIES OF REACTION RATES

The rates of many reactions increase with the rise in temperature. Arrhenius proposed the following empirical relationship between the rate constant, k, and temperature, T.

$$\ln k = \ln A - E_a/RT \qquad \text{...(18.132)}$$

or
$$\log k = \log A - E_a/2.303RT \qquad \text{...(18.133)}$$

As the reaction rate varies with temperature, temperature also must be specified while stating the values of rate constants.

where A is called the Arrhenius factor or frequency factor or pre-exponential factor and E_a is the activation energy. Activation energy is the threshold energy that the reactant molecules must have in order to react. If $\log k$ is plotted against $\frac{1}{T}$, a straight line (Fig. 18.10) is obtained for many reactions. In such cases, the slope of the line is $-E_a/2.303R$ and the intercept at $\frac{1}{T} = 0$ gives $\log A$.

Eqs. 18.132 is also written in the exponential form as follows:

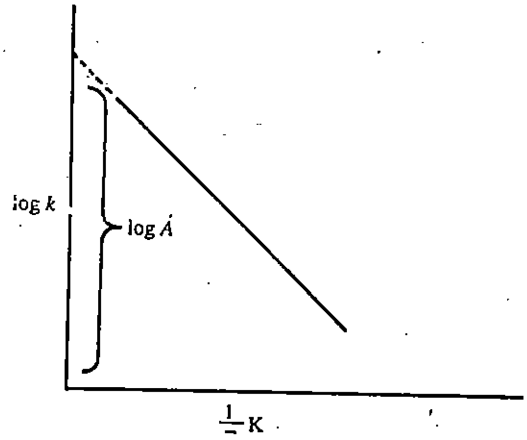


Fig. 18.10: Plot of log k against $\frac{1}{T}$

$$k = A\,e^{-E_a/RT} \qquad \text{...(18.134)}$$

A possible reason for the deviation from Arrhenius equation in some reactions is that A and E_a may vary with temperature. The temperature dependence of Arrhenius factor will be discussed in collision theory. In the present discussion, we consider that A and E_a are constants for a reaction. If the activation energy is high for a reaction, it means that the temperature dependence of the reaction rate is also high. In such cases, even a small change of temperature results in a large change in the rate constant.

Although activation energy of a reaction can be calculated from log k vs $1/T$ plot, another way of obtaining it is to calculate rate constants (k_1 and k_2) at two temperatures (T_1 and T_2). Assuming E_a and A to be constant and using Eq. 18.133, we get

$$\log k_1 = \log A - E_a/2.303RT_1 \qquad \text{...(18.135)}$$

and

$$\log k_2 = \log A - E_a/2.303RT_2 \qquad \text{...(18.136)}$$

The unit of A depends on the unit of k. For first order reactions, A has s^{-1} unit which is the same as the unit for frequency. This could be a reason for its name, frequency factor. A is also called the pre-exponential factor since it precedes the exponential term in Eq. 18.134.

Substracting the terms in Eq. 18.136 from those in Eq. 18.135,

$$\log \frac{k_2}{k_1} = \frac{-E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$= \frac{-E_a}{2.303R}\ \frac{(T_1 - T_2)}{T_1 T_2}$$

i.e.,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\ \frac{(T_2 - T_1)}{T_1 T_2} \qquad \text{...(18.137)}$$

Let us work out an example.

Example 16

The rate constants for the decomposition of SO_2Cl_2 are $1.01 \times 10^{-6}\ s^{-1}$ at 552 K and $3.85 \times 10^{-5}\ s^{-1}$ at 600 K. Calculate the activation energy and the frequency factor for the reaction, assuming them to be independent of temperature.

Solution

From Eq. 18.137,

$$E_a = 2.303\,\frac{RT_1T_2}{(T_2 - T_1)}\,\log\frac{k_2}{k_1}$$

$$E_a = \left(\frac{2.303 \times 8.314 \times 552 \times 600}{48}\ \log\frac{3.85 \times 10^{-5}}{1.01 \times 10^{-6}}\right) \text{J mol}^{-1}$$

$$E_a = 2.09 \times 10^5\ \text{J mol}^{-1}$$

Substituting for $T = 600$ K, $E_a = 2.09 \times 10^5$ J mol^{-1} and $k = 3.85 \times 10^{-5}\ s^{-1}$ in Eq. 18.133

we get,
$$\log A = \log k + E_a/2.303RT$$
$$= -4.4145 + \frac{2.09 \times 10^5}{2.303 \times 8.314 \times 600}$$
$$\log A = -4.4145 + 18.1924 = 13.7779$$
$$A = \text{Antilog of } 13.7779$$
$$A = 6.00 \times 10^{13}\ \text{s}^{-1}$$

We can understand the significance of the terms, E_a, A and $e^{-E_a/RT}$ during the discussion on collision theory of reaction rates.

Collision Theory

Collision theory is applicable to bimolecular reactions in gas phase. With some modifications, this can be applied to unimolecular (see Sec. 18.9) and termolecular reactions also. We explain collision theory using a gas-phase bimolecular elementary reaction of the following type:

$$X + Y \rightarrow \text{Products} \qquad \ldots(18.138)$$

To understand the significance of Eq. 18.139, see Appendix I.

As per collision theory, the rate of a bimolecular reaction depends on

- the total collision frequency and
- Boltzmann factor.

Although the steric factor is also to be considered while calculating the reaction rate, it will be treated under the refinement of collision theory.

Total Collision Frequency

Total collision frequency (Z_{XY}) is the number of collisions between the molecules of X and the molecules of Y in unit time in unit volume. Only X–Y collisions are counted but not X–X or Y–Y collisions, since only X–Y collisions are responsible for the reaction indicated in Eq. 18.138.

In Sec. 2.11 of Unit 2 of this course, we derived Eq. 2.52 for calculating the total collision frequency among the molecules of a single gas. The total collision frequency (Z) in general, can be derived using the following relationship:

$$Z = \left\{\begin{array}{l} \pi \times (\text{collision diameter})^2 \\ \times\ (\text{average relative speed of gas molecules}) \\ \times\ (\text{number density}) \\ \times\ (\text{number density}) \\ \times\ (\text{correction factor}) \end{array}\right. \qquad \ldots(18.139)$$

For calculating the total collision frequency (Z_{XY})among the molecules of X and Y, as per Eq. 18.139, we use the following relationships:

1) Collision diameter $= \sigma_{XY} = 1/2\,(\sigma_X + \sigma_Y)$ ...(18.140)

   where σ_X and σ_Y are the diameters of the molecules, X and Y, respectively. The collision diameter σ_{XY} is the distance of closest approach between a molecule of X and a molecule of Y.

ii) Average relative speed of the molecules of X and Y $= \left(\frac{8\,k_b T}{\pi\mu}\right)^{1/2}$ ...(18.141)

   where k_b is the Boltzmann constant (subscript b is added to k to differentiate it from the rate constant), T is temperature and μ is reduced mass.

   Note that $\frac{1}{\mu} = \frac{1}{m_X} + \frac{1}{m_Y}$ ...(18.142)

As per Eq. 2.47 of Sec. 2.9 of Unit 2,

$$\text{average speed of a gas molecule } (\bar{u}) = \left(\frac{8RT}{\pi M_m}\right)^{1/2}$$

i.e., $\text{Average speed of a gas molecule } (\bar{u}) = \left(\frac{8k_bT}{\pi m}\right)^{1/2}$ ... (18.144)

Since $R = N_A k_b$, $M_m = N_A m$

Where M_m is the molar mass and m is the mass of one molecule of gas and N_A is Avogadro constant.

While calculating the relative motion of particles, it is customary to use reduced mass in the place of mass of one molecule of the gas.

$$\left.\begin{array}{c}\text{Hence average relative} \\ \text{speed of the molecules} \\ \text{of X and Y}\end{array}\right] = \left(\frac{8k_bT}{\pi\mu}\right)^{1/2}$$

which is same as Eq. 18.141.

$$\mu = \frac{M_X M_Y}{M_X + M_Y} \cdot \frac{1}{N_A} \qquad \ldots(18.145)$$

where M_X, M_Y and N_A are the molar mass of X, molar mass of Y and Avogadro constant.

Eq. 18.145 comes from Eq. 18.143 since,

mass of one molecule of a substance $= \frac{\text{Molar mass}}{\text{Avogadro constant}}$

or $$\mu = \frac{m_X m_Y}{m_X + m_Y} \qquad ...(18.143)$$

where m_X and m_Y are the masses of one molecule of X and Y, respectively.

i) Let us now calculate the factor, (number density) × (number density). Since we have two types of molecules, X and Y, we have to consider number densities of both X and Y. Using Eq. 18.148,

(number density of X) × (number density of Y)

$$= N_A[X] \, . \, N_A[Y] = N_A^2[X][Y] \qquad ...(18.149)$$

Number density of a gas has been defined in Subsec. 2.8.2 of Unit 2.

$$\text{Number density} = \frac{\text{Number of molecules of the gas}}{\text{Volume of the gas}} = \frac{\text{Pressure of the gas}}{\text{Boltzmann constant} \times \text{temperature}} = \frac{p}{k_bT} \qquad ...(18.146)$$

Also note that from Eq. 2.41,

$$\text{concentration of a gas} = \frac{\text{Number of moles of the gas}}{\text{Volume of the gas}} = \frac{p}{RT}$$

$$\text{i.e., Concentration of a gas} = \frac{p}{N_A k_bT} = \frac{\text{Number density}}{N_A} \qquad ...(18.147)$$

where N_A is Avogadro constant.

i.e., Number density of a gas = N_A × (concentration of the gas) ...(18.148)

In the case of collision between the molecules of X and Y (i.e., between molecules of different gases), there is no necessity for the correction factor. It is because we calculate the collisions between each molecule of X and each molecule of Y. Each collision is counted only once. So omitting the correction factor and using Eqs. 18.139, 18.140, 18.141 and 18.149, we get,

$$Z_{XY} = \pi \sigma_{XY}^2 \left(\frac{8k_bT}{\pi\mu}\right)^{1/2} N_A^2[X][Y] \qquad ...(18.150)$$

Thus we have obtained a relationship useful in calculating the total collision frequency for the collisions between each molecule of X and each molecule of Y. Next we study the significance of Boltzmann factor.

Boltzmann Factor

You must realise that not all collisions between the molecules of X and Y would result in the product formation. Only those collisions, in which, the energy of the colliding molecules equals or exceeds some critical value E_a (known as activation energy as per Arrhenius equation), are effective in bringing about the reaction between X and Y. If $E_a >> RT$, then the Boltzmann factor, $e^{-E_a/RT}$, gives the fraction of the collisions in which the colliding molecules possess energy equal to or greater than the activation energy.

$$\text{Boltzmann factor} = e^{-E_a/RT} \qquad ...(18.151)$$

Boltzmann factor is helpful in calculating the number of molecules possessing energy equal to or greater than a particular value. Boltzmann factor, in other words, is helpful in calculating the population of the energy levels.

Calculation of Reaction Rate

The product of the total collision frequency and the Boltzmann factor gives the **number of molecules of X or Y in unit volume reacting per unit time**. This follows from the definitions of the terms, total collision frequency and the Boltzmann factor. In order to obtain the reaction rate in terms of concentrations of X or Y (or the **number of moles of X or Y in unit volume**) consumed per unit time, we have to divide the product, $Z_{XY} e^{-E_a/RT}$ by Avogadro constant.

$$[X] = \frac{\text{Number of moles of X}}{\text{Volume}} = \frac{\text{Number of molecules of X}}{N_A \times \text{Volume}} = \frac{\text{Number density of X}}{N_A}$$

$$\text{Reaction rate} = \frac{-d[X]}{dt} = \frac{-d[Y]}{dt}$$

$$= \frac{Z_{XY}\, e^{-E_a/RT}}{N_A} \qquad ...(18.152)$$

Using Eqs. 18.150 and 18.152,

$$\text{reaction rate} = \pi \sigma_{XY}^2 \left(\frac{8k_bT}{\pi\mu}\right)^{1/2} N_A^2[X][Y]\, e^{-E_a/RT} \times \frac{1}{N_A}$$

$$= \pi \sigma_{XY}^2 \left(\frac{8k_bT}{\pi\mu}\right)^{1/2} N_A[X][Y]\, e^{-E_a/RT} \qquad ...(18.153)$$

By definition, the reaction rate for a bimolecular elementary reaction as per Eq. 18.138 is as follows:

$$\text{Reaction rate} = k[X][Y] \qquad ...(18.154)$$

Comparing Eqs. 18.153 and 18.154,

$$k = \pi \sigma_{XY}^2 \left(\frac{8k_bT}{\pi \mu} \right)^{1/2} N_A \, e^{-E_a/RT} \qquad \text{...(18.155)}$$

Eq. 18.155 gives the theoretical value of the rate constant for a bimolecular reaction as per collision theory. $\pi \sigma_{XY}^2$ is called the mean collision cross-section.

Collision Theory and Arrhenius Theory–a Comparison

You compare Arrhenius Equation (Eq. 18.134) with Eq. 18.155. You can see that the frequency factor A is given by,

$$A = \pi \sigma_{XY}^2 \left(\frac{8k_bT}{\pi \mu} \right)^{1/2} N_A \qquad \text{...(18.156)}$$

From Eq. 18.156, you can see that A is not independent of temperature as predicted by Arrhenius equation. However, over a short range of temperature, the variation in A is not significant. Arrhenius factor can be written as a product of A' and $T^{1/2}$ where A' is a temperature-independent constant and T is temperature.

$$A = A' T^{1/2}$$

where $$A' = \pi \sigma_{XY}^2 \left(\frac{8k_b}{\pi \mu} \right)^{1/2} N_A$$

The factor $T^{1/2}$ indicates the temparature dependence of A as given in Eq. 18.156.

Hence $\log A = \log A' T^{1/2} = \log A' + 1/2 \log T$

Using this in Eq. 18.133,

$$\log k = \log A' + 1/2 \log T - E_a/2.303RT$$

or $$\log k - 1/2 \log T = \log A' - E_a/2.303RT$$

A better method of arriving at the experimental values of E_a and A is to plot $\log k - 1/2 \log T$ against $1/T$.

The slope of the plot gives E_a value since

$$\text{slope} = -E_a/2.303\,R$$

The intercept gives $\log A'$ value. From A' values, A at any temperature can be found out since

$$A = A' T^{1/2}$$

The value of A so obtained is the experimental value.

It was found that in the case of reactions between simple molecules, the agreement between the experimental value of A and the value obtained as per collision theory (Eq. 18.156) is fairly good. In the case of reactions involving complex molecules, there is a discrepancy between the two values of A. To explain the discrepancy between the two values of A, a refinement was suggested for Eqs. 18.155 and 18.156 in terms of steric factor.

Steric Factor

Although the molecular collisions may have requisite energy, the reaction would take place only if the molecules have proper orientation. In other words, the reacting species must have proper spatial orientation for the reaction to occur. In the case of complex molecules, the probability of attaining proper orientation for the reaction is much less as compared to simple molecules. To stress the need for the proper spatial requirement, **steric factor or probability factor** (P) was also added to the right hand side of Eq.18.155.

Hence $$k = P \pi \sigma_{XY}^2 \left(\frac{8k_bT}{\pi \mu} \right)^{1/2} N_A \, e^{-E_a/RT} \qquad \text{...(18.157)}$$

$$A = P \pi \sigma_{XY}^2 \left(\frac{8k_bT}{\pi \mu} \right)^{1/2} N_A \qquad ...(18.158)$$

Also, $$P = \frac{A_{\text{Experimental}}}{A_{\text{Theoretical}}} \qquad ...(18.159)$$

The steric factor is smaller for reaction between complex molecules. We expect the steric factor to be less than unity. But many fast reactions are known for which the steric factor is much greater than unity. Collision theory cannot explain such cases. Let us now study the **Activated Complex Theory** which gives a better method of calculating reaction rates.

Activated Complex Theory

The activated complex theory or the absolute theory of reaction rates depicts the formation of activated complex ($A^{\ddagger}$) from the reactants (X and Y) as a preceding step for the formation of the product, P.

$$X + Y \rightarrow A^{\ddagger}$$

$$A^{\ddagger} \rightarrow P$$

The main features of the activated complex theory are given here.

The reactant molecules come into contact with each other. In this process, a few bonds get distorted, some bonds start forming with the exchange or release of atoms or groups. The composite molecule so formed from the reactants prior to the formation of the product is called the activated complex. The activated complex then decomposes to give the product. The reaction sequence could be represented as in Fig.18.11.

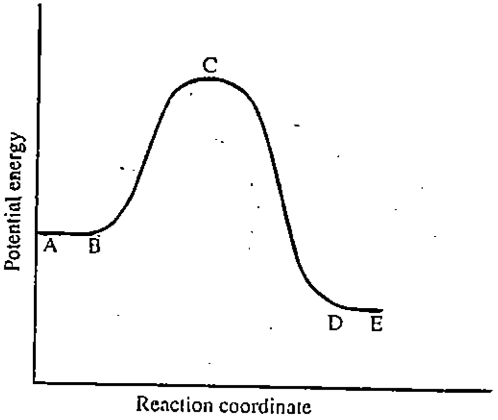


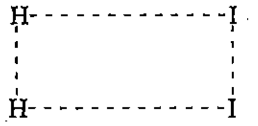
Fig.18.11: Graphical representation of the change in potential energy as a function of reaction coordinate.

Activated complex is the configuration of the atoms which the reactant molecules have near the top of the energy barrier that separates the reactants from the products. Transition state is the highest point in the potential energy curve.

The total potential energy of the system is depicted in the y-axis and the **reaction coordinate** in the x-axis. Reaction coordinate is the sequence of simultaneous changes in bond distances and bond angles. Such changes result during the formation of the products from the reactants.

Consider the reaction between a molecule of H_2 and a molecule of I_2. To start with, let us imagine that the two molecules are far part and the total potential energy of the system is the sum of the potential energies of H_2 and I_2. This part of the reaction course is represented by the horizontal portion AB of the curve in Fig. 18.11. As the two molecules approach each other to such an extent that the orbitals begin to overlap (point B in the curve), H–H and I–I bonds begin to stretch and H–I bond begins to form. The total potential energy starts increasing and this is represented by the rising portion of the curve BC. As the extent of H–H and I–I bond breakage and H–I bond formation increase, a point is reached when the potential energy is maximum (point C). The activated complex, represented below as a composite molecule, has the maximum potential energy.

The bond-breaking is an energy demanding process and the bond-making is an energy releasing process. The net energy requirement for the formation of the activated complex and its decomposition to products must be available through the translational or the vibrational energy of the reactants.



Activated Complex

The maxima point in the potential energy curve is called the transition state. Even a slight distortion of the bonds in the form of compression of H–I bond and stretching of H–H and I–I bonds enables the activated complex pass through the transition state. The path along CD represents the course of the events which result in the complete breakage of H–H and I–I bonds along with the formation of H–I bond. The horizontal portion DE represents the total potential energy of two H–I molecules. Although a fraction of the activated complex molecules could form the reactants (along the path CB) the formation of the products is almost a certainty, once the activated complex is at the transition state. The fraction of the activated complex converted into products is called the transmission coefficient and, in majority of cases, it is unity.

Energy Requirement for the Reaction

Now let us consider the energy criteria for the reaction. The energy requirement for the reactants to cross the energy barrier is to be met from translational or the vibrational energy of the molecules. At the transition state, the activated complex has some complicated vibration-like motion of all atoms. The activated complex has one particular mode of vibration along which it is unstable. If the activated complex vibrates with the frequency corresponding to this vibrational mode, the activated complex decomposes into products.

Rate Constant Calculation using Activated Complex Theory

Based on statistical thermodynamics, Eyring developed the activated complex theory. The basic postulate of the theory is that there exists an equilibrium between the activated complex and the reactants. Let us consider the **bimolecular gas phase reaction,**

$$X + Y \rightarrow A^{\ddagger} \qquad \text{...(18.160)}$$

where X and Y are the reactants, and $A^{\ddagger}$ is the activated complex. The activated complex then decomposes to give the product, P

$$A^{\ddagger} \rightarrow P \qquad \text{...(18.161)}$$

The rate of formation of the product depends on,

(i) the concentration of the activated complex and

ii) the frequency with which it is converted into the product. This is the frequency of one of the vibrational modes with respect to which the activated complex is unstable. Using detailed calculations, it is possible to derive an expression useful in calculating the rate constant (k) of the elementary reaction, X + Y → P (for which the steps are given in Eqs. 18.160 and 18.161). We shall only state the final expression without going through the derivation in full.

$$k = \frac{RT}{p^0} \cdot \frac{k_b T}{h} \cdot K_p = \frac{R k_b T^2}{p^0 h} \cdot K_p \qquad \text{...(18.162)}$$

where K_p = The equilibrium constant for the formation of the activated complex after adjusting for its vibration with respect to which it is unstable.

T = Temperature

k_b = Boltzmann constant

RT/p^0 is the correction term where p^0 is the standard pressure (1 bar)

h = Planck constant

R = Gas constant.

Using van't Hoff isotherm (Eq. 14.17 of Unit 14 of this course),

$$\Delta G^{\ddagger} = -RT \ln K_p \qquad \text{...(18.163)}$$

where $\Delta G^{\ddagger}$ is molar Gibbs energy of activation.

Hence,
$$K_p = e^{-\Delta G^{\ddagger}/RT} \qquad \text{...(18.164)}$$

Using Eq. 18.164 in Eq. 18.162,

$$k = \frac{Rk_bT^2}{hp^0} e^{-\Delta G^{\ddagger}/RT} \qquad \text{...(18.165)}$$

Using Eq. 9.15 of Unit 9,

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad \text{...(18.166)}$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the molar enthalpy of activation and molar entropy of activation, respectively.

Using Eq. 18.166 in Eq. 18.165,

$$k = \frac{Rk_bT^2}{hp^0} e^{-(\Delta H^{\ddagger} - T\Delta S^{\ddagger})/RT}$$

$$k = \frac{Rk_bT^2}{hp^0} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \qquad \text{...(18.167)}$$

$e = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \ldots$

$\simeq 2.718$

Note that 1!, 2!, etc., are to be read as factorial 1, factorial 2, etc.

Also $1! = 1$;
$2! = 1 \times 2$;
$3! = 1 \times 2 \times 3$

Finally '....' in the above expression means that it is a continuous series.

Using differential form of Eq. 18.132, it is possible to find the following relationship for a bimolecular gas phase reaction (See Appendix II):

$$\Delta H^{\ddagger} = E_a - 2RT \qquad \text{...(18.168)}$$

Using Eqs. 18.167 and 18.168,

$$k = \frac{Rk_b T^2}{hp^0} e^{-(E_a - 2RT)/RT} e^{\Delta S^{\ddagger}/R}$$

$$k = \frac{Rk_b T^2}{hp^0} e^{-E_a/RT} e^2 e^{\Delta S^{\ddagger}/R} \qquad \text{...(18.169)}$$

Comparing Arrhenius equation (Eq. 18.134) with Eq. 18.169,

$$A = \frac{Rk_b T^2}{hp^0} e^2 e^{\Delta S^{\ddagger}/R} \qquad \text{...(18.170)}$$

Hence
$$e^{\Delta S^{\ddagger}/R} = \frac{hp^0}{Rk_bT^2 e^2} \cdot A$$

i.e.,
$$e^{\Delta S^{\ddagger}/R} = 7.8119 \times 10^{-11} \frac{A}{T^2} \qquad \text{...(18.171)}$$

(substituting for the constants)

Taking natural logarithms,

$$\Delta S^{\ddagger}/R = \ln 7.8119 \times 10^{-11} \frac{A}{T^2}$$

$$\Delta S^{\ddagger} = 2.303R\,(\log 7.8119 \times 10^{-11} + \log A/T^2)$$

$$= (19.15 \log A/T^2 - 193.6)\ \text{J mol}^{-1}\,\text{K}^{-1} \qquad \text{...(18.172)}$$

Thus $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ can be calculated at any given temperature, if A and E_a are known from Arrhenius plot (Fig. 18.10).

While discussing collision theory or the activated complex theory, we consider only the gas-phase reactions. The study of rection rates in solutions is complicated due to the role of the solvent. In this course, we shall not discuss the reaction rates in solutions.

Comparison of Collision Theory and Activated Complex Theory

To account for the discrepancy between the experimentally obtained value of A and the value calculated as per collision theory, we had to introduce steric factor in Eq. 18.157. The activated complex theory has the factor, $e^{\Delta S^{\ddagger}/R}$, which takes care of the steric factor automatically.

It is observed that $\Delta S^{\ddagger}$ is negative for many reactions. Such a negative value indicates decrease in disorderliness. This is understandable since during collisions, the particles have to approach each other, thereby causing a decrease in randomness. The negative value of $\Delta S^{\ddagger}$ brings down the value of $e^{\Delta S^{\ddagger}/R}$ and hence of A as per Eq. 18.170. A large negative value for the entropy of activation is generally observed for reactions involving complex molecules. The demand for proper orientation is more in the case of a complex molecule and this causes larger reduction in randomness. Thus the entropy of activation, and hence, the frequency factor could be expected to be much less for reactions involving complex molecules.

SAQ 11

The second order rate constants of a reaction are given below at two temperatures:

T/K	298	308
$10^5 \times k/\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	8.8	28

Calculate the activation energy of the reaction.

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…………………………………………………………………………………………………

…………………………………………………………………………………………………

SAQ 12

For the reaction,

$$2\mathrm{NOCl} \rightarrow 2\mathrm{NO} + \mathrm{Cl_2}$$

Arrhenius factor at 298 K is $9.4 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$. Calculate entropy of activation for this reaction at 298 K.

…………………………………………………………………………………………………

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18.11 FAST REACTIONS

Many reactions are so fast that ordinary experimental methods mentioned in Sec. 18.3 are inadequate to make measurements of reaction rates or the rate constants. Such reactions are called fast reactions and the half-life periods of fast reactions are less than 10^{-2}s. Some of the special techniques used for measuring the rate constants of fast reactions are:

- flash photolysis,
- flow method, and
- relaxation method.

Of the above three, we shall discuss the first method in Unit 19 of this course. Now we consider the principles of the other two methods.

Flow Method

Two techniques are available under flow method. In continuous flow method (Fig. 18.12), the reacting solutions or gases are taken in separate containers (A and B) and are allowed to flow through the mixing chamber (C) into an observation tube (D). At various points along the observation tube, the composition of the mixture is determined by some physical methods.

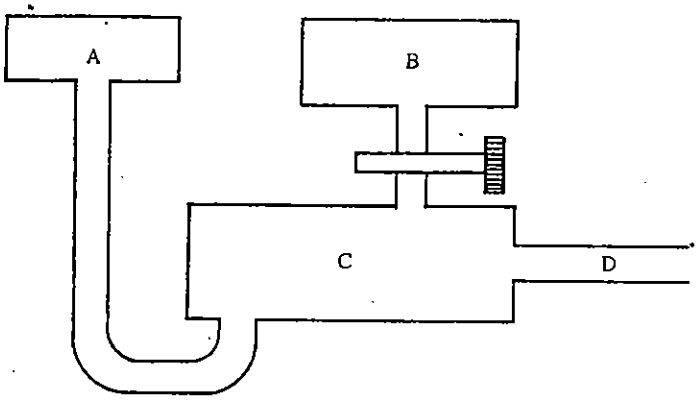


Fig. 18.12: Apparatus for continuous flow method

Using this method, reactions which get completed within 10^{-3}s can be studied. But this method requires a large volume of the reactants. In order to study the reaction rates using small volumes of samples, a refined method is used which is known as stopped-flow method. The reacting solutions are forced through jets into a mixing chamber where mixing occurs very rapidly (within 10^{-3}s). The solution passes at once into the reaction vessel from the mixing chamber. The flow is then stopped suddenly and measurements are made using suitable physical methods. This method is widely used for the study of enzyme kinetics.

Relaxation Method

For studying reactions, which are complete within 10^{-5} s or even less, one of the problems encountered is that the time of mixing the reactants should be much smaller than the time taken for the completion of the reaction. To avoid this problem, relaxation methods have been developed. In a relaxation method, we disturb a reaction at equilibrium using an external influence such as sudden variation of pressure or temperature (known as pressure jump or temperature jump). The system is said to be perturbed from its equilibrium position. The perturbed system then returns to a new equilibrium position. Relaxation refers to the passage of a perturbed system to the new equilibrium. The concentration of the perturbed system is recorded at various time intervals using suitable physical methods. From these measurements, it is possible to measure the rate constants.

18.12 SUMMARY

In this unit, we started with the definitions of the terms such as, rate of reaction, rate law, order of reaction and stoichiometry. We described experimenal methods for rate studies. We derived the integrated forms of rate expressions for first order, second order and zeroth order reactions. We defined and illustrated the pseudo first order reactions. We explained the methods of determination of order of reaction. We discussed the steps followed in arriving at the mechanisms of simple reactions. We described the theory of unimolecular reaction rates. Arrhenius equation, collision theory and the activated complex theory were discussed. Finally, we gave an outline of the methods of studying fast reactions.

18.13 TERMINAL QUESTIONS

1) In the formation of ammonia,

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

the rate of consumption of hydrogen at a particular instant is 4.78×10^{-4} M s^{-1}. What is the rate of formation of ammonia?

2) The rate constant for the decomposition of N_2O_5 at 340 K is 5.20×10^{-3} s^{-1}. This reaction follows first order kinetics. If the initial rate of decomposition of N_2O_5 is

2.60×10^{-4} M s^{-1}, calculate the initial concentration of N_2O_5.

3) What is the time required for 87.5% decomposition of N_2O_5 at 340 K? Use data from the previous question.

4) What is the half-life period for the first order decomposition of azomethane at 600 K if $k = 3.55 \times 10^{-4}\ s^{-1}$?

5) The reaction,

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

was studied at 298 K. The following results were obtained where

$$\text{rate} = -\frac{\Delta[S_2O_8^{2-}]}{\Delta t}$$

$[I^-]_0$ and $[S_2O_8^{2-}]_0$ denote the initial concentrations of the two species.

$10^2 \times [I^-]_0$/M	$10^2 \times [S_2O_8^{2-}]_0$/M	$10^6 \times$ Initial rate / M s^{-1}
8.0	4.0	12.50
4.0	4.0	6.25
4.0	2.0	3.12

Determine the rate law.

6) In the reaction

$$2NO_2Cl \longrightarrow 2NO_2 + Cl_2$$

the mechanism proposed below agrees with the experimentally observed rate law:

$$NO_2Cl \xrightarrow{k_1} NO_2 + Cl \qquad \text{(slow)}$$

$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2 \qquad \text{(fast)}$$

What is the rate law?.

7) For the decomposition of N_2O at 773 K, $k = 1.00 \times 10^{-5}\ s^{-1}$ and $E_a = 250$ kJ mol^{-1} Calculate A using Arrhenius equation.

8) For the reaction,

$$C_2H_4\,(g) + H_2\,(g) \longrightarrow C_2H_6\,(g)$$

the steric factor is 1.7×10^{-6} and mean collision cross- section ($\pi\sigma^2$) is 0.46 nm^2. Calculate A at 628 K. Use Eq.18.158.

Given: i) $k_b = 1.381 \times 10^{-23}$ J K^{-1}

ii) The relative molecular masses of ethylene and hydrogen are 28.05 and 2.016, respectively.

iii) $N_A = 6.022 \times 10^{23}\ mol^{-1}$

9) Explain the reason for the negative value of entropy of activation in the case of many reactions.

10) Explain two methods for the study of fast reactions.

11) The relaxation methods are suitable for measuring the rates of fast reactions. The experimental techniques (such as titrimetry mentioned in Sec. 18.3) are not useful for this purpose. Explain the reason.

18.14 ANSWERS

Self Assessment Questions

1) Using Eq. 18.2, $\frac{d[O_2]}{dt}$ = Rate

$$= 2.74 \times 10^{-4}\ \text{M s}^{-1}$$

2) $\frac{1}{2}\left(\frac{-d\,[HI]}{dt}\right) = \frac{d\,[H_2]}{dt}$

3) i) Spectrophotometry

ii) pH measurement, conductance or titration

iii) pressure measurement

4) Units of k :

zeroth order : M s^{-1}

first order : s^{-1}

second order : $\text{M}^{-1}\,\text{s}^{-1}$

5) Substituting in Eq.18.40,

$$\frac{1}{[A]_t} = \left(\frac{1}{[\,1.00 \times 10^{-2}\,]} + 1.83 \times 10^{-3} \times 1.68 \times 10^{5}\right)\text{M}^{-1}$$

$$[\,A\,]_t = 2.45 \times 10^{-3}\ \text{M}$$

6) Using Eq.18.60,

$$[A]_t = \frac{25}{100} \times 0.500\ \text{M} = 0.125\ \text{M}$$

$$t = \frac{(\,0.500 - 0.125\,)}{1.20 \times 10^{-4}}\ \text{s}$$

$$= 3.13 \times 10^{3}\ \text{s}$$

7) i) After obtaining V_0, V_t and V_∞ as explained in sec.18.6, log ($V_\infty - V_t$) is plotted against t.

$k' = -2.303 \times$ slope

where k' is the pseudeo first order rate constant for the acid hydrolysis of ester.

ii) Using r_0, r_t and r_∞ values, log ($r_t - r_\infty$) is plotted against t.

$k' = -2.303 \times$ slope

where k' is the pseudo first order rate constant for the inversion of sucrose.

8) Using Eq.18.71, $n = 1 + \frac{\log 300/240}{\log 5.00 \times 10^{-2}/4.00 \times 10^{-2}}$

$$n = 1 + \frac{0.0969}{0.0969} = 2$$

9) i) Rate = $k[O_3]$ [NO]

ii) Rate = $k[CH_3NC]$

iii) Rate = $k\,[Cl_2]$

10) The rate law is given below as per the proposed mechanism:

$$\text{Rate} = k_3\,[NO_3]\,[NO] \qquad \text{...(1)}$$

But $K = \frac{k_1}{k_2} = \frac{[NO_3]}{[NO]\,[O_2]}$

Hence, $[NO_3] = K\,[NO]\,[O_2]$ ...(2)

Using (2) in (1),

$$\text{rate} = k_3 K\,[NO]^2\,[O_2]$$

$$= k\,[NO]^2\,[O_2]$$

which is same as the rate law obtained experimentally.

11) Using Eq.18.137,

$$E_a = \frac{2.303\,RT_1\,T_2}{(T_2 - T_1)} \log k_2/k_1$$

$$= \frac{2.303 \times 8.314 \times 298 \times 308}{10} \log \frac{28 \times 10^{-5}}{8.8 \times 10^{-5}}$$

$$= 88.3 \text{ kJ mol}^{-1}$$

12) According to Eq.18.172,

$$\Delta S^{\ddagger} = (19.15 \log A/T^2 - 193.6)\text{ J mol}^{-1}\text{ K}^{-1}$$

$$= \left(19.15 \log \frac{9.4 \times 10^9}{298^2} - 193.6\right)\text{J mol}^{-1}\text{ K}^{-1}$$

$$\Delta S^{\ddagger} = -97.4 \text{ J mol}^{-1}\text{ K}^{-1}$$

Terminal Questions

1) $$\frac{1}{3}\left(\frac{-d[H_2]}{dt}\right) = \frac{1}{2}\frac{d[NH_3]}{dt}$$

Hence, $$\frac{d[NH_3]}{dt} = \frac{2}{3}\left(\frac{-d[H_2]}{dt}\right) = \frac{2}{3} \times 4.78 \times 10^{-4}\text{ M s}^{-1}$$

$$= 3.19 \times 10^{-4}\text{ M s}^{-1}$$

2) $$\frac{-d[N_2O_5]}{dt} = k[N_2O_5]$$

Hence, $$[N_2O_5] = \frac{1}{k}\frac{-d[N_2O_5]}{dt} = \frac{2.60 \times 10^{-4}\text{ M s}^{-1}}{5.20 \times 10^{-3}\text{ s}^{-1}}$$

$$= 5.00 \times 10^{-2}\text{ M}$$

3) $[A]_t = 12.5\%\,[A]_0 = [A]_0/8$

Using Eq. 18.20, $$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/8}$$

$$= \left(\frac{2.303}{5.20 \times 10^{-3}} \log 8\right)\text{s} = 400\text{ s}$$

4) Using Eq. 18.30, $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3.55 \times 10^{-4}}\text{ s} = 1950\text{ s}$$

5) Let us write the rate law as,

$$v = k[I^-]^m\,[S_2O_8^{2-}]^n$$

As in Example 11, $$m = \frac{\log 12.50 \times 10^{-6}/6.25 \times 10^{-6}}{\log 8.0 \times 10^{-2}/4.0 \times 10^{-2}} = 1$$

$$n = \frac{\log 6.25 \times 10^{-6}/3.12 \times 10^{-6}}{\log 4.0 \times 10^{-2}/2.0 \times 10^{-2}} = 1$$

The rate law is,

$$\text{rate} = k[I^-]\,[S_2O_8^{2-}]$$

6) Rate = $k_1[NO_2Cl]$

7) Using Eq.18.133, $\log A = E_a/2.303\,RT + \log k$

$$= (250 \times 10^3/2.303 \times 8.314 \times 773) + \log(1.00 \times 10^{-5})$$

i.e. $\log A = -5.00 + 16.89$

$$A = 7.8 \times 10^{11}\ \text{s}^{-1}$$

8) Mass of one molecule of a substance = $\dfrac{\text{Molar mass}}{N_A}$

Mass of one molecule of ethylene $= \dfrac{28.05 \times 10^{-3}}{6.022 \times 10^{23}}$ kg

Mass of one molecule of hydrogen $= \dfrac{2.016 \times 10^{-3}}{6.022 \times 10^{23}}$ kg

Using Eq. 18.143 $\mu = \dfrac{28.05 \times 2.016}{30.07 \times 6.022 \times 10^{26}}$ kg

$$= 3.12 \times 10^{-27}\ \text{kg}$$

$$\left(\frac{8k_bT}{\pi\mu}\right)^{1/2} = \left(\frac{8 \times 1.381 \times 10^{-23} \times 628}{3.143 \times 3.12 \times 10^{-27}}\right)^{1/2} \left(\frac{\text{J K}^{-1}\,\text{K}}{\text{kg}}\right)^{1/2}$$

$$= 2.66 \times 10^3\ \text{m}\ s^{-1}$$

Using Eq.18.158,

$$A = P\pi\sigma^2\left(\frac{8k_bT}{\pi\mu}\right)^{1/2} N_A$$

$$= 1.7 \times 10^{-6} \times 0.46 \times (10^{-9}\ \text{m})^2 \times 2.66 \times 10^3\ \text{m s}^{-1} \times 6.022 \times 10^{23}\ \text{mol}^{-1}$$

$$= 1.25 \times 10^3\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

$$= 1.25 \times 10^6\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \quad (1\ \text{m}^3 = 10^3\ \text{dm}^3)$$

$$= 1.25 \times 10^6\ \text{M}^{-1}\ \text{s}^{-1}$$

9) See under activated complex theory in sec.18.10.

10) See in Sec.18.11.

11) Methods such as titrimetry need mixing of the reactants. In the case of many fast reactions, the reaction is faster than the mixing time of the reactants. Hence, methods such as titrimetry are not useful for measuring rates of fast reactions. Relaxation method avoids the problem of mixing the solutions, and hence, is useful for measuring the rates of fast reactions.

APPENDIX I

Use of Eq. 18.139 in Calculating Total Collision Frequency

To understand the derivation of Eq. 18.150 for the total collision frequency among the molecules of two gases, X and Y, it is better to recapitulate the derivation of Eq. 2.52 given in Sec. 2.11 of Unit 2. Using a different procedure, Eq. 2.52 was derived for calculating the total collision frequency among the molecules of a single gas.

Eq. 18.139 can be used for deriving the total collision frequency among the molecules of a single or two different gases. Now, let us see how Eq. 18.139 could be used to derive the total collission frequency among the molecules of a single gas (i.e., Eq. 2.52).

Collision diameter of a sigle gas = σ (as given in Sec. 2.11 of Unit 2)

$$\left\{\begin{array}{l}\text{The reduced mass of a system}\\ \text{of two molecules of the same}\\ \text{gas which undergo collisions}\end{array}\right\} = \mu = \frac{m^2}{2m} = \frac{m}{2}$$

Note that while dealing with relative motion of molecules, we must use reduced mass of a system of two molecules but not the mass of a molecule. Using the μ value given above in Eq. 18.141,

Mass of each molecule (m) is same and $m_X = m_Y = m$ in Eq. 18.143.

$$\text{average relative speed of two molecules of a gas} = \left(\frac{8k_bT}{\pi m/2}\right)^{1/2} = 2^{1/2}\left(\frac{8k_bT}{\pi m}\right)^{1/2}$$

$$= 2^{1/2}\left(\frac{8k_bTN_A}{\pi m N_A}\right)^{1/2} = 2^{1/2}\left(\frac{8RT}{\pi M_m}\right)^{1/2}$$

Mass of one molecule of a gas (m) $= \dfrac{\text{Molar mass } (M_m)}{\text{Avogadro constant } (N_A)}$ and $k_bN_A = R$

$$\text{i.e., Average relative speed of two molecules of gas} = 2^{1/2}\left(\frac{8RT}{\pi M_m}\right)^{1/2}$$

$$= 2^{1/2}\bar{u} \quad \text{(Using Eq. 2.47)}$$

Number density of the gas = n_0 (using Eq.2.40).

Now, let us come to the correction factor required while calculating the total collision frequency among the molecules of a single gas. Suppose there are N molecules in a gas with labels, 1, 2, 3, 4, ... N. To calculate the total number of collisions, we use the following method:

First, imagine that molecule 1 is colliding with each of the molecules 2, 3, 4 .... N and count the number of collisions.

Then, assume that molecule 2 is colliding with each of the molecules, 1, 3, 4, ... N and count the number of collisions.

Continue the above procedure till the Nth molecule colliding with each of the molecules, 1, 2, 3, ... (N–1) and count the number of collisions in each case.

Add the number of collisions obtained in each case. In this procedure, each collision would have been counted twice. For example, the collision between molecules 1 and 2 is counted twice as if, molecule 1 is colliding with molecule 2 and, molecule 2 is colliding with molecule 1. Hence the correction factor, 1/2, must be included in Eq. 18.139 while calculating the total collision frequency among the molecules of a gas, so that each collision is counted only once.

i.e., correction factor = 1/2

Substituting the various factors in Eq. 18.139,

$$\left\{\begin{matrix}\text{Total collison frequency}\\ \text{among the molecules of a gas}\\ \text{(denoted as } Z_{11} \text{ in Sec. 2.11)}\end{matrix}\right\} = \pi\sigma^2 . 2^{1/2} . \bar{u} . n_0 . n_0 . 1/2$$

$$= \frac{1}{\sqrt{2}}\pi\sigma^2\bar{u}n_0^2$$

This equation is the same as Eq. 2.52.

While calculating the total collision frequency among the molecules of two different gases such as X and Y discussed in this section, there is no necessity for the corrector factor. We add up the number of collisions that each molecule of X will make with each molecule of Y as follows:

Let the molecules of gas X have labels,

X_1, X_2, X_3 ..... X_N

Let the molecules of gas Y have labels,

$Y_1, Y_2, Y_3,$ ..... Y_N

Count the number of collisions as indicated below:

Let the molecule X_1 collide with each of the molecules, Y_1, Y_2, Y_3, ... Y_N and count the number of collisions.

Repeat the process and count the number of collisions that X_2 makes with Y_1, Y_2, Y_3, ... Y_N. Continue the process and calculate the number of collisions upto the molecule X_N colliding with each of the molecules, Y_1, Y_2, Y_3, ... Y_N.

Add the number of collisions in each case.

In this process, each collision between a molecule of X and a molecule of Y is counted once only. Hence there is no necessity for correction factor while calculating the total collision frequency among the molecules of different gases. In this case, we have not **counted**

i) the collisions **among** the molecules of X only or

ii) the collisions **among** the molecules of Y only.

APPENDIX II

Derivation of Eq. 18.168 : $\Delta H^{\ddagger} = E_a - 2RT$

According to Eq. 18.132, $\ln k = \ln A - E_a/RT$. Differentiating with respect to temperature and assuming A and E_a to be independent of temperature,

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{E_a}{RT^2}$$

or

$$E_a = RT^2\,\frac{\mathrm{d}\ln k}{\mathrm{d}T}$$

This equation can be represented in the following form under constant volume conditions:

$$E_a = RT^2\left(\frac{\partial \ln k}{\partial T}\right)_V \qquad \text{...(A.1)}$$

$$= RT^2\left(\frac{\partial k/k}{\partial T}\right)_V = \frac{RT^2}{k}\left(\frac{\partial k}{\partial T}\right)_V \qquad \text{...(A.2)}$$

The change in concentration of a species is related to

- the change in the amount of the species and
- the change in the volume of the system.

If volume of the system is kept constant, the change in concentration of the species could be directly related to the change in the amount of species.

Keeping this in view, many reaction rates are measured under constant volume conditions. Reactions taking place in closed vessels are examples of this type.

Rewriting Eq. 18.162,

$$k = \frac{RT}{p^0}\,\frac{k_bT}{h}\,K_p$$

$$k = V^0\,\frac{k_bT}{h}\,K_p \qquad \text{...(A.3)}$$

where $\dfrac{RT}{p^0} = V^0 =$ standard volume

$$\left(\frac{\partial k}{\partial T}\right)_V = \frac{V^0 k_b}{h}\left(\frac{\partial\,(TK_p)}{\partial T}\right)_V$$

$$\left(\frac{\partial k}{\partial T}\right)_V = \frac{V^0 k_b}{h}\left[K_p + T\left[\frac{\partial K_p}{\partial T}\right]_V\right] \qquad \text{...(A.4)}$$

Using Eqs. A.3 and A.4,

$$\frac{1}{k}\left(\frac{\partial k}{\partial T}\right)_V = \frac{h}{V^0 k_b T K_p}\,\frac{V^0 k_b}{h}\left[K_p + T\left(\frac{\partial K_p}{\partial T}\right)_V\right]$$

$$= \frac{1}{TK_p}\left[K_p + T\left(\frac{\partial K_p}{\partial T}\right)_V\right] \qquad \text{...(A.5)}$$

$$\frac{RT^2}{k}\left(\frac{\partial k}{\partial T}\right)_V = \frac{RT^2}{TK_p}\left[K_p + T\left(\frac{\partial K_p}{\partial T}\right)_V\right]$$

$$= \frac{RT}{K_p}\left[K_p + T\left(\frac{\partial K_p}{\partial T}\right)_V\right]$$

$$= RT\left[1 + T.\frac{1}{K_p}\left(\frac{\partial K_p}{\partial T}\right)_V\right]$$

$$\frac{RT^2}{k}\left(\frac{\partial k}{\partial T}\right)_V = RT + RT^2\left(\frac{\partial \ln K_p}{\partial T}\right)_V \qquad \text{...(A.6)}$$

Using (A.2) and (A.6)

$$E_a = RT + RT^2\left(\frac{\partial \ln K_p}{\partial T}\right)_V \qquad \text{...(A.7)}$$

We are now going to use Eq. 14.33 of Unit 14 of this course. Under constant volume conditions, Eq. 14.33 then takes the form

$$RT^2\left(\frac{\partial \ln K_p}{\partial T}\right)_V = \Delta U^{\ddagger} \qquad \text{...(A.8)}$$

where $\Delta U^{\ddagger}$ is the molar activation internal energy.

From Eqs. A.7 and A.8,

$$E_a = RT + \Delta U^{\ddagger} \qquad \text{...(A.9)}$$

Applying Eq. 7.15 of Unit 7 for the formation of the activated complex,

$$\Delta H^{\ddagger} = \Delta U^{\ddagger} + \Delta n_g RT$$

Eq. 18.160 is written below specifying the physical state.
$X(g) + Y(g) \rightarrow A^{\ddagger}(g)$

Δn_g = Difference in the number of moles between the gaseous reactants and the gaseous products

= − 1(for the formation of the activated complex as per Eq. 18.160)

Hence $\Delta H^{\ddagger} = \Delta U^{\ddagger} - RT$ ...(A.10)

Using Eqs. A.9 and A.10,

$$E_a = \Delta H^{\ddagger} + 2RT$$

or $\Delta H^{\ddagger} = E_a - 2RT$

The last one is Eq. 18.168.

UNIT 19 PHOTOCHEMISTRY

Structure

19.1 INTRODUCTION

In Unit 9 of this course, we stated that free energy must decrease for a physical or a chemical process to be feasible. This is applicable to thermal reactions (also known as dark reactions). The conversion of carbon dioxide and water into starch is a reaction in which free energy increases. Under laboratory conditions, this reaction is not possible. But plants carry out starch synthesis using sunlight. Ozonisation of oxygen and decomposition of ammonia are also nonspontaneous reactions under laboratory conditions; but these could take place by using light of proper energy. Such possibilities of new reactions and new synthetic methods encouraged the scientists to probe into light-initiated reactions.

In photochemistry, we study the absorption and emission of light by matter. It consists of the study of various photophysical processes and photochemical reactions. Two important photophysical processes are fluorescence and phosphorescence. During fluorescence, light emission takes place in the presence of exciting radiation; but the light emission stops, once the exciting radiation is removed. In contrast to this, during phosphorescence, light emission takes place even after the removal of the exciting radiation.

In photochemical reactions, the substances acquire the necessary activation energy through light absorption. Again this is in contrast to the thermal reactions in which the reactants acquire their activation energy through collisions between molecules.

In this unit, we shall discuss the laws of photochemistry. We shall then describe some photochemical reactions and photophysical processes. We shall also explain some photosensitised reactions. Finally we shall discuss the applications of photochemical studies.

Objectives

After studying this unit, you should be able to

- explain the mathematical form of Beer-Lambert law,
- state Grotthuss-Draper law and Stark-Einstein law
- calculate the quantum yield of a reaction using the given experimental data,
- explain the reason for the higher energy requirement for the photochemical dissociation of a molecule as compared to its thermal dissociation,

- derive rate expressions for simple photochemical reactions,
- explain some photophysical properties such as fluorescence and phosphorescence,
- list some photosensitised reactions,
- state the applications of photochemical studies, and
- define chemiluminescence..

19.2 LAWS OF PHOTOCHEMISTRY

Grotthuss-Draper law and Stark-Einstein law are the two laws concerning the interaction between matter and light. Before discussing these two laws, let us state the mathematical form of Beer-Lambert law discussed in Unit 8 of Atoms and Molecules course.

Beer-Lambert law is useful in calculating the concentration of a solution on the basis of its light absorption. This law relates the intensity of the transmitted monochromatic light to the concentration of the solution and the thickness of the cell in which the solution is kept.

Mathematical form of Beer-Lambert law is given below:

$$\log I_0/I = A = \varepsilon c l \qquad \ldots (19.1)$$

where I_0 = Intensity of the incident radiation

I = Intensity of the transmitted radiation

$A = \log I_0/I$ = Absorbance or optical density of the solution

c = Concentration of the solution expressed in mol m^{-3} units

l = thickness of the cell

ε = Molar extinction coefficient; expressed in $m^2\ mol^{-1}$

The molar extinction coefficient of a substance can be determined using a colorimeter or a spectrophotometer as follows. The absorbances of a solution are measured at different known concentrations using a cell of known thickness (l). The plot of A against c gives a straight line (Fig. 19.1) and its slope is equal to $\varepsilon\, l$.

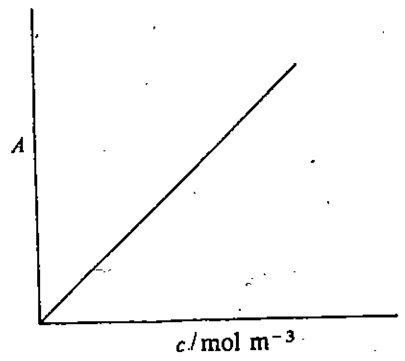


Fig. 19.1: A vs c plot.

$$\text{Hence, } \varepsilon = \frac{\text{slope}}{l}$$

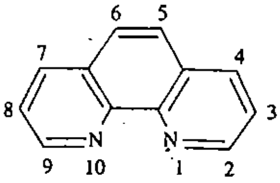
Since l is known, ε can be calculated. Using this ε value, the concentration of a solution can be determined by measuring its absorbance.

Colorimeters and spectrophotometers are commercially available for the measurement of absorbances. In colorimeters, colour filters are used to get the incident radiation in a particular wavelength range. Spectrophotometers have arrangements for obtaining nearly monochromatic incident radiation. Both colorimeters and spectrophotometers have devices for converting the light transmitted into suitable signal through detector devices (see Sec. 19.3). The signal generated from transmitted light is directly read as absorbance values.

Study the following example carefully. The calculation shown below is used in chemical actinometers (Example 3 in Sec. 19.3) for estimating the intensity of the light absorbed during a photochemical reaction. This example illustrates the use of Eq. 19.1 in calculating the concentration of a solution.

Example 1

A solution of the red complex formed by Fe^{2+} ion with 1,10-phenanthroline is taken in a cell of thickness 1.00 cm. If ε for the complex is 1.11×10^3 m^2 mol^{-1} and the absorbance of the solution is 0.391, calculate the concentration of the complex in mol m^{-3} units.



1,10 – Phenanthroline (Phen)

Solution

$$A = 0.391; \; l = 1.00 \text{ cm} = 1.00 \times 10^{-2} \text{ m};$$

$$\varepsilon = 1.11 \times 10^3 \text{ m}^2 \text{ mol}^{-1}$$

Rearranging Eq. 19.1, $c = \dfrac{A}{\varepsilon l} = \dfrac{0.391}{1.11 \times 10^3 \times 1.00 \times 10^{-2}} \text{ mol m}^{-3}$

$$= 0.0352 \text{ mol m}^{-3}$$

We shall now state the two laws of photochemistry.

Grotthuss-Draper Law

According to this law, only the light that is absorbed by a molecule can produce a photochemical change in it. This means that it is not sufficient to pass light through a substance to bring about a chemical reaction; but the light must be absorbed by it. Stark-Einstein law of photochemical equivalence provides a quantum mechanical form to Grotthuss-Draper law.

Stark-Einstein Law of Photochemical Equivalence

Stark-Einstein law of photochemical equivalence can be stated as follows:

Each molecule taking part in a photochemical reaction absorbs one quantum of radiation which causes the reaction.

This law is applicable to the primary act of excitation of a molecule by light absorption. This law helps in calculating the quantum efficiency (Φ) which is a measure of the efficiency of the use of light in a photochemical reaction.

Stark-Einstein law is applicable only if the intensity of light is not very high.

The quantum efficiencies for the formation of a product and for the disappearance of the reactant are defined below:

$$\left\{\begin{array}{l}\text{The quantum efficiency} \\ \text{for the formation of a} \\ \text{product } (\phi_P)\end{array}\right\} = \left\{\begin{array}{l}\dfrac{\text{Number of molecules of product formed in 1 second}}{\text{Number of quanta absorbed in 1 second}}\end{array}\right\} \qquad \ldots (19.2)$$

$$= \frac{dN_P/dt}{I_a}$$

In this equation, dN_P/dt denotes the rate of formation of the product. The units for $\dfrac{dN_P}{dt}$ are molecules per second. I_a refers to the number of photons absorbed per second. Similarly we can define the quantum efficiency for the disappearance of a reactant.

$$\left\{\begin{array}{l}\text{The quantum efficiency for} \\ \text{the disappearance of the} \\ \text{reactant } (\phi_R)\end{array}\right\} = \left\{\begin{array}{l}\dfrac{\text{Number of molecules of reactant consumed in 1 second}}{\text{Number of quanta absorbed in 1 second}}\end{array}\right\} \qquad \ldots (19.3)$$

$$= \frac{-dN_R/dt}{I_a}$$

where $-\mathrm{d}N_R/\mathrm{d}t$ is the rate of consumption of the reactant. The minus sign in $-\mathrm{d}N_R/\mathrm{d}t$ is due to the decrease in concentration of the reactant with time.

As per Stark - Einstein law, each reacting molecule absorbs one quantum of light. Hence,

$$\left\{\begin{array}{l}\text{the energy absorbed by one}\\ \text{mole of a substance undergoing}\\ \text{photochemical reaction}\end{array}\right\} = N_A h\nu = \frac{N_A h c}{\lambda} \qquad \dots (19.4)$$

This unit of energy is also called einstein and, as apparent from Eq. 19.4, the value of einstein depends on ν or λ.

where $N_A = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$

$h = 6.626 \times 10^{-34}\ \mathrm{J\,s}$

$c = 3 \times 10^{8}\ \mathrm{m\,s^{-1}}$

λ = wavelength of the light in m unit

ν = frequency in $\mathrm{s^{-1}}$ unit .

To calculate the quantum efficiency, use the following steps:

i) **Calculation of Energy Absorbed per Quantum**

$$\left\{\begin{array}{l}\text{Energy per quantum}\\ \text{of radiation absorbed}\end{array}\right\} = h\nu = \frac{hc}{\lambda}$$

ii) **Calculation of I_a**

Unit for energy per quantum = joule photon −1

Unit for $I_a = \dfrac{\text{joule second}^{-1}}{\text{joule photon}^{-1}}$

$=$ photon second^{-1}

Usually intensity of light absorbed is given in $\mathrm{J\,s^{-1}}$ units. From this, I_a could be calculated using the following equation :

$$\left\{\begin{array}{l}\text{Intensity in terms of}\\ \text{number of photons}\\ \text{absorbed in 1 second } (I_a)\end{array}\right\} = \frac{\text{Intensity in J s}^{-1}\text{units}}{\text{Energy per quantum}}$$

iii) **Calculation of $\dfrac{-\mathrm{d}N_R}{\mathrm{d}t}$ or $\dfrac{\mathrm{d}N_P}{\mathrm{d}t}$**

First we have to obtain the number of moles of reactant consumed or of product formed **in 1 second** by dividing the respective amount by the time in second unit.

In order to calculate the rate of formation or rate of disappearance in molecule per second units, we have to use the following equations:

$$\frac{-\mathrm{d}N_R}{\mathrm{d}t} = \left\{\begin{array}{l}\text{Number of moles of reactant}\\ \text{decomposed in 1 second}\end{array}\right\} \times N_A \qquad \dots (19.5)$$

Also,

$$\frac{\mathrm{d}N_P}{\mathrm{d}t} = \left\{\begin{array}{l}\text{Number of moles of product}\\ \text{formed in 1 second}\end{array}\right\} \times N_A \qquad \dots (19.6)$$

iv) **Calculation of Quantum Efficiency**

Using Eq. 19.2 or 19.3, ϕ_P or ϕ_R can be calculated.

Let us illustrate the calculation of quantum efficiency for a reaction.

Example 2

In photochemical decomposition of acetone using 313 nm light, 7.57×10^{-6} mol of carbon monoxide is formed in 20 minutes. If the light absorbed corresponds to $2.41 \times 10^{-3}\ \mathrm{J\,s^{-1}}$, calculate the quantum efficiency for the formation of carbon monoxide.

i) $$\left\{\begin{array}{l}\text{Energy absorbed}\\ \text{per quantum}\end{array}\right\} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{313 \times 10^{-9}}\ \text{joule photon}^{-1}$$

$$= 6.35 \times 10^{-19}\ \text{joule photon}^{-1}$$

ii) $$I_a = \frac{\text{Intensity in joule second}^{-1}}{6.35 \times 10^{-19} \text{ joule photon}^{-1}}$$

$$= \frac{2.14 \times 10^{-3} \text{ joule second}^{-1}}{6.35 \times 10^{-19} \text{ joule photon}^{-1}}$$

i.e., $I_a = 3.80 \times 10^{15}$ photons second^{-1}

iii) Amount of carbon monoxide formed in 1 second $= \dfrac{7.57 \times 10^{-6} \text{ mol}}{20 \times 60 \text{ s}}$

$$= 6.31 \times 10^{-9} \text{ mol s}^{-1}$$

$$\frac{dN_{CO}}{dt} = 6.31 \times 10^{-9} \times 6.022 \times 10^{23} \text{ molecule second}^{-1}$$

$$= 3.80 \times 10^{15} \text{ molecule second}^{-1}$$

iv) Using Eq. 19.2, ϕ_{CO} = Quantum efficiency for the formation of carbon monoxide

$$= \frac{\frac{dN_{CO}}{dt}}{I_a} = 1$$

In the next section, we shall discuss the experimental method of determining the quantum efficiency of a reaction. Before studying this, work out the following SAQ.

SAQ 1

A radiation of 250 nm incident on HI results in the decomposition 1.85×10^{-2} mol within a particular time interval. Light energy absorbed during this time interval is 4.18 k J. Calculate the quantum efficiency for the decomposition of HI.

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19.3 EXPERIMENTAL DETERMINATION OF QUANTUM EFFICIENCY

For the determination of quantum efficiency of a photochemical reaction, we must measure the following:

- the rate of decomposition of the reactants or the rate of formation of the products ; this can be done using any of the methods discussed in Unit 18.
- the number of quanta absorbed in the given time.

In short, we need a method for measuring the amount of light absorbed. If we can devise a method for estimating the intensity of the incident light (I_0) and the intensity of the light transmitted (I) by the reaction mixture, the intensity of the light absorbed (I_a) can be calculated using the relationship ;

$$I_a = I_0 - I$$

For measuring I_0 and I, same cell is used. I_0 corresponds to the measurement of intensity with empty cell (known as blank) and I, to the measurement using the cell containing the reaction mixture.

The experimental set-up used for measuring the intensity of light is shown in Fig. 19.2.

As a source (A) of visible light, a high intensity tungsten lamp or quartz halogen lamp or xenon arc lamp can be used. For obtaining ultraviolet light, hydrogen or deuterium lamps are good sources. The light is first passed through a lens, B (to get a parallel beam of light), and then through a monochromator (C). The monochromator yields a narrow band of light in the desired wavelength. The monochromatic light then passes through the reaction cell (D). The light transmitted by the reaction cell reaches the detector (E).

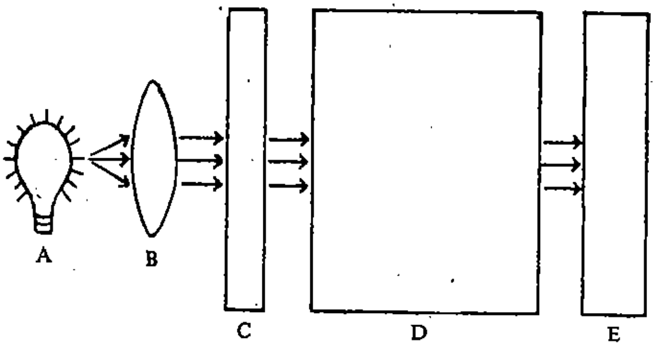

Fig. 19.2 : Measurement of intensity of light during a photochemical reaction.

While using ultraviolet light as a source of radiation, quartz cuvettes (cells) and lenses must be used.

Since pyrex glass absorbs light below 300 nm, it can be used for radiation above 300 nm only.

The visible light has the wavelength region, 800-380 nm. The ultraviolet light has wavelength below 380 nm and above 10 nm.

The detector is used for measuring the intensity of light. The quantitative measurement of light intensity based on energy conversion or on chemical reaction is called **actinometry**. Detectors such as thermopiles and the photoelectric cells function on energy conversion principle. We discuss each of them in brief below :

Thermopile

Thermopile consists of thermocouples connected in series and it generates electricity on heating.

Thermopile (Fig. 19.3) is a device useful for converting light into heat, and then, heat into electricity. It has a set of junctions of different metals having a blackened surface. This black coating is to ensure absorption of all radiation falling on it. The energy so absorbed increases the temperature of the metals. Thermopile converts this temperature increase into a potential difference. Light intensity is related to electricity generated by it. The detector device must be calibrated against a standard light source. Thermopile could be used as a detector for light of any wavelength.

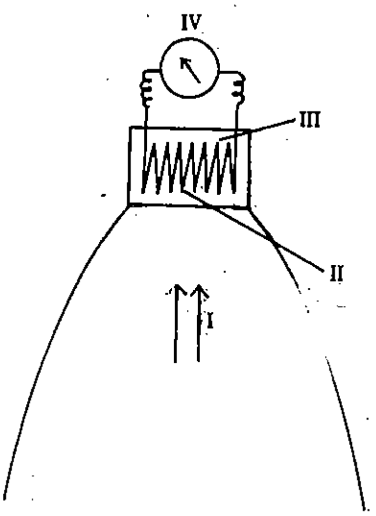

Fig. 19. 3 : Thermopile : I. light radiation, II. blackened surface exposed to radiation; III. unexposed surface at the back; IV galvanometer.

Photoelectric Cells

Photoelectric cell converts light directly into electricity. The current generated is directly proportional to light intensity. Photoelectric cell is an evacuated bulb with a photosensitive cathode. Light radiation results in the emission of electrons from the cathode which get collected at the anode. Thus the flow of current is caused. The photoelectric cell is sensitive to the wavelength of the light used and must be calibrated using a thermopile.

Chemical Actinometers

Light intensity could be estimated by a quantitative estimation of a substance formed or decomposed by light. The photochemical decomposition of $K_3Fe(C_2O_4)_3$ is a widely used chemical method for estimating intensity of light between the wavelength range 250 nm and 577 nm. Light within this wavelength range causes $K_3Fe(C_2O_4)_3$ dissolved in sulphuric acid to react as follows:

$$2\,Fe^{3+} + 2\,e^- \rightarrow 2\,Fe^{2+}$$

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

The concentration of Fe^{2+} is estimated colorimetrically through complex formation with 1,10-phenanthroline. (See Example 1). This complex has a deep red colour. The concentration of the complex is equal to the concentration of Fe^{2+} present before complexation. The following example is worked out to illustrate this method.

Example 3

In a potassium ferrioxalate actinometer, the quantum efficiency for Fe^{2+} production (ϕ_{FS}) at 480 nm wavelength is 0.95. After irradiating the potassium ferrioxalate solution for 20 minutes, it is completely transferred to a 200 cm^3 volumetric flask, mixed with required quantity of 1,10-phenanthroline for complex formation and made up to mark with a buffer solution. For colorimetric estimation, a sample of this complex is taken in a cell of 1.00 cm thickness. The complex has an absorbance value of 0.391 and its ε is $1.11 \times 10^3\ m^2\ mol^{-1}$. Calculate

i) the concentration of the complex,

ii) the number of Fe^{2+} ions formed in the actinometer due to irradiation,

iii) the rate of formation of Fe^{2+} ions (dN_{FS}/dt)

iv) I_a (number of photons absorbed per second).

Assume that one Fe^{2+} ion forms one complex molecule with 1,10-phenanthroline.

Solution

i) Note that the concentration of the complex is same as that calculated in Example 1 using Eq. 19.1; c = concentration of complex = $0.0352\ mol\ m^{-3}$

Also, concentration of Fe^{2+} ion = concentration of the complex

$$= 0.0352\ mol\ m^{-3}$$

ii)

$$\left\{\begin{array}{l}\text{Number of moles of } Fe^{2+} \text{ ion}\\ \text{present in 200 cm}^3 \text{ of the}\\ \text{solution}\end{array}\right\} = \left\{\begin{array}{l}\text{Concentration}\\ \text{of } Fe^{2+} \text{ ion}\end{array}\right\} \times \left\{\begin{array}{l}\text{volume of the}\\ \text{solution in m}^3\\ \text{unit}\end{array}\right\}$$

$$= 0.0352 \times 200 \times 10^{-6}\ mol$$

$$= 7.04 \times 10^{-6}\ mol \quad \left\{\begin{array}{l}\text{because, 200 cm}^3\\ = 200 \times 10^{-6}\ m^3\end{array}\right\}$$

$$\left\{\begin{array}{l}\text{Hence the number of moles}\\ \text{of } Fe^{+2} \text{ ion formed in the}\\ \text{actinometer}\end{array}\right\} = 7.04 \times 10^{-6}\ mol$$

$$\begin{array}{l}\text{The number of } Fe^{2+} \text{ ions}\\ \text{formed in the actinometer}\end{array} = 7.04 \times 10^{-6} \times 6.022 \times 10^{23}\ \text{ions}$$

$$= 4.24 \times 10^{18}\ \text{ions}$$

iii)

$$\frac{dN_{FS}}{dt} = \frac{\text{Number of } Fe^{2+} \text{ ions formed}}{\text{Time in seconds}} = \frac{4.24 \times 10^{18}}{1200}\ \text{ions second}^{-1}$$

$$= 3.53 \times 10^{15}\ \text{ions second}^{-1}$$

iv) Using Eq. 19.2, $\phi_{FS} = \dfrac{dN_{FS}/dt}{I_a}$

Given that $\phi_{FS} = 0.95$

$$\text{Hence } I_a = \frac{dN_{FS}}{dt} \times \frac{1}{0.95}$$

$$= \frac{3.53 \times 10^{15}}{0.95} \text{ photons second}^{-1}$$

$$= 3.72 \times 10^{15} \text{ photons second}^{-1}$$

The Quantum Efficiencies of Some Reactions

If a photochemical reaction follows Stark-Einstein law, then ϕ ust be unity. Studies on a large number of photochemical reactions indicate that while some of them follow Stark-Einstein law, many others do not. The quantum efficiencies of some photochemical reactions along with their effective wavelengths are given in Table 19.1.

Table 19.1: Quantum Efficiencies and Effective Wavelengths of Some Photochemical Reactions

Reaction	Effective wavelength / nm	ϕ
$2NH_3 \rightarrow N_2 + 3H_2$	<210	0.2
$2NO_2 \rightarrow 2NO + O_2$	<366	0.7
$H_2 + Br_2 \rightarrow 2HBr$	<511	0.01
$H_2S \rightarrow H_2 + S$	<208	1.0
$2HI \rightarrow H_2 + I_2$	<327	2.0
$3O_2 \rightarrow 2O_3$	<175	3.0
$H_2 + Cl_2 \rightarrow 2HCl$	<478	10^6

The photochemical reactions for which quantum efficiency is a small integer are said to follow Stark-Einstein law. Examples are the dissociation of H_2S or ozonisation of oxygen etc. Reactions like the formation of hydrogen chloride or hydrogen bromide do not follow Stark-Einstein law. The quantum efficiency for the former reaction ($H_2 + Cl_2 \rightarrow 2\,HCl$) is very high while it is much low for the latter ($H_2 + Br_2 \rightarrow 2\,HBr$). In order to explain these discrepancies, Bodenstein pointed out that photochemical reactions involve two distinct processes:

i) In the primary process, absorption of one quantum of light results in the excitation of one molecule or an atom (A) to form the excited species, A^*

$$\underset{\text{Atom or molecule}}{A} + h\nu \rightarrow \underset{\text{Excited species}}{A^*}$$

ii) In the secondary process, the excited species undergoes a chemical change

$$A^* \rightarrow \text{Products}$$

According to Bodenstein, the deviations from Stark-Einstein law are due to the secondary processes.

In the case of reactions having low quantum yields, the number of molecules decomposed by the absorption of one quantum of radiation is less than one. The probable reasons for the low quantum yields are given below:

- The excited species formed at the first step may be deactivated by collisions before the product could be formed. This process is called **quenching**. Sometimes the presence of paramagnetic substances like oxygen or nitric oxide could result in quenching leading to low quantum yield for a chemical reaction.

- One or more of the reactions in the secondary processes may be endothermic. High energy requirement could decrease the reaction rate. In Sec. 19.5, we will see that the quantum yield for the formation of hydrogen bromide is low due to the endothermic nature of the reaction between Br and H_2 (see Example 5 in Sec. 19.5).

- The excited species may recombine to give the reactant molecule. In the hydrogen bromide formation, another reason for the low quantum yield is the recombination of bromine atoms which are formed in the primary step.

In the case of reactions with high quantum yields, the excited species formed in the first step could initiate a series of chain reactions. This causes a large number of molecules to react by absorption of one quantum of light, as in the case of hydrogen chloride formation (see Sec. 19.5).

The following SAQ could be answered correctly, if you have understood the materials in this section.

SAQ 2

The quantum yield for the photochemical formation of hydrogen chloride is high in the absence of oxygen but low when oxygen is present. Explain.

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19.4 PHOTOCHEMICAL DISSOCIATION

In Unit 3 of Atoms and Molecules course, it has been stated that the bond enthalpy gives an estimate of the average energy required to break a particular bond. These bond enthalpies are derived from thermochemical calculations (see Sec. 7.8 of Unit 7 of this course). It is generally seen that the energy required for the dissociation of a particular bond by light absorption is much greater than its bond enthalpy value. In Table 19.2, we illustrate this for some diatomic molecules.

Table 19.2: Comparison of Photochemical Dissociation Energies and Bond Enthalpies

Dissociating molecule	nm*	(Photochemical dissociation** energy) / kJ mol^{-1}	Bond enthalpy*** / kJ mol^{-1}
H_2	84.5	1420	436
Cl_2	478	250	242
Br_2	511	235	193
HI	327	367	299
O_2	176	682	497

* λ value corresponds to maximum wavelength of light required for decomposition by direct irradiation.

** Photochemical dissociation energy for one mole is calculated by substituting for λ in Eq. 19.4.

*** Bond enthalpies except for HI are taken from Table 3.9 of Unit 3 of Atoms and Molecules course.

Bond enthalpy of a diatomic molecule indicates the energy requirement for its thermal dissociation.

The reasons for the higher photochemical dissociation energies as compared to bond enthalpies are given below:

- For dissociating a molecule through light absorption, there must be an upper electronic state with appropriate energy levels. There is no such restriction for thermal decomposition.

- During photochemical dissociation, the product species could be in an excited state and / or in ground state. For example, decomposition of bromine by absorption of light of wavelength 511 nm can be shown as below:

$$Br_2 + h\nu \rightarrow Br^* + Br \qquad \lambda = 511 \text{ nm}$$

The atom with asterisk sign indicates excited state. Thus, photochemical decomposition of bromine needs 235 kJ mol^{-1}. But thermal decomposition of bromine needs 193 kJ mol^{-1} only, since both the bromine atoms are formed in ground state.

The photochemical dissociation of molecules is also known as **photolysis.** The photolysis can be understood using potential energy diagrams of the type discussed in Unit 4 of Atoms and Molecules course. In Fig. 19.4, the ground state and the excited state are represented using potential energy diagrams I and II, respectively. The quantised vibrational sublevels in each state are shown by horizontal lines such as AB, EF etc.

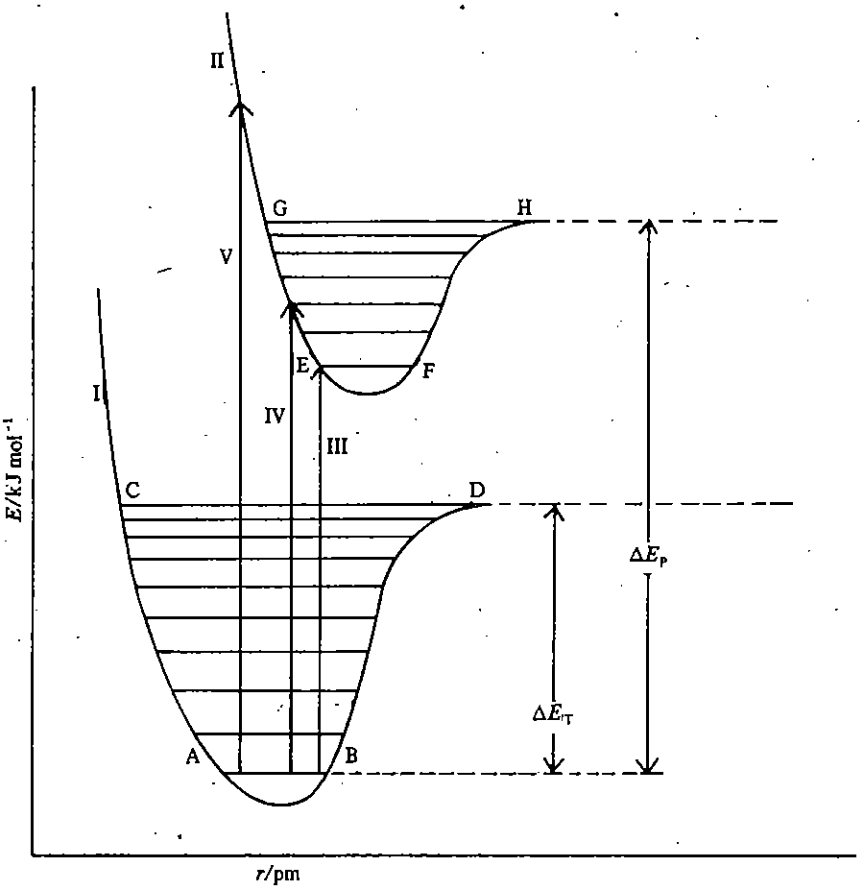

Fig. 19.4: Electronic excitation; *E* (potential energy) vs *r* (internuclear distance).

When a molecule is excited from zero vibrational level AB of ground electronic state to any of the vibrational levels **below GH** in the upper electronic state, the resultant electronic spectrum shows an absorption band with vibration — rotation fine structure. The fine structure is due to numerous transitions (such as III, IV etc.) possible from the zero vibrational level (AB) in the lower electronic state to any of the quantised vibrational levels in the upper electronic state. This can further be understood from the fact that each vibrational level has its own rotational sublevels.

When a molecule absorbs sufficient energy such that it is transferred from the ground state to or above GH in the upper electronic state, then the molecule undergoes photochemical dissociation. The spectrum shows a continuum (lack of discrete lines), once the molecule dissociates. The difference in energy between the levels AB and GH (ΔE_P) is the **photochemical dissociation energy. The thermal dissociation energy** (ΔE_T) is equal to the bond enthalpy in the case of diatomic molecules and it is the energy difference between the lowest and uppermost vibrational levels (AB and CD) in the ground state. Note that $\Delta E_P > \Delta E_T$.

We have discussed photolysis in detail so far because it is the initial reaction in many photochemical reactions. The excited atom or radical formed due to photolysis of a molecule often starts a chain reaction. We shall use this principle in the next section in the study of some photochemical reactions. Before studying that, answer the following SAQ which will help you in understanding Example 4.

SAQ 3

In the photochemical dissociation of HI, the first step is given below:

$$HI + h\nu \rightarrow H + I$$

Assume that H atom formed is in excited state while I atom is in ground state. Calculate the excess energy that the excited hydrogen atom carries as (use Table 19.2) compared to a ground state hydrogen atom.

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The excess energy ($\Delta E_r - \Delta E_T$) that a photochemical decomposition demands as compared to thermal decomposition is given to one of the atoms formed. This atom is said to be in the excited state.

19.5 SOME PHOTOCHEMICAL REACTIONS

In this section, we discuss the mechanism of some photochemical reactions and then explain flash photolysis. For the first two reactions given below, we derive rate equations also. You go through these derivations carefully. These two examples could give you an idea as to how the photochemical rate expressions are written.

The first step in both the examples is photolysis. The rate of the photolysis step is expressed as I_a which is the rate of absorption of light (number of quanta absorbed per second). The initial photolysis is followed by thermal (or dark) reactions for which kinetic expressions are similar to those discussed in Unit 18.

Example 4

Photochemical Decomposition of Hydrogen Iodide

Let us derive expressions useful in calculating the rate of decomposition of HI and the quantum efficiency for this reaction. HI undergoes photochemical decomposition below 327 nm. The mechanism is given below:

$$HI + h\nu \rightarrow H + I \quad \text{Rate of photolysis} = I_a \qquad ..(19.7)$$

$$H + HI \xrightarrow{k_2} H_2 + I \qquad ..(19.8)$$

$$I + I \xrightarrow{k_3} I_2 \qquad ...(19.9)$$

Such steps are written based on energy considerations. If you have answered SAQ in the last section correctly, you could follow why in the second step H atom attacks HI whereas I does not.

While deriving rate expressions, we try to eliminate terms containing active species using steady state principle.

HI is consumed in two ways as per Eqs. 19.7 and 19.8. The rate of disappearance of HI can be written as follows :

$$\frac{-d[HI]}{dt} = I_a + k_2[H][HI] \qquad ...(19.10)$$

As per steady state approximation discussed in Unit 18, the concentration of the active species H is constant. In other words, its concentration does not vary with time.

i.e., $$\frac{d[H]}{dt} = 0 = I_a - k_2[H][HI] \qquad ...(19.11)$$

Note that H is formed as per Eq. 19.7 and is used as per Eq. 19.8.

or $$k_2[H][HI] = I_a \qquad ...(19.12)$$

Using Eqs. 19.10 and 19.12, we get,

$$\frac{-d[HI]}{dt} = 2I_a \qquad ...(19.13)$$

Experimentally it has been observed that the quantum efficiency for HI decomposition is 2 (Have you worked out SAQ 1?). It is worth noting that the rate of decomposition of HI depends on the intensity of the absorbed light as per Eq. 19.13.

Example 5

Photochemical Reaction between H_2 and Br_2

Hydrogen and bromine combine at wavelengths below 511 nm to give HBr as per the mechanism given below. Let us calculate the rate of formation of HBr and also the quantum efficiency for this reaction.

$$Br_2 + h\nu \rightarrow Br + Br \qquad \text{Rate of photolysis} = I_a \qquad \text{... (19.14)}$$

$$Br + H_2 \xrightarrow{k_2} HBr + H \qquad \text{... (19.15)}$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br \qquad \text{... (19.16)}$$

$$H + HBr \xrightarrow{k_4} H_2 + Br \qquad \text{... (19.17)}$$

$$Br + Br \xrightarrow{k_5} Br_2 \qquad \text{... (19.18)}$$

The rate of formation of HBr can be written as,

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \qquad \text{.. (19.19)}$$

Note that Br and H are active species and we can apply steady state approximation for these two.

$$\frac{d[Br]}{dt} = 0 = 2I_a - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2 \qquad \text{...(19.20)}$$

The coefficient 2 in $2I_a$ and $2k_5[Br]^2$ are due to the formation or disappearance of two bromine atoms in the respective steps.

$$\frac{d[H]}{dt} = 0 = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] \qquad \text{... (19.21)}$$

Adding Eqs. 19.20 and 19.21 and rearranging we get

$$2k_5[Br]^2 = 2I_a \qquad \text{... (19.22)}$$

or

$$[Br] = (I_a/k_5)^{1/2} \qquad \text{... (19.23)}$$

Rearranging Eq. 19.21 and using Eq. 19.23 we get,

$$[H] = \frac{k_2[Br][H_2]}{k_4[HBr] + k_3[Br_2]} = \frac{k_2[H_2]\,(I_a/k_5)^{1/2}}{k_4[HBr] + k_3[Br_2]} \qquad \text{... (19.24)}$$

Using Eqs. 19.19, 19.23 and 19.24,

$$\frac{d[HBr]}{dt} = k_2(I_a/k_5)^{1/2}[H_2] + \{k_3[Br_2] - k_4[HBr]\}\left[\frac{k_2[H_2]\,(I_a/k_5)^{1/2}}{k_4[HBr] + k_3[Br_2]}\right]$$

$$= \frac{2k_2k_3(I_a/k_5)^{1/2}[H_2][Br_2]}{k_4[HBr] + k_3[Br_2]}$$

Dividing the numerator and the denominator of R.H.S by $k_3[Br_2]$,

$$\frac{d[HBr]}{dt} = \frac{2k_2k_5^{-1/2} I_a^{1/2}[H_2]}{1 + k_4[HBr]/k_3[Br_2]} \qquad \text{...(19.25)}$$

$$\frac{d[HBr]}{dt} \propto I_a^{1/2} \qquad \text{... (19.26)}$$

This shows that the rate of hydrogen bromide formation is proportional to the square root of absorbed intensity. This has been proved experimentally.

In the above two cases, we derived rate expressions. Next, we shall study the reaction between H_2 and Cl_2 in a qualitative way, and then, study the principles of flash photolysis.

Hydrogen-chlorine Reaction

The quantum efficiency for the photochemical combination of hydrogen and chlorine is very high. When exposed to light of wavelength 478 nm, the primary process in the photochemical reaction is the decomposition of chlorine,

$$Cl_2 + h\nu \rightarrow 2\,Cl \qquad \text{... (19.27)}$$

This is followed by the following secondary processes:

$$Cl + H_2 \rightarrow HCl + H \qquad \text{... (19.28)}$$

$$H + Cl_2 \rightarrow HCl + Cl \qquad \text{... (19.29)}$$

The reaction between Cl and H_2 (Eq. 19.28) is exothermic and much fast. This results in the propagation of chain reaction with high quantum efficiency. The chain-terminating step is the recombination of chlorine atoms on the walls of the vessel to form chlorine molecule.

$$Cl + Cl \rightarrow Cl_2 \qquad \text{... (19.30)}$$

Next we shall explain briefly the main features of flash photolysis. Flash photolysis is useful in detecting the short-lived intermediates in a reaction sequence. The reaction mechanisms are proposed based on flash photolysis results.

Flash Photolysis

Flash photolysis was developed by Norrish and Porter in 1949. In ordinary photolysis, the steady state concentrations of the intermediates are so small that these cannot be detected by absorption spectrophotometers. In flash photolysis, a high-intensity flash of microsecond duration is used for photolysing the substance and the products are identified using absorption spectrophotometers. The flash duration must match the decay rate of the intermediates. Flash lamps work for a time of around 15 μs. This restricts their use to the study of intermediates of life time around 100 μs. In recent years, laser flash sources have been developed. The flash duration is around 10^{-9} s.

As far as this section is concerned, make sure that you understand the derivations for calculating the rate of decomposition of hydrogen iodide and the rate of formation of hydrogen bromide. This could help you in arriving at the rate expressions for simple photochemical reactions for which reaction sequence (like Eq. 19.14 to Eq. 19.18) is known. You can build up confidence by answering the SAQ given below. The aim of this SAQ is to make you derive expression for the rate of formation of carbon monoxide in the photolysis of acetaldehyde. You are guided through a series of steps with helpful hints. This guidance has added to the length of the problem. Don't mind it!

SAQ 4

Look at the reaction sequence for the photolysis of acetaldehyde:

$$CH_3CHO + h\nu \rightarrow CH_3 + CHO \quad \begin{matrix}\text{Rate of}\\ \text{photolysis}\end{matrix} = I_a \qquad \text{...(1)}$$

$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO \qquad \text{...(2)}$$

$$CH_3CO \xrightarrow{k_3} CH_3 + CO \qquad \text{...(3)}$$

$$CH_3 + CH_3 \xrightarrow{k_4} C_2H_6 \qquad \text{...(4)}$$

I_a is the absorbed light intensity and it represents the rate of photochemical excitation (as per Eq. (1)).

Using the above mechanism, derive expressions for the following:

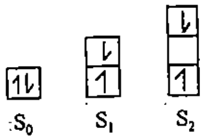
i) $\frac{d[CH_3CO]}{dt}$ ii) $\frac{d[CH_3]}{dt}$

(**Hints:** CH_3CO and CH_3 are active species. CH_3CO is formed as per Eq. (2) and consumed as per Eq. (3). CH_3 is formed as per Eqs. (1) and (3), and used up as per Eqs. (2) and (4). The answers for (i) and (ii) are to be arrived at using Eqs. 19.21 and 19.22 as models. Note that as per Eq. (4), two CH_3 radicals are consumed for every molecule of ethane formed).

iii) Derive the combined expression for $\frac{d[CH_3CO]}{dt} + \frac{d[CH_3]}{dt}$

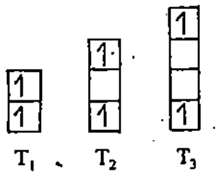
(**Hint:** Add up the expressions you have got as answers for (i) and (ii)).

For a 2-electron system, the first three singlet states are represented below :



Note that $E_{s_2} > E_{s_1} > E_{s_0}$, where E stands for the energy of a particular level.

Similarly, the first three triplet states are represented below for a 2-electron system:



$E_{T_3} > E_{T_2} > E_{T_1}$

iv) Find the relationship between $[CH_3]$ and I_a.

(**Hint:** Rearrange the answer for (iii)).

v) State the relationship between $\frac{d[CO]}{dt}$ and $[CH_3CO]$.

(**Hint:** Use Eq. (3)).

vi) Find the relationship between the rate of formation of CO and the absorbed light intensity.

(**Hints:** First combine answers for (v) and (i). Then use the answer for (iv)).

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19.6 PHOTOPHYSICAL PROCESSES

The light absorbed by a molecule is not always used up in producing a chemical reaction. The absorbed energy can be lost through various physical processes also. In this section, we examine such physical processes.

The absorption of ultraviolet or visible light results in the increase of electronic energy from the ground state to the excited state. Usually electronic excitation is also accompanied by an increase in the rotational and vibrational energy levels. In our discussion, for convenience, we depict only transitions between electronic energy levels. In order to understand the nature of electronic transitions, it is essential to know the concept of spin multiplicity. A molecule with electrons paired and with anti-parallel spins is said to be in the singlet ground state (S_o). An excited molecule with **two of its electrons unpaired and, with anti-parallel spins** is said to be in the excited singlet state such as S_1, S_2, S_3, ... etc. An excited molecule with **two of its electrons unpaired, but with parallel spins** is said to be in the excited triplet state such as T_1, T_2, T_3, ... etc.

Normally excitation of a ground state molecule leads only to one of the excited singlet states. But in some specified cases, direct excitation from S_o to a triplet level is possible. We restrict our discussion to $S_o \rightarrow S_1$, $S_o \rightarrow S_2$ etc. transitions only.

Multiplicity of state is given by the expression $2S + 1$, where S (note the italicised type) is the sum of spin values of electrons. This symbol S should not be confused with S (Roman type) for singlet state.

Normally a molecule in the S_o state on absorbing a quantum of light gets two of its paired electrons unpaired and gets transferred to S_1 or S_2 or S_3 .... etc. levels, but not to T_1 or T_2 or T_3 .... etc levels. That is, due to excitation, spin multiplicity is not generally altered. This condition is called the selection rule for electronic transition. In other words, absorption of energy by the molecule in the ground state leads to allowed transition such as $S_o \rightarrow S_1$, $S_o \rightarrow S_2$, $S_o \rightarrow S_3$ and so on. Such excitations and the subsequent energy loss while reaching the ground state are shown by Jablonski diagram (Fig. 19.5). The solid arrows pointing upwards refer to absorption of energy. The solid arrows pointing downwards refer to energy emission as light, known as radiative transitions. The wavy horizontal arrows stand for transition between excited singlet and triplet states without energy loss, while wavy vertical arrows stand for transitions between singlet-singlet or triplet-triplet levels with energy loss as heat (the later is not shown in Fig. 19.5). These wavy arrows stand for nonradiative transitions (transitions without light emission).

Imagine a molecule in the singlet state. It has two electrons with anti-parallel spins (such as ↑↓). Then, sum of the electron spins

$$S = +\frac{1}{2} - \frac{1}{2} = 0$$

Hence multiplicity

$$= 2S + 1 = (2 \times 0) + 1 = 1$$

In Fig. 19.5, the excitation from the singlet ground state to the excited singlet levels

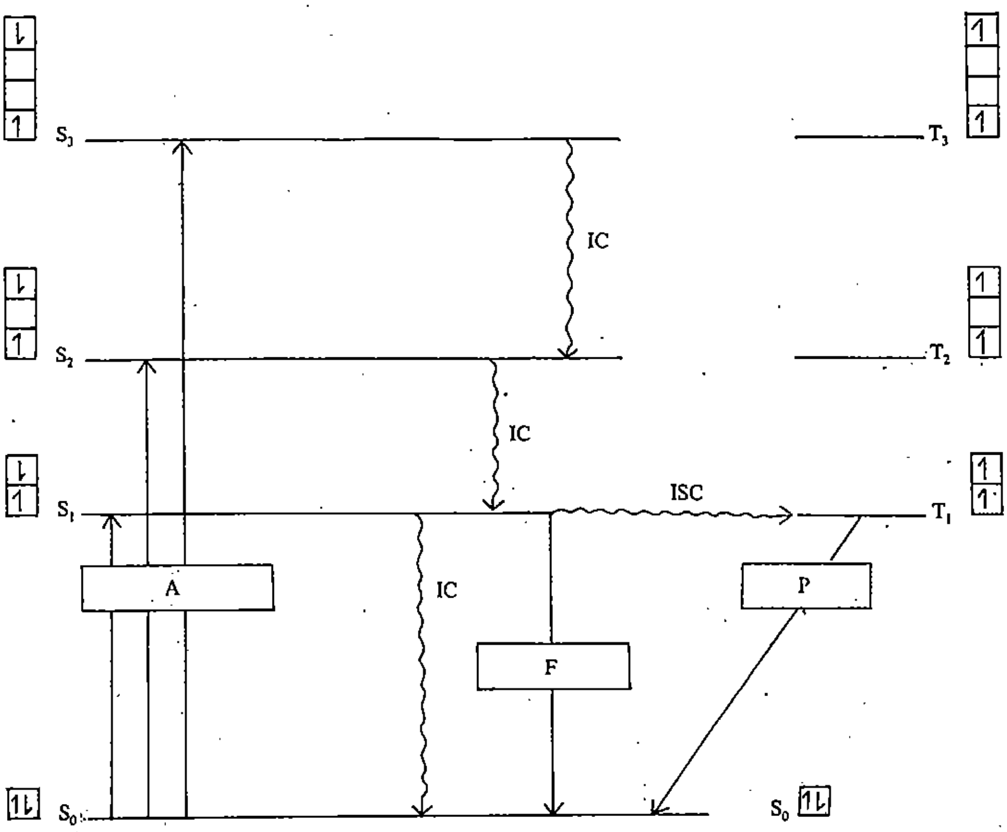


Fig. 19.5: Jablonski diagram

Thus the singlet state has two electrons with anti-parallel spins and its $(2S+1)$ value is equal to 1. In the presence of a magnetic field, a singlet state does not split further.

A molecule in the triplet state has two electrons with parallel spins (such as $\uparrow\uparrow$). The sum of electron spins

$$= S = \frac{1}{2}+\frac{1}{2} = 1$$

Hence the multiplicity $= (2S+1) = 3$

So, a molecule in the triplet state has two electrons with parallel spins and its $(2S+1)$ value is equal to 3. In the presence of a magnetic field, a triplet state splits into three energy levels.

S_1, S_2 and S_3 are shown by vertical arrows marked A. The excited species at S_2 and S_3 have very short lifetimes and these species, quickly lose their energy as heat to the medium in about 10^{-11} second and reach S_1 level. Such a singlet-singlet transition is called an internal conversion (IC). The molecule at S_1 state has a life time of $10^{-8} - 10^{-10}$ second. The system at S_1 may undergo any of the following transitions:

A = Absorption of quanta leading to excitation to S_1, S_2 and S_3 levels. Note the antiparallel spins at various S levels.

IC = Internal conversion from S_3 to S_2, from S_2 to S_1 and from S_1 to S_o.

F = Fluorescence; a transition from $S_1 \rightarrow S_o$ with light emission.

ISC = Intersystem crossing ; $S_1 \rightarrow T_1$ transition. Note the parallel spins at various T levels.

P = Phosphorescence; a transition from $T_1 \rightarrow S_o$ with light emission.

For clarity, transitions to and fro T_2 and T_3 are not shown.

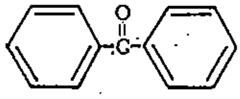
The name "fluorescence" is derived from the name of the mineral, "fluorite", which emits visible light on exposure to ultraviolet radiation.

i) Fluorescence

The excited molecule could undergo the transition, $S_1 \rightarrow S_o$, with the emission of light. This phenomenon is called fluorescence (F). Since $S_1 \rightarrow S_o$ transition is allowed by selection rule, it is very fast. In other words, substances fluoresce in the presence of the exciting radiation. Once the exciting radiation is stopped, fluorescence stops.

ii) Internal Conversion

The excess energy may be lost as heat while $S_1 \rightarrow S_o$ transition takes place which is again a case of internal conversion and a radiationless transition.



Benzophenone.

iii) Intersystem Crossing

The excited molecule could cross over to the first triplet state through $S_1 \rightarrow T_1$ transition. Such a transition involves spin inversion. For such intersystem crossing (ISC) to be efficient, the energy gap between S_1 and T_1 levels must be low.

Ketones have very low energy gap between S_1 and T_1 levels and have high efficiency for intersystem crossing. Thus benzophenone has 100% efficiency for intersystem crossing. Compared to ketones, aromatic hydrocarbons are less efficient in intersystem crossing and olefins are still less efficient. Let us now study two of the processes by which the molecule in the triplet state could reach the ground state.

1) **Phosphorescence**

An interesting physical process by which an excited species at T_1 level may undergo transition to S_o level is by emitting light ; $T_1 \rightarrow S_o$ transition with emission of light is called **phosphorescence (P).** This is a process with a spin change and is a forbidden transition. Hence, in contrast to fluorescence, light emission during phosphorescence is slow and it lasts even after the removal of exciting radiation.

"Phosphorescenc" is derived from "phosphorus" which glows in dark although it is not strictly phosphorescent (see Sec. 19.9).

2) **Energy Transfer**

Another process by which a molecule in the triplet state (called a donor molecule) may lose its excess energy is by energy transfer to an acceptor molecule.This is an instance of **sensitisation** which we shall discuss in Sec. 19.7.

Fluorescence and phosphorescence are exhibited by those substances which do not undergo chemical reaction at the wavelength of radiation.

In this section, we have dealt with some of the important physical processes only. Let us now see some of the applications of the study of the physical processes. Study of fluorescent behaviour of substances has led to the development of fluorescence spectroscopy. Using spectrofluorometers, it is possible to identify several fluorescing substances present in the same solution, provided they have sufficiently different fluorescent spectra. This method is both sensitive and selective. Even substances with a low concentration such as 10^{-9} g/cm^3 could be detected. For example, this method is quite useful in the analysis of drugs, pesticides and atmospheric pollutants which are present in trace amounts. Studies based on fluorescence and phosphorescence provide important data on the properties of excited states such as lifetime, energy and electronic configuration.

On the commercial side, fluorescent lamp is one of the applications of the phenomenon of fluorescence. A fluorescent lamp consists of a glass tube with

- a small amount of mercury,
- two electrodes, and
- a coating of phosphor.

A phosphor is a solid substance which emits fluorescent light when excited by ultraviolet radiation. The electrodes initiate an electric arc which helps in vaporizing and exciting mercury atoms. The excited mercury atoms emit ultraviolet radiation. The phosphor, being excited by ultraviolet radiation, emits fluorescence.

Some other commercial applications of fluorescence are given below:

- Optical brighteners are added to detergents to give extra–brightness to the clothes. Optical brighteners fluoresce in sunlight.
- Fluorescent paints are manufactured using suitable additives.
- TV screens of different colours are produced using phosphors.

Although molecules in the excited singlet and triplet states could show interesting chemical behaviour, their studies are included in Unit 14 of the course on Organic Reaction Mechanisms. In the next section, we shall discuss photosensitisation ; this discussion could make you understand how a substance gains photochemical activity in the presence of another photochemically excited substance. Based on the materials of this section, answer the following SAQ.

SAQ 5

State two differences between fluorescence and phosphorescence.

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19.7 PHOTOSENSITISATION

Photosensitisation is the process of exciting a molecule by energy transfer from an excited molecule. In this process, a donor molecule (D) absorbs a quantum light and forms an excited molecule (D^*). The excited donor molecule then transfers its excitation energy to an acceptor molecule (A) in the ground state in order to excite it. This can be explained using the following reaction sequence:

Light absorption : $D + h\nu \rightarrow D^*$

Sensitisation : $D^* + A \rightarrow A^* + D$

The donor molecule is called the **sensitiser**. In Sec. 19.6, we mentioned about such energy transfer by the excited molecule. The excited acceptor molecule A^* could take part either in chemical reactions or in physical processes which we shall discuss now.

Photosensitised Chemical Reactions

If the excited molecule A^* has obtained sufficient energy, it will get dissociated and start a chemical reaction. The advantage in photosensitised dissociation of a molecule is that it is enough to transfer energy equivalent to its bond enthalpy to dissociate it. It is so since the photosensitised molecule gets dissociated in the ground state. This is in contrast to direct photochemical decomposition for which much higher energy is required due to the necessity of exciting a molecule to upper electronic state (see Sec. 19.4). Thus the energy required for photosensitised dissociation of a molecule is less than that for photochemical dissociation.

Let us consider an example. When irradiated with 253.7 nm light, hydrogen and oxygen react in presence of mercury vapour but not in its absence. Mercury vapour acts as a sensitiser. The reaction sequence is given below:

$$Hg + h\nu \rightarrow Hg^*$$

$$Hg^* + H_2 \rightarrow H + H + Hg$$

$$H + O_2 \rightarrow OH + O$$

The chain reaction continues further. The energy transferred to hydrogen molecule by excited mercury atom is equal to 472 kJ mol^{-1} (as per Eq. 19.4 where $\lambda = 253.7$ nm). This energy is sufficient for thermal dissociation of hydrogen since its bond enthalpy is 436 kJ mol^{-1}(see Table 19.2). Note that excited mercury atom cannot directly dissociate oxygen molecule since its bond enthalpy is higher (497 kJ mol^{-1}). Further in the absence of mercury vapour, light of 253.7 nm (or 472 kJ mol^{-1} energy) cannot photolyse hydrogen or oxygen directly, since the energies needed for their photochemical dissociation are much higher (1420 kJ mol^{-1} and 682 kJ mol^{-1}, respectively). Hence mercury vapour is essential as a sensitiser for H_2–O_2 photochemical reaction at λ = 253.7 nm.

A well-known photosensitised reaction is photosynthesis. Chlorophyll ("chl") and other plant pigments act as photosensitisers in the synthesis of starch from carbon dioxide and water. A simplified reaction sequence is as follows:

$$chl + h\nu \rightarrow chl^* \quad \text{Starch}$$

$$chl^* + CO_2 + H_2O \rightarrow \frac{1}{n}(CH_2O)_n + O_2 + chl$$

Chlorophyll is the name given for a group of compounds with minor variation in structure. Chlorophyll-*a* absorbs effectively in the red region of sunlight; the red light is in abundance in sunlight.

The reaction mechanism is very complex. Energy calculations show that apart from chlorophyll, there must be other coloured light-absorbing materials (pigments) which also provide energy required for the synthesis of starch.

Photosensitisation is frequently used by chemists for preparing compounds which cannot be formed by thermal or direct irradiation methods.

Sensitised Fluorescence

Let us now discuss a physical process which proceeds through sensitisation. Thallium vapour does not give rise to fluorescence when directly irradiated with light of wavelength 253.7 nm. But if mercury vapour is also included in the reaction vessel, thallium exhibits fluorescence. Mercury atoms get excited first and transfer energy to thallium atoms to excite them. The excited thallium atoms emit fluorescence as they go down to the ground level.

Using the ideas learnt in this section, answer the following SAQ.

SAQ 6

Oxalic acid is not decomposed directly by light of wavelength, 335 nm. Irradiation in presence of uranyl (UO_2^+) ion results in the decomposition of oxalic acid to carbon monoxide and carbon dioxide.

i) How do you explain this reaction?

ii) Suggest a reaction sequence.

(**Note:** The above procedure was used in the earlier chemical actinometric method of determining the light intensity. Oxalic acid solution of known concentration was irradiated in presence of uranyl ion and the unreacted oxalic acid was estimated using potassium permanganate solution. From the amount of oxalic acid reacted, the intensity of light was calculated using ϕ for a particular wavelength.)

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19.8 APPLICATIONS OF PHOTOCHEMISTRY

We have earlier indicated the applications of the study of fluorescence, phosphorescence, flash photolysis and photosensitisation. Apart from the above, a few are worth mentioning.

Synthetic organic chemists have increasingly started using photochemical methods for synthesis due to greater efficiency and selectivity as compared to dark reactions. Photochemistry offers a method of conducting reactions which are not possible thermodynamically.

In the analysis of pollutants, photochemistry plays an important role. For example, photochemical studies have indicated how ozone layer is affected by chlorofluorocarbons (freon) used as refrigerants, solvents and spray- propellants. The simplest freon is CF_2Cl_2. Freon is chemically inert and remains as such for years. But when it reaches stratosphere (10 km to 50 km above the earth's surface), freon decomposes and gives out free chlorine atoms. These chlorine atoms can react with ozone decomposing it. This can cause depletion of ozone layer. It is a matter of serious concern since ozone layer protects our planet from low wavelength portion of sun's rays (290 nm-320 nm wavelength). Irradiation with such high energy radiation could produce skin cancer. As a result of photochemical studies, alternatives are tried for freon.

Three common types of cells used for converting light into electricity are given below :

i) Photoelectric cells or photo cells convert light into electricity using photosensitive cathode. (see Sec.19.3).

ii) Photovoltaic cells have two dissimilar silicon (or germanium) crystals in close contact. Irradiation of light causes flow of electrons from one crystal to other. Solar cells used in calculators are photovoltaic cells.

iii) Photogalvanic cells convert light into electricity through chemical reactions.

The present energy crisis has compelled the scientists to look for alternatives. Solar energy, if properly utilised through suitable photochemical reactions, could offer a solution for this energy problem. In this connection we now discuss the functioning of a photogalvanic cell which is helpful for solar energy conversion through chemical reactions.

Photogalvanic Cell

A reversible cell which converts light into electricity through an intermediate chemical reaction is called photogalvanic cell. It undergoes cyclic charging and recharging processes as explained below:

Charging in presence of light

Two substances undergo oxidation — reduction in presence of light.

$$OA_1 + RA_2 \xrightarrow{h\nu} OA_2 + RA_1$$

In this OA_1 and RA_1 refer to oxidised and reduced forms of substance 1, while OA_2 and RA_2 to those of substance 2. In this process, light is used in conducting a chemical reaction. This photochemical reaction is thermodynamically non-spontaneous ($\Delta G > 0$). By the above photochemical process, the cell is charged.

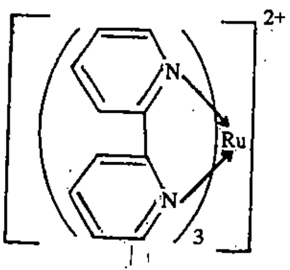
Discharging in the absence of light

In the absence of light, the reaction reverses spontaneously ($\Delta G < 0$).

$$OA_2 + RA_1 \rightarrow OA_1 + RA_2$$

The chemical energy gained during charging is converted into electrical energy and the cell is discharged.

An example of such a system is given below:



tris - (2, 2′ - bipyridine) ruthenium (II) ion

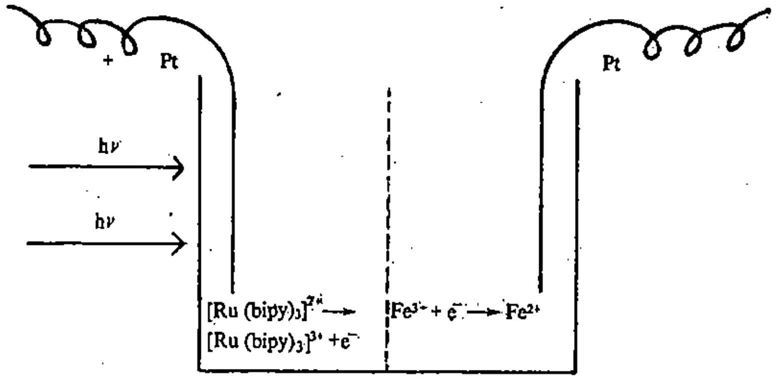


Fig. 19.6: Photogalvanic cell.

$$Fe^{3+} + \left[Ru(bipy)_3 \right]^{2+} \underset{dark}{\overset{h\nu}{\rightleftharpoons}} \left[Ru(bipy)_3 \right]^{3+} + Fe^{2+}$$

In this system, tris- (2,2′-bipyridine) ruthenium (II) - tris- (2,2′-bipyridine) ruthenium (III) and iron (II) - iron(III) are the two redox pairs. The platinum electrodes serve as electrical contacts (Fig. 19.6).

In the next section, we shall discuss chemiluminescence, which in a way, is the reverse of photochemical reaction.

Photochromism is the light induced reversible colour change. The colour change is brought about by reversible reactions. Photochromic sunglasses darken in sunlight and protect the eyes from the excess light. The sunglasses contain Ag^+ and Cu^+ ions and react reversibly as follows:

In presence of sunlight:

$Ag^+(s) + Cu^+(s) \rightarrow Ag(s) + Cu^{2+}(s)$

Silver formed is responsible for the darkening of the glasses.

In the absence of sunlight:

$Ag(s) + Cu^{2+}(s) \rightarrow Ag^+(s) + Cu^+(s)$

SAQ 7

Suggest a basic difference between galvanic cells (discussed in Unit 17) and photogalvanic cells.

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19.9 CHEMILUMINESCENCE

Chemiluminescence is the emission of light as a result of chemical reaction at room temperature. It must be clearly understood that chemiluminescence is not due to any photophysical process like fluorescence or phosphorescence. Some examples of chemiluminescence are given below :

- Glow of phosphorus is due to slow oxidation ; it is not due to phosphorescence as name suggests.
- Oxidation of Grignard compounds by air or oxygen results in greenish-blue luminescence.
- *Will-o-the-wisp* (mistaken as light produced by evil spirits) is the glow caused by the oxidation of decaying wood in marshy places.
- Emission of light by firefly is due to oxidation of some proteins in its body (this is also called bioluminescence).

19.10 SUMMARY

In this unit, we have discussed the physical and chemical processes accompanying light absorption.

- The laws of photochemistry have been stated and explained.
- Quantum yield has been defined and the method of determining it has been explained.
- The variation in energy requirements for photochemical and thermal dissociation has been discussed.
- The rate expressions have been derived for some photochemical reactions.

- The photophysical processes have been explained. The applications of fluorescence and phosphorescence have been stated.
- Photosensitisation has been explained with examples.
- Applications of photochemical studies have been listed.
- Chemiluminescence has been defined.

19.11 TERMINAL QUESTIONS

1) State two differences between a chemical reaction and a photochemical reaction.

2) If 10% of the energy of a 100 W incandescent bulb generates visible light having average wavelength 600 nm, how many quanta of light are emitted in 10 minutes?

$$(1\,W = 1\,J\,s^{-1})$$

(Hint: A tungsten filament bulb is an example of incandescent bulb. Incandescence is light emission due to intense heat.)

3) The extinction coefficient (ε) value of a substance is 4.66 $m^2\ mol^{-1}$. Calculate the concentration of its solution (in molarity) which has $\frac{I}{I_0} = 0.2$. The thickness of the cell is 1.00 cm.

4) At 478 nm, hydrogen and chlorine combine to give hydrogen chloride with a quantum efficiency of 1.00×10^6. If the absorbed intensity is $2.50 \times 10^{-3}\ J\ s^{-1}$, calculate the amount of hydrogen chloride formed in 10 minutes.

(Hint: The unit for amount is mole.)

5) State some of the applications of fluorescence and phosphorescence studies.

6) In the photochemical reaction between hydrogen and bromine at 511 nm wavelength, the first step is the photolysis of bromine but not of hydrogen. Why?

(Hint: Use Table 19.2.)

7) Fill in the blanks:
   i) Light emission through $S_1 \rightarrow S_o$ transition is called ....
   ii) Light emission through $T_1 \rightarrow S_o$ transition is called ....
   iii) The energy required for photolysis of bromine is ...... than its bond enthalpy.

8) Suggest a condition that should be fulfilled in order to photolyse a molecule using a sensitiser.

19.12 ANSWERS

Self-assessment Questions

1) Energy absorbed per photon $= \dfrac{6.626 \times 10^{-34} \times 3 \times 10^8}{250 \times 10^{-9}}$ joule photon^{-1}

$$= 7.95 \times 10^{-19} \text{ joule photon}^{-1}$$

Assume that the reaction is conducted for t seconds.

$$\text{Hence, } I_a = \frac{\text{Intensity in joule second}^{-1}}{7.95 \times 10^{-19} \text{ joule photon}^{-1}}$$

$$= \frac{4.18 \times 10^3 \text{ joule}/t \text{ second}}{7.95 \times 10^{-19} \text{ joule photon}^{-1}}$$

$$= \frac{5.26 \times 10^{21}}{t} \text{ photon second}^{-1}$$

$$\text{Amount of HI decomposed in 1 second} = \frac{1.85 \times 10^{-2}\ \text{mol}}{t\ \text{second}}$$

$$\frac{-dN_{HI}}{dt} = \frac{1.85 \times 10^{-2}}{t} \times 6.022 \times 10^{23}\ \text{molecule second}^{-1}$$

$$= \frac{1.114 \times 10^{22}}{t}\ \text{molecule second}^{-1}$$

$$\text{Using Eq. 19.3,}\ \phi_{HI} = \frac{-dN_{HI}/dt}{I_a} = \frac{1.114 \times 10^{22}/t}{5.26 \times 10^{21}/t}$$

$$= 2.12$$

2) Oxygen molecules could quench the excited species. Hence in presence of oxygen, ϕ_{HCl} is low.

3) For HI, the difference between photochemical dissociation energy and bond enthalpy is 68 kJ mol^{-1} and the excited hydrogen atom carries this excess energy.

4) i) $\frac{d[CH_3CO]}{dt} = 0 = k_2[CH_3][CH_3CHO] - k_3[CH_3CO]$

ii) $\frac{d[CH_3]}{dt} = 0 = I_a - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] - 2k_4[CH_3]^2$

iii) $\frac{d[CH_3CO]}{dt} + \frac{d[CH_3]}{dt} = 0 = I_a - 2k_4[CH_3]^2$

iv) $[CH_3] = \left(\frac{I_a}{2k_4}\right)^{1/2}$

v) $\frac{d[CO]}{dt} = k_3[CH_3CO]$

vi) $\frac{d[CO]}{dt} = k_2[CH_3][CH_3CHO]$

$$= k_2\left(\frac{I_a}{2k_4}\right)^{1/2}[CH_3CHO]$$

5) The light emission during fluorescence is due to $S_1 \rightarrow S_o$ transition. Fluorescence, being due to an allowed transition, is quite fast and stops as soon as exciting source is removed.

The light emission during phosphorescence is due to $T_1 \rightarrow S_o$ transition. Since this transition is forbidden, it is slow and it persists even if the exciting source is removed.

6) i) UO_2^+ ion acts as a photosensitiser and facilitates the decomposition of oxalic acid.

ii) $UO_2^+ + h\nu \rightarrow (UO_2^+)^*$

$(UO_2^+)^* + H_2C_2O_4 \rightarrow UO_2^+ + H_2O + CO + CO_2$

7) In a galvanic cell, the potential difference is due to conversion of chemical energy into electrical energy.

In a photogalvanic cell, light energy is converted into chemical energy, which is then, converted into electrical energy.

Terminal Questions

1) A photochemical reaction could take place even if ΔG is positive. For a chemical reaction to take place, ΔG must be negative at a given temperature and pressure.

In a photochemical reaction, the reacting molecules get the excitation energy through light absorption. In a chemical reaction, the reacting molecules get the activation energy through collisions.

2) A 100 W bulb emits 100 J s^{-1} of which 10 J s^{-1} comes out as light.

$$\text{Energy per quantum} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{600 \times 10^{-9}} \text{ joule photon}^{-1}$$

$$= 3.31 \times 10^{-19} \text{ joule photon}^{-1}$$

$$\left\{\begin{matrix}\text{Number of quanta} \\ \text{emitted per second}\end{matrix}\right\} = \frac{\text{Energy emitted per second}}{\text{Energy per photon}}$$

$$= \frac{10 \text{ joule second}^{-1}}{3.31 \times 10^{-19} \text{ joule photon}^{-1}}$$

$$= 3.02 \times 10^{19} \text{ photons second}^{-1}$$

$$\left\{\begin{matrix}\text{Number of quanta emitted} \\ \text{in 10 minutes}\end{matrix}\right\} = 3.02 \times 10^{19} \times 600 \text{ photons}$$

$$= 1.81 \times 10^{22} \text{ photons}$$

3) $I/I_o = 0.2$; so, $\frac{I_o}{I} = 5$

$$A = \log I_o/I = 0.699 = \varepsilon c l$$

$$c = \frac{0.699}{\varepsilon l} = \frac{0.699}{4.66 \times 1.00 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}}$$

$$= 15 \text{ mol m}^{-3}$$

$$= 15 \times 10^{-3} \text{ mol dm}^{-3} = 0.015 \text{ M}$$

$1 \text{ M} = 1 \text{ mol dm}^{-3}$ and
$1 \text{ m}^{-3} = (10 \text{ dm})^{-3}$
$= 10^{-3} \text{ dm}^{-3}$

4) $$\text{Energy per quantum} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{478 \times 10^{-9}} \text{ joule photon}^{-1}$$

$$= 4.16 \times 10^{-19} \text{ joule photon}^{-1}$$

$$I_a \begin{pmatrix}\text{Number of quanta} \\ \text{per second}\end{pmatrix} = \frac{\text{Intensity in joule second}^{-1}}{\text{Energy per photon}}$$

$$= \frac{2.50 \times 10^{-3} \text{ joule second}^{-1}}{4.16 \times 10^{-19} \text{ joule photon}^{-1}}$$

$$= 6.01 \times 10^{15} \text{ photons second}^{-1}$$

$$\phi_{HCl} = \frac{\frac{dN_{HCl}}{dt}}{I_a}; \text{ hence, } \frac{dN_{HCl}}{dt} = \phi_{HCl} \cdot I_a$$

$$\text{i.e., } \frac{dN_{HCl}}{dt} = 6.01 \times 10^{15} \times 1.00 \times 10^{6} \text{ molecules second}^{-1}$$

$$= 6.01 \times 10^{21} \text{ molecules second}^{-1}$$

$$\left\{\begin{matrix}\text{Number of molecules of HCl} \\ \text{formed in 10 minutes}\end{matrix}\right\} = 6.01 \times 10^{12} \times 600 \text{ molecules}$$

$$= 3.61 \times 10^{24} \text{ molecules}$$

$$\left\{\begin{matrix}\text{Amount of HCl formed} \\ \text{in 10 minutes}\end{matrix}\right\} = \frac{3.61 \times 10^{24}}{6.022 \times 10^{23}} \text{ mole}$$

$$= 5.99 \text{ mole.}$$

5) See Sec. 19.6.

6) Light of wavelength 511 nm is just sufficient to photolyse bromine molecule. To photolyse hydrogen molecule directly, light of higher energy is required.

7) i) fluorescence ii) phosphorescence

iii) higher

8) The energy emitted by the excited sensitiser during its return to ground state should be atleast equal to the energy required for the thermal decomposition of the molecule.

UNIT 20: COLLOIDS AND MACROMOLECULES

Structure

20.1 INTRODUCTION

In unit 10 of this course we have discussed the properties of solutions. In a true solution, the solute particles are homogeneously distributed and are of the same molecular dimension as solvent particles. For example, a sugar solution contains sugar and water molecules. homogeneously distributed over the whole volume. Such solutions are called **molecular solutions** in order to distinguish them from solutions of macromolecules (i.e., molecules having large molar masses). On the other hand we have **coarse suspensions**; these are formed from substances which do not dissolve in the solvent but form two or more distinct phases with the solvent. An example is adding $CaCO_3$ to water. However, there does exist a third possibility where the size of the solute particle is much bigger than that of the solvent molecule, but is not large enough to be seen with naked eyes. Such a dispersion of particles of one material in another is called **Colloid**. In the early days, colloids were defined as a suspension of small particles in a continuous medium. However, we define a system to be in the colloidal state if particles of one or more of its components have dimensions in the range of 1 to 1000 nm. These are classified into three categories:

1) Colloidal dispersions,

2) Associated colloids, and

3) Solutions of macromolecules.

We shall discuss each of the above in this unit. Further we shall study the preparation of colloids, their properties and uses.

Objectives

After studying this unit, you should be able to

- define colloids and distinguish them from true solutions and coarse suspensions,
- describe methods for the preparation and purification of colloids,
- explain the characteristic properties of colloids,
- discuss factors responsible for the stability of colloids,
- describe various methods for the determination of the molar masses of polymers, and
- state some applications of colloids.

20.2 DIFFERENCES AMONG THE COLLOIDS, SOLUTIONS AND COARSE SUSPENSIONS

The colloidal systems differ from coarse suspensions and true solutions in a number of ways. The following discussion will make the differences clear.

i) Size

As mentioned earlier, the particle size of one of the phases in a colloid lies in the range 1 to 1000 nm. In the coarse suspensions, the size of the suspended particles is always larger than 1000 nm, whereas the dimensions of solute molecules in true homogeneous solutions are less than 1 nm.

ii) Filterability

Coarse suspensions can be easily filtered using ordinary filter papers so as to separate into two phases. The colloidal system cannot be filtered using ordinary filter papers but need special ultrafilter papers (See Subsec. 20.3.2). Molecular solutions pass even through ultrafilter papers.

iii) Appearance

Coarse suspensions appear heterogeneous even to the naked eye whereas colloidal systems and molecular solutions appear clear and homogeneous (See Subsec. 20.6.3).

Membranes are thin, soft layer of animal or plant tissue or synthetic polymer.

iv) Diffusibility

Solute molecules in molecular solutions diffuse through membranes rather rapidly, while the particles in a coarse suspension or in a colloidal system diffuse very slowly.

In the next section, we shall discuss different types of colloidal dispersions.

20.3 COLLOIDAL DISPERSIONS

Some gas mixtures show inhomogeneous regions at extremely high pressures.

A colloidal dispersion is a heterogeneous system in which the colloidal particles (the dispersed phase) are dispersed in a continuous phase (the dispersion medium). The colloidal dispersions can be further classified on the basis of the state of matter in which the two phases exist. Table 20.1 lists the colloidal dispersions of various types with their common names and suitable examples.

It may be noted that due to the mutual solubility of all gases in all proportions, it is not possible to have a colloidal dispersion of one gas in another gas.

In some cases where the dispersion medium is either a liquid or gas, the colloidal dispersions are called sols. The dispersion medium is characterised by the addition of a prefix to the word, sol. Some examples are hydrosol, aerosol and alcosol.

Table 20.1 : Various Types of Colloidal Dispersions

Dispersed phase	Dispersion medium	Common name	Example
Liquid	Gas	Aerosol (of liquid particles)	Mist
Liquid	Liquid	Emulsion	Cream
Liquid	Solid	Solid Emulsions and Gels	Jellies
Solid	Gas	Aerosol (of solid particles)	Smoke
Solid	Liquid	Sol	Hydrosol of $Fe(OH)_3$.
Solid	Solid	Solid suspensions	Precious stones
Gas	Liquid	Foam	Whipped Cream
Gas	Solid	Solid foam	Polystyrene

Based on the interaction between the colloidal particles and the medium, the solid-liquid sol could be further classified as (1) lyophilic and (2) lyophobic. "Lyophilic" literally means solvent loving. The lyophilic colloids are dispersions of polymeric molecules. There is a strong interaction between the dispersed particles and the dispersion medium.

In most cases, the lyophilic colloids are called gels. A gel is a semisolid mass of lyophilic sol in which all the solvent has been absorbed by the particles.

Examples

Starch in water, rubber in benzene, cellulose nitrate (collodion) in acetone, etc.

The word "lyophobic" means solvent hating. The lyophobic colloids are prepared by dispersing insoluble substances in a solvent. The lyophobic colloids are a collection of small molecules or formula units (where it is difficult to classify as a molecule).

Examples

Sols of gold, sulphur, ferric hydroxide, silver iodide, etc. Let us now discuss the methods of preparation of lyophilic and lyophobic sols.

20.3.1 Methods of Preparation

The preparation of lyophilic colloidal dispersions are quite straightforward. Generally, vigorous shaking of the dispersed phase with the dispersion medium results in lyophilic sols. Lyophobic sols, due to their low stability, present greater difficulty in their preparation. Such sols are usually prepared by the following methods:

A) **Condensation methods**

In these methods, small particles are coalesced together so as to produce particles of colloidal dimensions. Let us consider some examples.

1. **Bredig's Arc Method**

This is particularly suitable for the preparation of colloidal sols of metals. Two rods of the same metal (say, gold, or platinum) are placed in a suitable liquid (water or an organic solvent) containing small amount of alkali (Fig. 20.1).

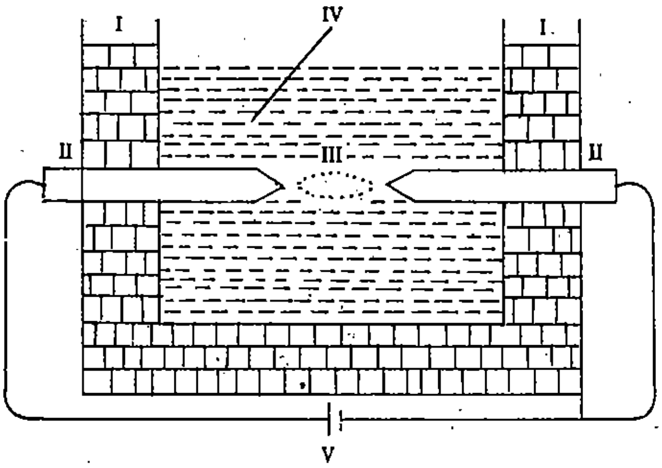

Fig. 20.1 Bredig's arc method: I. ice ; II. electrodes ; III. arc ; IV. solvent + alkali; V. power supply.

From metal sols, it is possible to precipitate metals by suitable methods (Sec. 20.6). The metals thus precipitated are in a finely divided state. In such a finely divided state, the metallic particles have a large surface area and are effective catalysts. (See Sec. 20.10)

An electric arc is struck between them. The heat produced by the arc converts metal into vapours. These vapours condense into liquid to give the required colloidal sol.

2. Through Chemical Reactions

Many molecules produced in a chemical reaction aggregate to give particles of colloidal dimensions. For example, sulfur sols can be prepared by the oxidation of hydrogen sulphide:

$$2\,H_2S + O_2 \rightarrow 2\,S + 2\,H_2O$$

The gold sol can be prepared by the reduction of $HAuCl_4$ ($AuCl_3 + HCl$) using reducing agents like formaldehyde or hydrazine. Metal sols and metal hydroxide sols, which are found to be very useful in many industries, are normally prepared by this method.

3. Use of a Second Solvent

A substance may form a molecular solution in one liquid but may be insoluble in another liquid. If the saturated solution of a substance is diluted with another liquid in which it is insoluble, it may lead to the formation of colloidal sol. The two liquids, however, should be miscible. Thus when a saturated solution of sulphur in alcohol is diluted with water, we get sol of sulphur in water.

B) Dispersion Methods

In this method, larger particles are broken down into smaller particles of colloidal dimensions. This can be achieved either by mechanical means or by the use of some reagents known as peptizing agents.

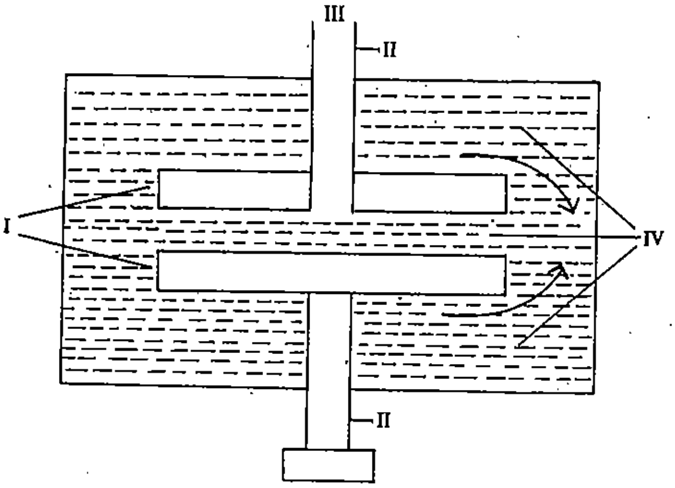

Fig. 20.2: A colloidal mill : I. heavy discs ; II. axle ; III. inlet for introducing the suspension of solid in the dispersion medium ; IV. sol ; the two arrows denote motion in the opposite directions.

1. Mechanical Method

The material to be converted into colloidal particles is introduced into a colloidal mill in which two discs rotate rapidly in opposite directions on a common axle (Fig. 20.2). The size reduction takes place due to the large force between the two discs. Many commercial colloids like printing ink and paints are prepared by this method.

2. Peptization

In this process, a precipitate is converted into colloidal dispersion by the addition of an electrolyte to the dispersion medium. The adsorption of suitable ions from the electrolyte causes the stabilisation of the colloidal particles. The electrolyte is called the peptizing agent. For example, in the preparation of ferric hydroxide sol, the freshly prepared precipitate of ferric hydroxide is taken in a beaker containing water and very small amount of peptizing agent, ferric chloride. The ferric ions, arising from the ionisation of ferric chloride, are preferentially adsorbed on the surface of the $Fe(OH)_3$ particles. The positively charged particles of ferric hydroxide repel each other and are easily dispersed throughout the medium giving colloidal sol of ferric hydroxide. Similarly the addition of a common ion to precipitates of many other substances can lead to the formation of colloidal sols.

20.3.2 Methods of Purification

Any impurities present in a colloidal sol renders it unstable and therefore it is necessary to purify it before undertaking any studies on it. The following methods are generally used for the purification of sols.

1. Ultrafiltration

We know that a colloidal system cannot be filtered using ordinary filter papers but need special ultrafilter papers which can be prepared by reducing the pore size of ordinary filter papers or other porous materials. It is achieved by impregnating the filter paper with a solution of gelatin or collodion. Colloidal systems can then be filtered through ultrafilters and the process is known as ultrafiltration.

Gelatin : Animal protein which could form gel.

Collodion : Cellulose nitrate.

A pure sol is obtained by passing the impure sample through ultrafilters which allow the soluble impurities to pass but not the colloidal particles. However, the method is very slow and not always successful.

2. Dialysis

A much better method of purification is dialysis. It is seen that colloidal particles cannot pass through certain semipermeable membranes like **parchment bag** while smaller particles or ions pass through them. In dialysis, we use such a membrane to separate the smaller particles from the colloidal particles. The method is illustrated in Fig. 20.3.

Parchment : The skin of a sheep, goat or other animal prepared for writing.

A bag of a suitable membrane containing the sol is suspended in a container through which fresh liquid is passed continuously. The ions or smaller molecules inside the bag diffuse out leaving the pure sol behind. The process of diffusion is made faster by using hot water instead of cold water in the process. It must however be kept in mind that excessive dialysis can lead to destabilisation of the sol and a precipitate may be obtained.

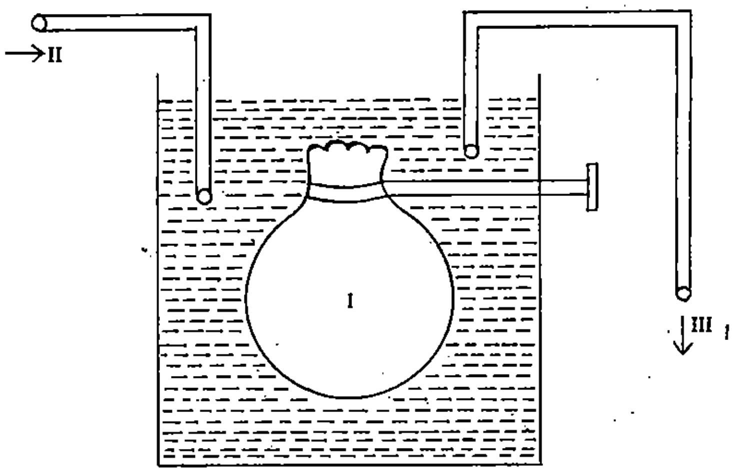

Fig. 20.3: Dialysis apparatus: I. sol in parchment bag ; II. water inlet; III. water outlet.

3. Electrodialysis

This modification of the process of dialysis is specially used when the impurities are ionic. The apparatus is shown in Fig. 20.4.

A parchment bag containing the sol is kept immersed in a liquid (generally water). Two electrodes are dipped in this liquid. When an electric field is applied across the electrodes, the positive ions move towards the cathode and the negative ions towards the anode through the membrane in the liquid. The rate of diffusion is considerably increased by the application of electric field and the process is quite quick.

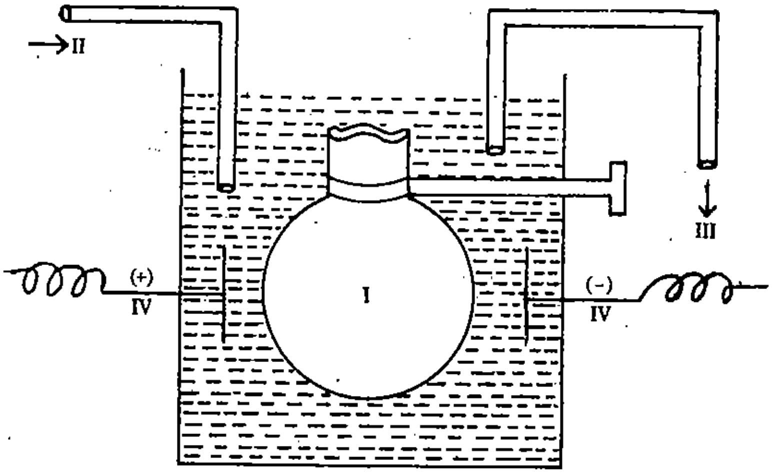

Fig. 20.4: Electrodialysis apparatus : I. sol in parchment bag; II. water inlet; III. water outlet; IV. electrodes.

SAQ 1

In order to prepare platinum in a finely divided state, a platinum sol is prepared using 1.00×10^{-6} m^3 of platinum. Assuming that each platinum particle in the dispersion is a sphere of radius 50 nm., calculate the total surface area of all the platinum particles in the sol in cm^2 unit.

Hints : i) Volume of each platinum particle is given by the formula, $4/3\ \pi r^3$.

ii) Calculate the number of particles that could be formed from 1.00×10^{-6} m^3 platinum

$$\left(= \frac{1 \times 10^{-6}}{4/3\ \pi r^3} = n \text{ (say)} \right)$$

iii) Surface area of each platinum particle is given by the formula, $4\pi r^2$

iv) Total surface area of all the platinum particles in the sol $= 4\pi r^2 n$

Finally change the unit into cm^2.

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SAQ 2

Suggest a peptizing agent useful in preparing silver chloride sol from solid silver chloride.

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20.4 ASSOCIATED COLLOIDS

The molecules of certain substances (soaps, dyes etc.) on dissolution in a solvent have strong tendency to aggregate (or associate). The size of these aggregates lies in the colloidal range. These aggregates are called micelles. The systems in which the solute molecules aggregate to give particles of colloidal dimensions are called associated colloids. The molecules of associated colloids have both lyophobic and lyophilic groups. Let us consider one example in detail. Soap molecules have a general formula, $RCOO^- M^+$, where R is a straight chain of 10 to 20 carbon atoms and M^+ is Na^+ or K^+. We find that many properties of soap solutions such as surface tension, electrical conductivity and osmotic pressure show abrupt changes at a particular concentration of soap. This concentration is called critical micelle concentration (CMC). These observations have been explained by assuming that above the CMC, a substantial portion of the solute ions ($RCOO^-$) aggregate to form particles of colloidal dimension, called micelles. Experiments have confirmed the formation of micelles which usually contain 20 to 100 units depending on the concentration of soap and other substances in solution. The structure of soap micelle is shown in Fig. 20.5.

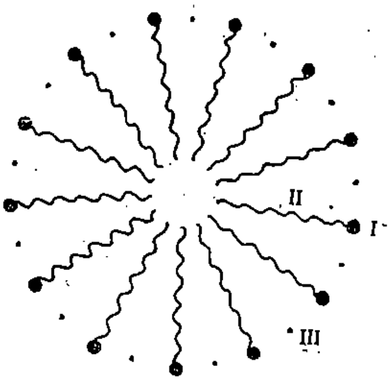


Fig. 20.5: Structure of a micelle: I. polar group; II. nonpolar group; III. counter ion.

A soap micelle has a spherical structure with the nonpolar hydrocarbon part inside the sphere and the polar RCOO$^-$group on its surface. The polar group strongly interacts with the water molecules. A number of M$^+$ ions are bound to the surface of the micelle as counter ions and this helps in reducing its charge considerably.The formation of micelle is reversible. The formation of micelle reduces the electrical conductivity of the electrolyte as well as the osmotic pressure of the solution. The soap solution acts as a solvent for hydrocarbons (grease) by incorporating the molecules of hydrocarbons into the interior of the micelle. The action of soap as a cleanser depends on this property of soap. We shall discuss this in Sec. 20.7.

These days **reverse micelles** are of great help in the study of enzyme–catalysed reactions. As their name implies, the polar part is inside (Fig.20.6) dipping in a small part of water and the nonpolar part is surrounded by an organic phase.

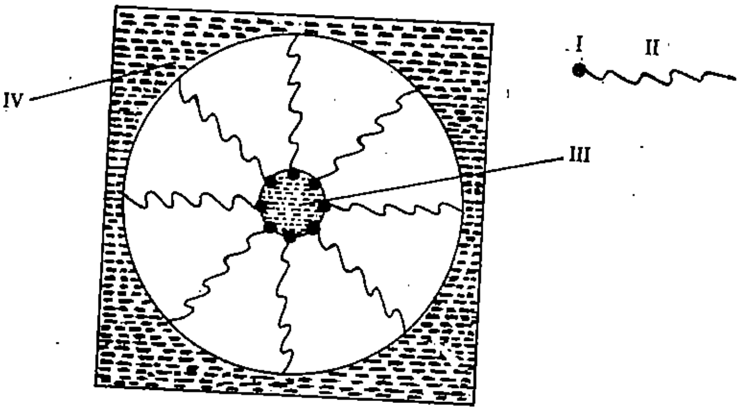


Fig. 20.6: Structure of a reverse micelle: I. polar group ; II. nonpolar group; III. water pool ; IV. organic phase.

The reverse miscelles have structural similarities to a cell in a living system.

The following SAQ is based on the charge calculation of a micelle. Try it.

SAQ 3

Imagine that initially there are 100 Na$^+$ ions and 100 RCOO$^-$ ions and that all the RCOO$^-$ ions aggregate into a micelle which binds 80 Na$^+$ ions on the surface as counter ions.

i) What is the charge on the micellar ion ?

Hint : Charge on the micellar ion

= Charge due to all the RCOO$^-$ ions– Charge due to Na$^+$ ions present as counter ions.

During the formation of the micellar ion, charge due to all the RCOO$^-$ ions is decreased by the counter ions .

ii) Calculate the number of ions present after micelle formation

Hint : Count the aggregate of $RCOO^-$ ions and the counter ions as one ion only.

iii) Can you explain the fact that micelle formation leads to decrease in electrical conductivity and osmotic pressure ?

....

....

....

20.5 MACROMOLECULAR SOLUTIONS

In addition polymerisation, the repeating unit has the same chemical composition as the monomer.

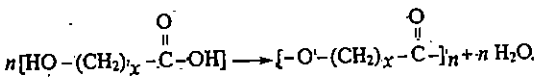
In condensation polymerisation, the repeating unit is different in chemical composition from the monomer. Water or a small molecule is eliminated during the formation of condensation polymer.

When a component in a true solution has molecules large enough (e.g., the molecule of a protein) to be in the colloidal range, even this is considered a colloidal solution. The reason is that the solutions of such macromolecules have properties similar to colloidal dispersions and same techniques are used to study them. Some of the naturally occurring macromolecules are starch, protein, rubber, cellulose, silicates, polyphosphates, plastic sulphur—just to name a few out of a large number. In addition, there is a large variety of macromolecules which are prepared synthetically. These macromolecules are commonly called polymers implying thereby that they are multiples of a monomeric unit. Generally, such molecules are formed by the polymerisation of a single monomer by the addition reaction as shown below :

$$n\ CH_2 = CHCl \rightarrow (-CH_2CHCl-)_n$$

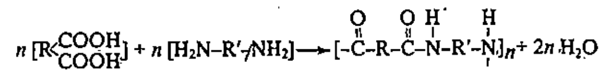
Vinyl chloride Polyvinyl chloride or PVC

However, some of the polymers are formed by condensation process e.g.,



$$n[HO-(CH_2)_x-\overset{\overset{O}{\|}}{C}-OH] \longrightarrow [-O-(CH_2)_x-\overset{\overset{O}{\|}}{C}-]_n + n\ H_2O$$

Hydroxy acid Polyester



$$n\,[R\!<^{COOH}_{COOH}] + n\,[H_2N-R'-NH_2] \longrightarrow [-\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R'-\overset{\overset{H}{|}}{N}]_n + 2n\,H_2O$$

Dicarboxylic acid Diamine Nylon (a polyamide)

The purpose of including polymers here is just to indicate that their behaviour in solution is similar to colloids but we will not study them in detail. The properties of macromolecular solutions depend to a great deal on the size and distribution of macromolecules in a sample. In the synthesis of polymers we get macromolecules with different molar masses depending on the reaction conditions. Thus, the determination of average molar mass becomes important in the studies of polymers. The average molar mass can be defined in different ways and experimentally obtained values depend on the method of determination. The two most commonly used ways to define the average molar mass are discussed below.

20.5.1 The Number Average Molar Mass

The average molar mass of the a polymer can be defined in a number of ways and even the experimentally obtained average molar mass values depend on the method of determination.

Let us assume that a sample contains many species of polymers where N_1, N_2, N_3 ...., are the number of polymer molecules of molar masses M_1, M_2, M_3 ....., respectively. Then the total mass of the sample is $N_1M_1 + N_2M_2 +$ .... and the total number of molecules is $N_1 + N_2 + N_3$ .... We define the number average molar mass, $\overline{M}_n$, of the sample as:

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + ...}{N_1 + N_2 + N_3 + ...} = \frac{\sum_i N_i M_i}{\sum_i N_i} \qquad ...(20.1)$$

where N_i is the number of molecules of the i^{th} species having molar mass M_i. If we divide each term in numerator and denominator by Avogadro number (N_A) we can write

$$\overline{M}_n = \frac{\sum_i \frac{N_i}{N_A} M_i}{\sum_i \frac{N_i}{N_A}} = \frac{\sum_i n_i M_i}{\sum_i n_i} \qquad \ldots (20.2)$$

In Eq. 20.2, N_i/N_A is the number of moles of ith polymer species.

where $n_i = N_i/N_A$ is the amount (number of moles) of a species having molar mass, M_i. Thus $\overline{M}_n$ is equal to the total mass of the sample divided by the total number of moles, n, of the sample or

$$\overline{M}_n = \frac{\sum_i n_i M_i}{n} = \sum_i \frac{n_i M_i}{n_i} = \sum_i x_i M_i \qquad \ldots (20.3)$$

where $n = \sum_i n_i$ and

$$x_i = \frac{n_i}{n}$$

= the mole fraction of the molecules for which molar mass is M_i.

This should become clear from the following example :

Example 1

Determine the number average molar mass of a polymer sample with the following distribution of molar masses :

N_i	5	5	10	10	5	5
$\frac{M_i}{\text{kg mol}^{-1}}$	1.000	2.000	50.000	10.000	12.000	20.000

Solution

Using Eq. 20.1 we get,

$$\overline{M}_n = \frac{(5 \times 1.000) + (5 \times 2.000) + (10 \times 50.000) + (10 \times 10.000) + (5 \times 12.000) + (5 \times 20.000)\ \text{kg mol}^{-1}}{5 + 5 + 10 + 10 + 5 + 5}$$

$$= 19.375 \text{ kg mol}^{-1}$$

The number average molar mass is sensitive to the species having low molar mass. The presence of such species as impurities can lead to very low estimates of average molar mass. The experimental determination of average molar mass is given in Sec. 20.9.

20.5.2 The Mass Average Molar Mass

Some methods for the determination of the molar mass depend on the effect produced by the masses of the polymer molecules instead of their numbers. Therefore, in the averaging process, the molar mass (M_i) of any particular molecule (i) is multiplied by its mass (w_i). The sum, $\sum_i w_i M_i$, for all the molecules is then divided by the total mass of the sample $\left(\sum_i w_i\right)$. Thus the mass average molar mass ($\overline{M}_w$) is given by

$$\overline{M}_w = \frac{\sum_i w_i M_i}{\sum_i w_i} \qquad \ldots (20.4)$$

$$\text{But } w_i = n_i M_i \qquad \ldots (20.5)$$

where n_i is the number of moles of the i^{th} species.

$$\overline{M}_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \qquad \ldots(20.6)$$

$$\text{or } \overline{M}_w = \frac{n_1 M_1^2 + n_2 M_2^2 + \ldots}{n_1 M_1 + n_2 M_2 + \ldots} \qquad \ldots(20.7)$$

where n_1, n_2, ... are the number of moles of species with molar mass M_1, M_2 ...., respectively in the polymer sample.

We can multiply the numerator and denominator in the R.H.S. of Eq.20.6 by Avogadro number, and get,

The transformation from Eq. 20.8 to Eq. 20.9 uses the following relationship :

$$n_i = \frac{N_i}{N_A}$$

or

$$N_i = n_i N_A$$

$$\overline{M}_w = \frac{\sum_i n_i N_A M_i^2}{\sum_i n_i N_A M_i} \qquad \ldots(20.8)$$

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \qquad \ldots(20.9)$$

where N_i is the number of molecules of i^{th} type.

Example 2

Calculate the mass average molar mass from the data given in Example 1.

Solution

Using Eq. 20.9,

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

$$= \frac{5(1.000)^2 + 5\,(2.000)^2 + 10\,(50.000)^2 + 10\,(10.000)^2 + 5\,(12.000)^2 + 5\,(20.000)^2}{(5 \times 1.000) + (5 \times 2.000) + (10 \times 50.000) + (10 \times 10.000) + (5 \times 12.000) + (5 \times 20.000)} \text{ kg mol}$$

i.e., $\overline{M}_w = 37.09 \text{ kg mol}^{-1}$

It can be seen that $\overline{M}_w$ is larger than $\overline{M}_n$. The ratio of $\overline{M}_w/\overline{M}_n$ is known as polydispersity index. In the next section,we shall discuss some of the properties of colloidal dispersions.

In addition to the above two molar mass equations, we sometimes use the following relationships also which we are not going to discuss in detail:

$$M_{rms} = \text{Root mean square molar mass} = \frac{\sum_i n_i M_i^2}{\sum_i n_i} \qquad \ldots(20.10)$$

$$\overline{M}_v = \text{Viscosity average molar mass} = \left(\frac{\sum_i n_i M_i^{(1+\alpha)}}{\sum_i n_i M_i} \right)^{1/\alpha} \qquad \ldots(20.11)$$

where α is a constant lying between 0.5 and 0.8.

Before proceeding to the next section, try to solve the following SAQ's.

SAQ 4

When will the polydispersity index be equal to one?

....

....

....

SAQ 5

Show that $M_{rms} = \overline{M}_n \times \overline{M}_w$.

....

....

....

20.6 PROPERTIES OF COLLOIDAL SYSTEMS

As mentioned earlier, colloidal systems show some characteristic properties which are different from true solutions and coarse dispersions. These properties can be classified as (1) physical (2) optical and (3) electrical. We shall study each of them separately.

20.6.1 Physical Properties

Sedimentation

Colloidal dispersions are usually quite stable and, do not settle easily. The rate of sedimentation can be increased by the use of an ultracentrifuge. The ultracentrifuge consists of a cylinder provided with a rotor that can be driven at a high speed. The rotational motion of the cylinder about its axis causes the particles to settle. The centrifugal force on the particles is generated by the rotational motion which is opposed by the frictional force. Due to these forces, the colloidal particles move outwards causing more concentration of the particles near the edge of the cylinder compared to the centre. The rate of sedimentation depends upon the size and shape of the particles.

Sedimentation: Deposition of an undissolved material

2. **Diffusibility**

We have already discussed in Sec. 20.2 that particles in a colloidal suspension diffuse very slowly through a membrane. Note that the colloidal particles cannot pass through ultrafilter papers or semipermeable membranes (like parchment bag) as mentioned in Sec. 20.3.

3. **Viscosity**

The viscocity of a solution containing macromolecules is high even at low concentrations. The measurement of viscosity of such a solution provides us a way of obtaining the molar mass of macromolecules (See Sec. 20.9).

4. **Colligative Properties**

Colloidal dispersions also show colligative properties just like a true solution. Out of the four colligative properties namely (i) the lowering of vapour pressure (ii) the depression of freezing point (iii) the elevation of boiling point, and (iv) the osmotic pressure, only the last one gives measurable values. The other three give too small a change to be usefully employed (See Sec. 20.9).

20.6.2 Kinetic Properties

Brown in 1827 observed that pollen grains suspended in water show continuous random motion. This motion is along short straight paths of different lengths and directions, as shown in Fig. 20.7.

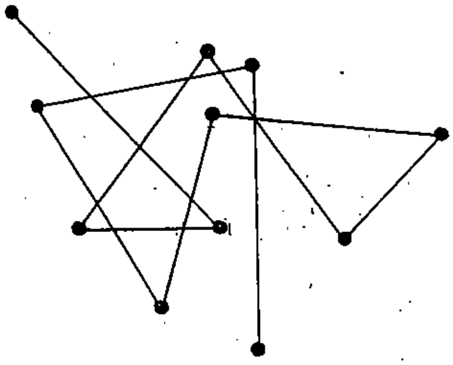


Fig. 20.7 : Brownian motion.

This type of motion is called Brownian motion in recognition of its discoverer. With proper lighting, Brownian motion of colloidal particles can also be viewed. This motion is not due to convection current in the fluid.

The Brownian motion of a colloidal particle is due to its bombardment by the molecules of the medium. A colloidal particle will acquire the same average kinetic energy (= 3/2 kT) as all other molecules in such motion. But due to its heavy mass, its speed will be much less compared to those of the molecules of the medium.

Example 3

Compare the root mean square speed of a water molecule with that of a colloidal particle having mass, 1.00×10^{-23} kg.

Solution

$$\text{Mass of water molecule } (m_1) = \frac{\text{Molar mass}}{\text{Avogadro constant}}$$

$$= \frac{0.018 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$\simeq 2.99 \times 10^{-26} \text{ kg}$$

$$\text{Mass of colloidal particle } (m_2) = 1.00 \times 10^{-23} \text{ kg}$$

From kinetic theory, we know

$$\frac{1}{2} m_1 \overline{u_1^2} = \frac{1}{2} m_2 \overline{u_2^2}$$

You could recollect that we derived the relationship between u_{rms} and the molar mass in Eq. 2.43 of Unit 2 of this course, although it was meant for gases.

where $\overline{u_1^2}$ and $\overline{u_2^2}$ are the mean square speeds of water molecules and colloidal particles respectively. Then their respective root mean square speeds (u_{rms1} and u_{rms2}) can be written as,

$$\sqrt{\frac{\overline{u_1^2}}{\overline{u_2^2}}} = \frac{u_{rms1}}{u_{rms2}} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{1.00 \times 10^{-23}}{2.99 \times 10^{-26}}} = 18.3$$

Thus the root mean square speed of water molecules is about 18.3 times that of the colloidal particles.

20.6.3 Optical Properties

When a beam of light is passed through a clear solution and viewed from a direction at right angles to the direction of the beam of light, it appears completely dark. However, in the case of a colloidal sol we observe bright spots of light against this dark background. This is due to the scattering of light by the colloidal particles and is known as Tyndall effect. Although the phenomenon is also prevalent in most gases, liquids and solutions, the intensity of the scattered light is negligible. This is attributed to the small size of the particles in these cases. However, colloidal particles are large enough to cause considerable scattering of light. It is observed that spots of light keep on continuously changing which indicates the heterogeneous character of the sol and the continuous motion of the particles.

A very common example of Tyndall effect can be seen in a cinema hall. You can see clearly the projection beam all the way from the projector to the screen due to scattering of light by the suspended dust particles in the cinema hall.

The Tyndall effect depends on the refractive indices of both the dispersed phase and the dispersion medium. It is best observed when the refractive indices of the two differ appreciably from each other and the size of the particles is in the same region as the wavelength of light used.

The Tyndall effect has been put to a number of practical uses, one of which is the construction of ultramicroscope (Fig. 20.8).

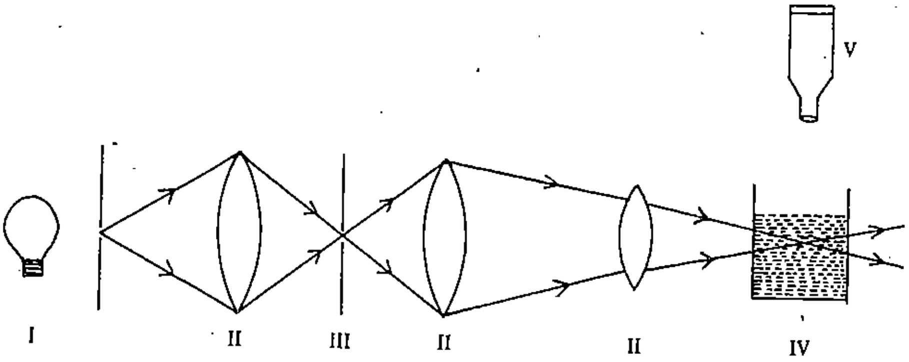


Fig. 20.8: Ultramicroscope: I. light source; II. lens ; III. slit ; IV. sol; V. microscope.

When a narrow beam of light is observed at right angles to its path through a sol, the particles can be viewed in the form of blocks of light moving continuously in all directions. Using ultramicroscope, we can distinguish the different colloidal particles on the basis of light scattered by them.

20.6.4 Electrical Properties

Colloidal particles in a dispersion medium carry charges on their surfaces. These charges can be positive (as in the case of ferric hydroxide sol) or negative (as in the case of arsenious sulphide sol). The total charge on the colloidal particles is, however, fully balanced by the charge on the particles of the dispersion medium thus preserving the electrical neutrality of the sol. The origin of charge can be traced mainly to two causes:

1. **Direct ionisation of surface groups**

Proteins contain many acidic and basic groups and, these groups are ionisable. Depending on the acidity of the medium, the particles in a protein sol may acquire a positive or negative charge. Similarly in the cases of associated colloids like soaps and detergents, the ionised molecules associate to give micelles whose outer surface will be charged (See Sec.20.4).

2. **Adsorption**

In certain cases positive or negative ions present in the medium are specifically adsorbed on the surface of the colloidal particles. For example, in silver iodide sol, the particles adsorb the iodide ions from the solution and, acquire a negative charge.

Similarly, some molecules may get adsorbed on the surface of the colloidal particles, dissociate and leave a charge on the surface. Arsenious sulphide sol adsorbs H_2S molecules which dissociate leaving a negatively charged sol.

3. **Electrical double layer**

The charges on the colloidal particles will affect the charge distribution in the dispersion medium. Thus the charges on the colloidal particles will attract ions of opposite charges (counter ions) and repel the ions having similar charge (coions).

This is the basis of the formation of double layer of charges. In the vicinity of the colloidal particles, there would be a higher concentration of counter ions compared to that of coions. The concentration of counter ions starts decreasing gradually at greater distances, till the concentration of counter ions and coions becomes equal.

In Fig. 20.9, the double layer around a colloidal particle (I) with positively charged adsorbed ions is shown. The double layer consists of,

i) a compact layer (II) made up of excess of counter ions,

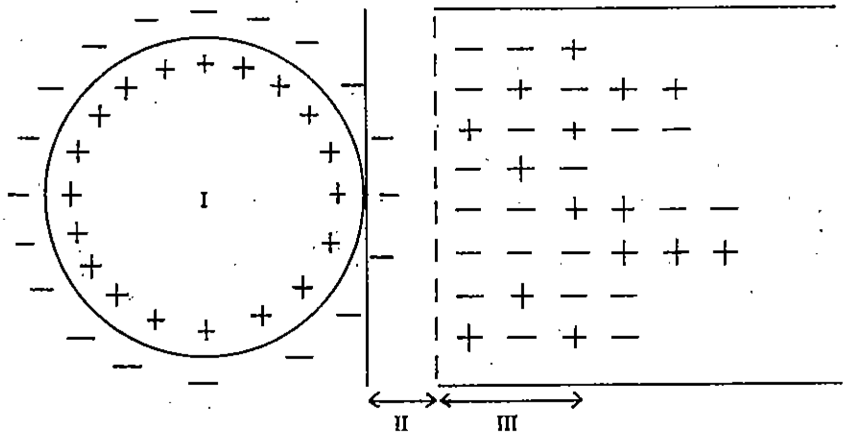


Fig. 20.9 : The double layer around a colloidal particle with positively charged adsorbed ions.

ii) a diffused layer (III) consisting of increasing concentrations of coions, as distance increases. At a particular distance, the concentration of coions and counter ions becomes equal. The diffused layer is loosely held and is therefore mobile.

Although the double layer theory could help us in explaining,

- electrophoresis,
- electro-osmosis and
- stability of lyophobic sols,

We give only a simple description of these phenomenon.

4. Electrophoresis

Due to the charge on the colloidal particles they move towards the suitable electrode when

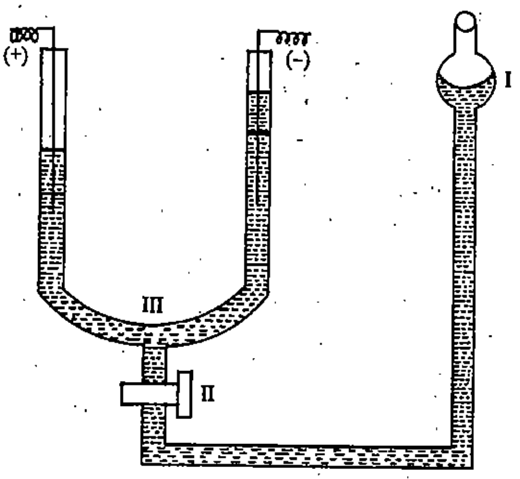


Fig. 20.10 : Apparatus for electrophoresis : I. reservoir of sol ; II. stopcock ; III. water; note the rise in level in the cathode section; the colloidal particles are positively charged.

an electrical potential is applied. This migration of colloidal particles towards either cathode or anode under the influence of an electrical field is known as electrophoresis. Electrophoresis can be observed in a U-tube fitted with a stopcock and connected to a reservoir of sol (Fig. 20.10).

Two platinum electrodes are fitted, one in each limb of U-tube. The U-ube is partially filled with the solvent. The sol is gently introduced from the reservoir into the U-tube through the stopcock. The electrodes should be dipping in the solvent. A direct current voltage in the range of 50 V to 250 V is applied across the electrodes. If the colloidal particles have a positive charge on their surface, they will move towards the cathode and the level in the cathodic limb will rise whereas the level in the anodic limb will correspondingly move downwards. On the other hand, if the particles are negatively charged, movement will take place in the opposite direction in the two limbs.

Potential gradient is defined in Sec. 16.7 of Unit 16 of this course.

From the direction of the movements in the two limbs we can find whether the particles are positively or negatively charged. The velocity with which the particles move depends on the applied voltage. We can find out the speed of the particle under unit potential gradient which is called the 'electrophoretic mobility'.

Electrophoresis has been used for the separation of various types of colloidal particles from a mixture. Since different particles move with different velocities, their separation becomes easy.

5. **Electro-osmosis**

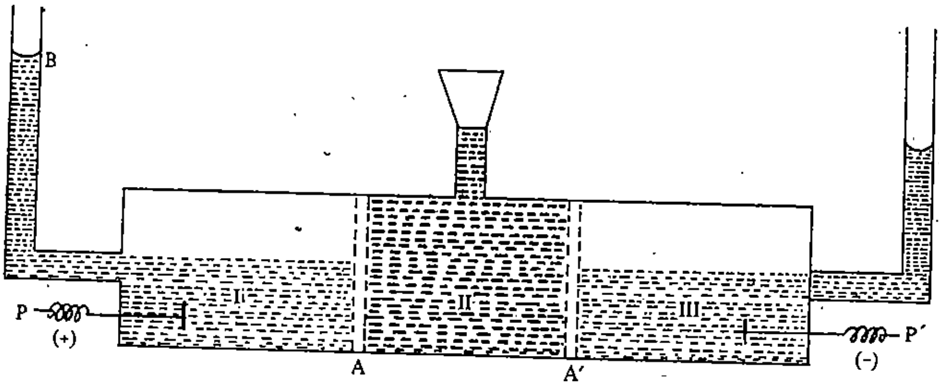


Fig. 20.11 : Apparatus for electro-osmosis : note the solvent level rise in anode compartment ; the colloidal particles in the sol (kept in compartment II) are positively charged.

If the colloidal particles are not allowed to move under the influence of an electrical field due to certain physical barriers, then the dispersion medium itself moves. This phenomenon is known as electro-osmosis. It can be studied by using a simple apparatus shown in Fig. 20.11.

It consists of a vessel divided into three compartments I, II and III by means of semipermeable membranes A and A′. The two outer compartments I and III are fitted with capillary tubes B and B′ and platinum electrodes P and P′. The compartments I and III are filled with the solvent. On passing electricity through P and P′, solvent level rises in one tube and falls in the other. The difference in the levels of the solvent in these tubes is a measure of the motion of the dispersion medium under the influence of the electrical field. If the colloidal particles are positively charged, the dispersion medium will be negatively charged and the level will rise in the tube connected to the anode compartment. Similarly, if the colloidal particles are negatively charged, the level will rise in the tube connected to the cathode compartment.

20.6.5 Stability of Colloids

Sometimes we want to separate colloidal particles from the dispersion medium. This is usually done by the formation of bigger particles due to aggregation. This process is known as coagulation. However, at times, we want to preserve the colloidal sol and prevent its coagulation. This is done by the protection of colloids. Let us study these two processes separately.

1. Coagulation

Let us study the coagulation of lyophilic and lyophobic sols separately.

Lyophilic Sols

Lyophilic sols are more stable than lyophobic sols. In lyophilic sols there is a strong interaction between the colloidal particles and the molecules of the dispersion medium. As a result, lyophilic sols contain highly solvated particles. In order to bring about the coagulation in such a system, we must remove the solvent molecules which surround the particles so that the particles can come near each other. This is done by introducing a competing agent for the solvent molecule. There are two ways of doing it–either by using a second solvent or by adding an electrolyte.

i) Introduction of a Suitable Solvent

If a second solvent, which interacts strongly with the dispersion medium, is added to lyophilic sol, coagulation takes place. Thus protein–in water sol can be coagulated by the introduction of alcohol. The water molecules interact strongly with alcohol molecules and the protein molecules are desolvated (i.e., surrounding solvent molecules are removed).

ii) Introduction of Electrolytes

When electrolytes are added to lyophilic sols, the ions of the electrolyte compete for the solvent molecules. If sufficient amount of electrolyte is added, the sol coagulates. This is called the salting out of the sol.

It has been stated in Sec. 20.3 that lyophobic colloids are made up of substances insoluble in the dispersion medium. If the double layer were absent, you can expect the particles of insoluble material to come close because of attraction due to van der Waals forces. This would have destabilised the lyophobic colloid and resulted in the precipitation of the colloid. The presence of double layer causes repulsion between particles. This is helpful in avoiding precipitation and in stabilising the lyophobic colloids.

Lyophobic sols

Lyophobic sols differ in stability from lyophilic sols. The stability of lyophobic sols is due to the electrical double layer and, their coagulation will thus involve the depletion or the complete removal of this double layer.

One way of doing this is the mixing together of two sols which have particles carrying opposite charges when both the sols are coagulated. For example, the mixing of ferric hydroxide sol with arsenious sulphide sol results in the neutralisation of the charges on both the sols and both of them are coagulated.

The other method involves, once again, the addition of electrolytes but here the mechanism of coagulation is different. In this case, the ions of the electrolyte are taken up by the colloidal particles. This results in the neutralisation of the charge on the particles and the reduction of the repulsion between different colloidal particles. The coagulation of colloidal particles is sometimes also referred to as flocculation. The capacity of an electrolyte to cause flocculation is given by its flocculation value It is defined as the concentration of an electrolyte in millimoles per litre (or cubic decimeter) which is required to flocculate a sol. **The flocculation values of some common electrolytes for arsenious sulphide and ferric hydroxide** sols are given in Table 20.2.

Table 20.2: The Flocculation Values of Some Common Electrolytes for Arsenious Sulphide and Ferric Hydroxide Sols.

Arsenious sulphide (negatively charged)		Ferric hydroxide (positively charged)	
Electrolyte	(Flocculation value) (10^{-3} mol dm^{-3})	Electrolyte	(Flocculation value) (10^{-3} mol dm^{-3})
NaCl	51	NaCl	9.0
KNO_3	50	KCl	9.0
KCl	50	KNO_3	12.0
$CaCl_2$	0.65	K_2SO_4	0.21
$Al(NO_3)_3$	0.095	Tl_2SO_4	0.22

The effect of the charge of the counter ions on the flocculation value is given by Schulze-Hardy rule. This rule states that the counter ions having a higher charge have a greater power to cause flocculation of a sol. According to this law, the flocculation value of an electrolyte is inversely proportional to the sixth power of the valency of the counter ions. For arsenious sulphide sol (a negatively charged sol), for example, the flocculation value of sodium chloride solution is 51×10^{-3} mol dm^{-3} and that of potassium chloride solution is 50×10^{-3} mol dm^{-3}. These values are more or less the same since the charges on the counter ions, Na^+ and K^+, are the same. But if calcium chloride solution is used as the electrolyte for the flocculation of the arsenious sulphide sol, the flocculation value is much less (0.65×10^{-3} mol dm^{-3}); it is so since the charge on the counter ion, i.e., calcium ion, is +2 which thereby is more effective than the unipositive ions, K^+ or Na^+, in the flocculation of the negatively charged sol of arsenious sulphide. Many of the electrolytes follow this rule as seen from Table 20.2. Only in a few cases, it is not followed and in these cases, both the ions of the electrolytes determine the flocculation value.

2. Protection of Colloids

It has been observed that lyophobic sols, in contrast to lyophilic sols, are easily flocculated on the addition of a small amount of electrolyte. The relatively higher stability of lyophilic sols is due to the attraction between the dispersed particles and the dispersion medium. Some lyophilic sols are so stable that their addition to lyophobic sols increases the stability of even lyophobic sols. Such lyophilic sols are called protective colloids. Their stabilising action towards the lyophobic colloids is called protective action. The stabilisation is due to adsorption. In other words, lyophilic colloidal particles get adsorbed on the surface of lyophobic colloidal particles. This increases their capability to interact with the dispersion medium. Usually macromolecules like gelatin, starch etc. are used as protective colloids. The protection of colloids is of great industrial importance. The protective power of a colloid is given in terms of gold number. It is defined as "the number of milligrams of the protective colloid which prevents the coagulation of 10 ml of a gold sol on adding 1 ml of a 10% solution of sodium chloride". The start of the flocculation is taken as the point at which the colour of the gold sol changes from red to blue. The size of the gold particles is smaller in red sol and bigger in the blue sol. Formation of blue colour means partial flocculation. It is clear that smaller the gold number of a colloid, larger will be its protective power. The values of gold number for a few hydrophilic ("water loving") sols are given in Table 20.3.

Table 20.3 Gold number of Some Hydrophilic Sols

Sol	Gold number
Gelatin	0.005 — 0.010
Egg albumin	0.08 — 0.10
Gum arabic	0.10 — 0.15
Soluble starch	10 — 15

Egg albumin: A water soluble protein found in egg

Gum arabic: A gum obtained from a particular type of trees.

Soluble starch: Starch is composed 75% of water-soluble portion known as amylopectin. It has a branced chain structure in which many glucose units are connected.

So far we studied the properties of sols. In the next section, we shall study the formation and the characteristics of emulsions. Before proceeding to the next section, answer the following SAQ's.

SAQ 6

Differentiate between electrophoresis and electro-osmosis.

....

....

....

SAQ 7

Addition of sodium chloride solution to gold sol results in its coagulation. But if this reaction is carried out in presence of a certain amount of soluble starch, precipitation of gold does not take place. Explain.

....

....

....

20.7 EMULSIONS

Emulsions are colloidal systems in which both the dispersed phase and the dispersion medium are liquids.

Emulsions can be formed between any two immiscible liquids but normally we come across those which are composed of water and an oil. They can be either oil-in-water type, in which the dispersion medium is water or water-in-oil type in which the dispersion medium is oil. The two types can be distinguished by any of the following methods:

1. A small amount of an oil-soluble dye is added to the emulsion and observed under microscope. If the whole background is coloured,then it is water-in-oil type but if you observe only coloured drops, then it must be oil-in-water type.
2. Oil-in-water type emulsions generally have high conductivity as compared to those of water-in-oil type. This is so because organic liquids have much lower conductance than water.
3. Oil-in-water emulsions will not spread on an oily surface whereas water-in-oil will do so, and hence, a distinction can be made.

In an emulsion, globules of one liquid are found suspended in the other liquid. However, in majority of cases, these globules are unstable and the system separates into two liquid layers. In order to stabilise emulsions we have to add substances known as emulsifiers or emulsifying agents. These are generally long hydrocarbon chain molecules having a polar group at one end. Thus, soaps, proteins, long chain sulphonic acids etc. act as emulsifiers. The stabilisation of an emulsion by means of the addition of an emulsifier is known as emulsification. The emulsifier is first shaken with one of the liquids and then, the other liquid is added.

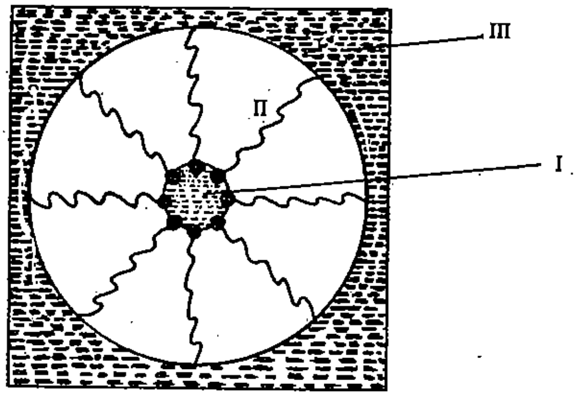


Fig.20.12: Orientations of an emulsifier: I. water ; II. emulsifier molecules with the polar group towards water and nonpolar group towards oil ; III. oil.

The role of an emulsifier is primarily to lower the interfacial tension between the two liquids so as to promote greater interaction between them. The interfacial tension is lowered because of the adsorption of the emulsifier at the interface. This is followed by the preferential orientation of the emulsifier molecules with their polar groups towards water and the long hydrocarbon chain towards the oil as shown in Fig. 20.12.

Emulsions are often used in pharmaceutical preparations, disinfectants etc. Emulsification of greasy material by soap solutions is the mechanism on which the cleansing action of soap depends. The stability of the emulsions can be reduced by adding a substance which destroys the emulsifier. Sometimes centrifuging or freezing may also help in destabilising an emulsion.

Cleansing Action of Soaps and Detergents

$$\underset{\longleftrightarrow\ \text{(Nonpolar hydrocarbon tail)}}{CH_3-(CH_2)_{16}}-\underset{\longleftrightarrow\ \text{(Polar head)}}{COO^-}\ Na^+$$

(Sodium stearate)

As explained in Sec. 20.4, soaps are salts of long-chain fatty acids, the most common example being sodium stearate, $C_{17}H_{35}COO^- Na^+$.

Let us now discuss the cleansing action of soaps.

The dirt particles that cling to the textile fibres are generally covered by a layer of oil molecules, called grease. These oil molecules are nonpolar and, so repel water. Hence, water cannot wash such dirt particles out of cloth by itself.

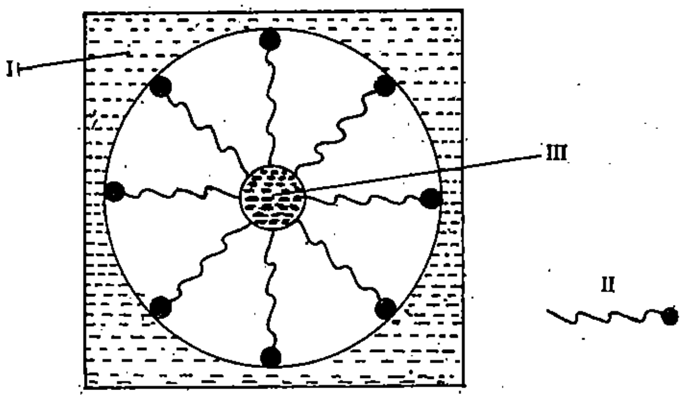


Fig. 20.13 : Soap micelles interacting with grease : I. water ; II. stearate anion ; III. grease molecules attached to the nonpolar tail of the stearate anion.

On the addition of soap, (i) grease molecules get attached to the nonpolar hydrocarbon tail of the stearate anion (due to London forces) and (ii) the polar head of the stearate anion is directed towards water (due to ion-dipole interaction). This results in the lowering of interfacial tension between grease and water. Because of this emulsifying action of soap, grease and hence, dirt is washed out of clothes (Fig. 20.13).

Because of the ability to assist water in wetting and suspending the nonpolar (grease) molecules by lowering the interfacial tension, soaps and detergents are called wetting agents or surfactants.

Soaps are not effective as cleansers when used in hard water. This is because the calcium and magnesium ions present in hard water form a precipitate of calcium and magnesium stearates. This results in

- the loss of cleansing action of soap due to decrease in stearate ion concentrations in water,
- increase of binding of the grease to the cloth, giving it a dull colour.

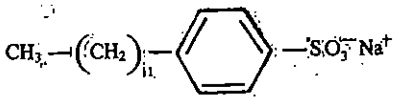


Fig. 20.14 : A linear alkylbenzene sulphonate (sodium salt).

To solve this problem of hard water, detergents are used in the place of soaps. Detergents are of two types–anionic and cationic. The anionic detergents are generally the sodium salts of linear alkylbenzene (LAB) sulphonic acids (Fig. 20.14).

The cationic detergents are generally quaternary ammonium salts of the type,

$(CH_3)_3RN^+ Cl^-$

where R is a long chain of alkyl groups containing between 12 and 18 carbon atoms.

As far as cleansing action is concerned, detergents, like soaps, act as emulsifiers between grease and water. Further in presence of hard water, detergents do not form precipitates. For example, calcium or magnesium salts of LAB sulphonates are soluble in water. Hence detergents can be used even in hard water.

Your study of this section could help you in answering the following SAQ. In the next section, we shall discuss the characteristics of gels.

SAQ 8

Explain the detergent action of linear alkylbenzene sulphonates (RSO_3^-).

....

....

....

20.8 GELS

Hot solutions of some substances, when cooled, form a semisolid mass. These are the substances which normally form lyophilic sols. As the solution cools, the molecules of the solute tend to come together to form bigger aggregates. In doing so, they form a network with much open space between the aggregates. Solvent gets trapped in these small spaces of the network. These gels can be of two types: In one case, the gels on standing may lose water and become a solid. However, this solid on mixing water can again turn into a gel. Such substances are called elastic gels. A common example of elastic gel would be the gum or glue we use for pasting paper. The other kind of gel on dehydration gives a powder which cannot be converted back into gel again. These are known as nonelastic gels. So far in this unit, we discussed the characteristics of some colloidal dispertions.

In the next section, we shall discuss the methods of determination of molar mass of macromolecular systems. These methods are based on the characteristics of colloidal dispersions.

20.9 METHODS FOR THE DETERMINATION OF MOLAR MASS

It has been pointed out in Sec. 20.5 that in macromolecular solutions, the distribution of macromolecules is not uniform. Hence, some kind of average molar mass value is obtained experimentally. For these measurements we use such a property of the sample which is directly related to the molar mass. We shall discuss a few of these methods in the present section.

1. **Viscosity Method**

The macromolecular solutions show high viscosities even when the concentrations are low. This may be due

- either to the high solvation of the solute molecules which do not allow the solvent to move freely, or,
- to the macromolecules getting entangled with each other due to their large size and thus restricting the movement of the solvent.

Relative molecular mass is commonly known as molecular weight.

Molar mass $= \frac{(\text{Relative molecular mass})}{1000}\ \text{kg mol}^{-1}$

Due to the simplicity of the measurement of viscosity, this method is widely used in determining the molar masses of the polymers. The first step involves the determination of the viscosities of polymer solutions of different concentrations. From these measurements, we derive the value of intrinsic viscocity which is defined below:

$$\text{Intrinsic viscosity } [\eta] = \underset{d \to 0}{Lt}\left[\frac{(\eta - \eta_0)}{d\,\eta_0}\right] \quad \ldots(20.12)$$

where η and η_0 are the viscosities of the solution and of the solvent, respectively and d is the concentration of the polymer solution (expressed as mass of the polymer per given volume of the solution).

In order to obtain the value of $[\eta]$ a graph is plotted with $\frac{\eta - \eta_0}{d\eta_0}$ against d which gives a straight line. The line is extrapolated to zero concentration so that the intercept gives the value of intrinsic viscocity. The intrinsic viscosity is related to the relative molecular mass (M) by the following equation:

$$\left.\begin{array}{l} [\eta] = KM^{\alpha} \\ \text{or } [\eta] = \log K + \alpha \log M \end{array}\right\} \quad \ldots(20.13)$$

where K and α are constants which depend on the nature of the polymer, solvent and the temperature. For the determination of K and α values, we first take solutions of a polymer of known relative molecular mass, and draw a graph between log $[\eta]$ and log M values for this polymer. The slope of the line gives α and the intercept gives log K. Using these values of K and α we can determine the relative molecular mass for a similar polymer.

This gives us the viscosity average molar mass $\overline{M}_v$ of the polymer. Let us study an example.

Example 4

The intrinsic viscosity of a given polymer sample is 0.96 dm^3 kg^{-1}. If the value of K and α are 1.2×10^{-4} dm^3 kg^{-1} and 0.75, respectively, find the relative molecular mass of the polymer.

Solution

$$[\eta] = KM^{\alpha}$$

$$0.96 \text{ dm}^3 \text{ kg}^{-1} = 1.2 \times 10^{-4} \text{ dm}^3 \text{ kg}^{-1} \; M^{0.75}$$

$$M^{0.75} = \frac{0.96}{1.2 \times 10^{-4}} \text{ or } M = \left(\frac{0.96}{1.2 \times 10^{-4}}\right)^{\frac{4}{3}}$$

or

Relative molecular mass = 1,60,000

or

Molar mass = 160 kg mol^{-1}

2. **Osmotic Pressure Method**

The osmotic pressures produced by solutions of even low molarity are easily measurable and, this method is widely used for the determination of molar masses of polymers. For dilute solutions, we can write the relationship between the osmotic pressure and the molar mass of the polymer based on Eq. 12.49 as follows:

$$\Pi = \frac{wRT}{MV} \qquad \text{...(20.14)}$$

$$\Pi = \frac{wRT}{VM} \qquad \text{...(20.15)}$$

Eq. 12.49 was derived in Unit 12 for correlating the molar mass of a nonvolatile solute with the osmotic pressure of the solution.

w and M are the mass and molar mass of the polymer, R is gas constant, T is temperature, V is the volume of the solution and Π is its osmotic pressure.

Replacing w / V by d we can rewrite Eq. 20.15 as,

$$\Pi = \frac{dRT}{M} \qquad \text{...(20.16)}$$

or

$$\frac{\Pi}{d} = \frac{RT}{M} \qquad \text{...(20.17)}$$

where d is the concentration of a solution given in kg m^{-3} units.

This equation is applicable only to dilute solutions which do not show deviation from normal behaviour. Such cases are represented using the limiting condition, $d \rightarrow 0$, i.e., the concentration of the solution approaches zero,

$$\underset{d \to 0}{Lt} \frac{\Pi}{d} = \frac{RT}{M} \qquad \text{...(20.18)}$$

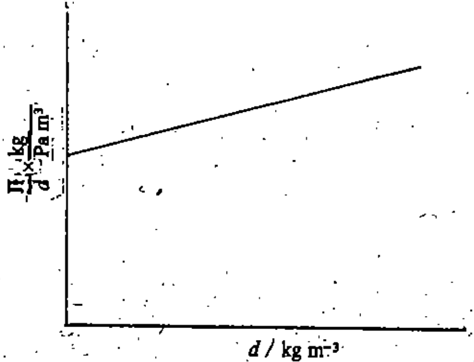


Fig. 20.15 : Plot of Π/d vs. d

The polymer solutions of measurable concentration exibit deviation from ideal behaviour and a correction term, Bd, is to be included in Eq. 20.17, where B depends on the polymer-solvent system and the extent of interaction between the two.

Hence,

$$\frac{\Pi}{d} = \frac{RT}{M} + Bd \qquad \ldots (20.19)$$

The method of measurement of osmotic pressure has been discussed in Unit 12. A graph is plotted between Π/d and d which gives a straight line (Fig. 20.15).

By extrapolating the line to zero d value, the intercept, which is equal to L.H.S of Eq. 20.18 and also to RT/M, is obtained. From this, we get the value of M, the number average molar mass of the polymer.

3. Light Scattering Method

In the case of pure fluids light scattering takes place due to local changes of density from time to time. This results in fluctuations in the refractive index of the medium. In case of solutions, these fluctuations are of higher magnitude. Thus, when a ray of light enters the solution, it suffers scattering in all directions thereby giving the solution a turbid appearance. The turbidity (τ) is related as per Eq. 20.20 to the intensity of incident light (I_0) the intensity of scattered light (I) and the distance(x) through which light has passed in the solution:

$$I = I_0 \, e^{-\tau/x}$$

or

$$\frac{I}{I_0} = e^{-\tau/x} \qquad \ldots (20.20)$$

Also, I/I_0 value is related to the refractive index of the solvent, angle of scattering, the change in the refractive index of the solution with concentration, wavelength of the incident light etc. Without going into the derivation, we can write the following relationship:

$$\tau = HMc \qquad \ldots (20.21)$$

where H includes all the factors mentioned above for which values are known, M is the molar mass and c the concentration of the polymer. This expression has been derived for highly idealised systems and for its application to real systems, we must add another concentration term giving,

$$\frac{Hc}{\tau} = \frac{1}{M} + 2\,Bc \qquad \ldots (20.22)$$

where B is a constant.

By plotting Hc/τ against the concentration, we get a straight line which when extrapolated to zero concentration, gives an intercept equal to $1/M$. The scattering method is suitable for the determination of very high molar masses. The apparatus for measuring turbidity are commercially available these days. By this method, we obtain the mass average molar mass.

4. Sedimentation Method

When a polymer or a colloidal sol is left in a vessel, the colloidal particles settle to the bottom under the force of gravity. This process can be accelerated by subjecting the sol to a very high gravitational force by putting the cell containing the sol in an ultracentrifuge and subjecting to high speed of rotation. In analytical centrifuges there is optical arrangement for the determination of the concentration of the polymer molecules at different depths of the cell. The use of ultracentrifuge for the determination of molar mass of a polymer is done either by sedimentation velocity method or sedimentation equilibrium method. However, we shall not discuss these methods in detail.

If you have understood the osmotic pressure method of determining the molar mass of a polymer, you could answer the following SAQ.

SAQ 9

1.00 m^3 of a solution containing 2.50 kg of a polymer has an osmotic pressure of 250 Pa at 298 K. Assuming that the solution does not deviate from ideal behaviour, calculate the molar mass of the polymer.

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20.10 APPLICATIONS

There are many applications of colloids in day to day life and in industry. Some important applications are given below:

Food : The study of colloidal systems has helped in the processing of milk, butter, starch, proteins, curd, ice-cream and cheese.

Medicine : Many medicines are emulsions and colloidal sols. Their preparation and stabilisation require a knowledge of colloidal science. Most biological fluids like blood etc are colloidal dispersions.

Agriculture : Soil is a mixture of clay, organic materials, and salts which shows colloidal behaviour. The study of colloids becomes important in understanding the nature of soil, its moisture adsorption properties, formation of protective colloid by humus, exchange of ions etc.

Rubber : Rubber latex is a colloidal suspension. Since the rubber particles are negatively charged, they can be directly deposited on a mould of any size or shape by making it the anode in an electrophoretic process.

Water Treatment : Water from rivers, lakes etc. contain large amounts of colloidal impurities which are usually purified by the addition of alum which coagulates the colloidal particles.

Sewage disposal : Water in the sewage contains dust, garbage and other impurities as a colloidal suspension. The sewage disposal tanks are fitted with charged electrodes. The colloidal particles move towards the suitable electrode and get discharged. Thus these particles coagulate at the electrodes. The sewage sludge after further treatment can be used as manure. Clear water from the tanks is used for irrigation purposes.

Smoke removal : Industrial towns are saved from smoke pollution to a large extent by fitting Cottrell's apparatus at the chimney of the factories. This apparatus consists of two electrodes, (one being cylindrical and the other being a co-axial pointed rod). These electrodes are maintained at a very high potential difference (50,000 volts). The smoke particles while passing between the electrodes are precipitated on a suitable electrode from where they are scrapped down and removed.

Preparation of catalysts : Catalysts, we know, are most effective when used in the form of finely divided particles (See SAQ 1). These are first obtained in a colloidal state from which they are coagulated on a suitable supporting material.

Leather Industry: Hides contain proteins in colloidal state which are precipitated in the tanning process. Leather is usually chrome-tanned by allowing the positively charged particles of hydrous chromic oxide into the animal hides.

Hide : Skin removed from a dead animal.

Tanning : Changing hide into leather by chemical treatment.

Chrome-tanning: Tanning by using chromium compounds.

Soaps, Detergents and Dyes : The colloidal chemistry of soaps and detergents is important in understanding their cleansing property. They are also used as emulsifiers. Many dyes form associated colloids.

Other Industries : Many industrial products like paints, varnishes, printing inks, gums, resins and adhesives are all colloidal in nature. The list of such industrial goods is so long that it cannot be given fully.

Smoke Screens : Finely divided titanium dioxide particles dispersed in air are used in modern warfare as smoke screens for the purpose of camouflaging.

20.11 SUMMARY

In this unit, we have discussed the main features of colloidal systems:

- We have first defined the colloidal systems and then given their classification.

- We have described the characteristic properties of colloids.
- The origin of charge on the colloidal particles has been discussed.
- The characteristics of macromolecular solutions are discussed. The number average molar mass and the mass average molar mass are then defined.
- The methods for the determination of molar masses are described.
- A short discussion on the applications of colloids in industry as well as in our daily life has been given.

20.12 TERMINAL QUESTIONS

1) 1.00 m^3 of a sol has 10^{16} particles of radius 100 nm. Calculate the mass of a solid required to prepare 1.00 dm^3 of the sol. The density of the solid is 1.50×10^3 kg m^{-3}.

   (Hints: i) Consider the particles in the sol to be spherical and calculate the volume of each particle using the formula,

   $$\frac{4}{3}\pi r^3$$

   ii) Calculate the volume occupied by the particles in 1.00 m^3 of the sol; for this, multiply the answer for (i) by 10^{16}.

   iii) Calculate the mass of the substance dispersed in 1 m^3 of the sol.

   $$\left\{\begin{array}{l}\text{Mass of the}\\ \text{substance in } 1m^3 \text{ of the sol}\end{array}\right\} = \left\{\begin{array}{l}\text{Volume of the particles}\\ \text{in } 1m^3 \text{ of the sol}\end{array}\right\} \times \left\{\begin{array}{l}\text{density of}\\ \text{the substance}\end{array}\right\}$$

   iv) Calculate the mass of the substance required to prepare 1 dm^3 of the sol ; multiply the answer for (iii) by 10^{-3} to get the answer for this step).

2) Give a few examples of colloids used by you in daily life.

3) What is the origin of charge on a colloidal particle? How are coions and counter ions distributed around the charged colloidal particles?

4) Calculate the volume of 0.1 M $BaCl_2$ solution (in cm^3 unit) required to coagulate 1 dm^3 of arsenious sulphide sol, if the flocculation value of $BaCl_2$ is 4.

5) What is Tyndall effect? Suggest an application for this effect.

6) Caculate the number average and mass average molar masses of a polymer sample with the following distribution of molar masses:

N_i	100	250	400	300	200	100
M_i/kg mol^{-1}	2.000	3.000	5.000	7.000	10.000	15.000

   Also calculate the polydispersity index.

7. What do you understand by protection of colloids? Explain the mechanism of protection of colloids.

8. Explain the term, 'electrophoresis'. State two of its applications.

20.13 ANSWERS

Self Assessment Questions

1) $$\left\{\begin{array}{l}\text{Volume of each platinum}\\ \text{particle}\end{array}\right\} = \frac{4}{3} \times 3.14 \times (50 \times 10^{-9})^3\ m^3$$

$$= 5.23 \times 10^{-22}\ m^3$$

$$\left\{\begin{array}{c}\text{Number of particles that}\\ \text{could be formed from}\\ 1.00\times10^{-6}\ \text{m}^3\ \text{platinum}\end{array}\right\} = \frac{1.00\times10^{-6}\ \text{m}^3}{5.23\times10^{-22}\ \text{m}^3}$$

$$= 1.91\times10^{15}$$

$$\left\{\begin{array}{c}\text{Surface area of each}\\ \text{platinum particle}\end{array}\right\} = 4\pi r^2$$

$$= 4\times3.14\times(50\times10^{-9})^2\ \text{m}^2$$

$$= 3.14\times10^{-14}\ \text{m}^2$$

$$\left\{\begin{array}{c}\text{Total surface area of all}\\ \text{the platinum particles}\end{array}\right\} = 1.91\times10^{15}\times3.14\times10^{-14}\ \text{m}^2$$

$$= 60.0\ \text{m}^2 = 6.00\times10^5\ \text{cm}^2$$

2) A dilute solution containing Cl^- ion or Ag^+ ion could function as peptizing agent in the preparation of silver chloride sol from solid silver chloride.

3) i) Charge on the micellar ion = [(–100)–(+80)] units

= –20 units

ii) $$\left\{\begin{array}{c}\text{Number of ions present}\\ \text{after micelle formation}\end{array}\right\} = \left\{\begin{array}{c}\text{1 (due to micelle) +}\\ \text{(20 due to free Na}^+\text{ ions)}\end{array}\right\}$$

$$= 21$$

iii) The number of ions before micelle formation = 200

The number of ions after micelle formation = 21

The decrease in the number of ions, which carry current, evidently results in the decrease of conductivity. Since osmotic pressure is a colligative property, its decrease due to the decrease in the number of species is understandable.

4) The polydispersity index will be equal to one, if the molar masses of all the polymers are same. You can get this result if you write M_i as M and take it out of $\sum$ sign in Eqs.20.1 and 20.9.

5) $$\overline{M}_n\,\overline{M}_w = \frac{\sum_i n_i M_i}{\sum_i n_i}\cdot\frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} = \frac{\sum_i n_i M_i^2}{\sum_i n_i} = M_{\text{rms}}\ \text{(as per Eq. 20.10).}$$

6) During electrophoresis, colloidal particles move towards an electrode whereas during electro-osmosis, dispersion medium moves.

7) The addition of sodium chloride solution to gold sol neutralises the charge on the colloidal particles and causes coagulation. Soluble starch particles get adsorbed on the surface of gold sol particles and increase their capability to interact with the dispersion medium thereby preventing coagulation.

8) The detergent action of linear alkylbenzene sulphonates is similar to stearates. The main difference is that the sulphonate ion forms the polar part in the former whereas the carboxylate ion forms the polar part in the latter.

9) As per Eq. 20.15, $M = \frac{wRT}{V\Pi}$

$$= \frac{2.50\ \text{kg}\times8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\times298\ \text{K}}{1.00\ \text{m}^3\times250\ \text{Pa}}$$

$$= 24.8\ \text{kg mol}^{-1}$$

Terminal Questions

1) Volume of each particle $= \frac{4}{3}\pi r^3 = \frac{4}{3}\times3.14\times(100\times10^{-9}\ \text{m})^3$

$$= 4.19 \times 10^{-21}\ \text{m}^3$$

There are 10^{16} particles in 1.00 m^3 of the sol.

$$\left\{\begin{array}{l}\text{Volume of the particles}\\ \text{in 1 m}^3\text{ of the sol}\end{array}\right\} = 4.19 \times 10^{-21} \times 10^{16}\ \text{m}^3$$

$$= 4.19 \times 10^{-5}\ \text{m}^3$$

$$\left\{\begin{array}{l}\text{Mass of the substance}\\ \text{required to prepare}\\ \text{1 m}^3\text{ of the sol}\end{array}\right\} = 4.19 \times 10^{-5}\ \text{m}^3 \times 1.50 \times 10^{3}\ \text{kg m}^{-3}$$

$$= 6.29 \times 10^{-2}\ \text{kg}$$

$$\left\{\begin{array}{l}\text{Mass of the substance}\\ \text{required to prepare}\\ \text{1 dm}^3\text{ of the sol}\end{array}\right\} = 6.29 \times 10^{-2} \times 10^{-3}\ \text{kg}$$

$$= 6.29 \times 10^{-5}\ \text{kg}$$

2) Curd, cheese, butter, ice-cream, paints, ink, tooth paste and adhesives are some examples.

3) See Subsec. 20.6.4.

4) The flocculation value of barium chloride is 4. Hence, 4 millimoles of $BaCl_2$ are required to coagulate 1 dm^3 of arsenious sulphide sol. 1 dm^3 of 0.1 M $BaCl_2$ solution contains 0.1 mole of $BaCl_2$.

Hence, 1 cm^3 of 0.1 M $BaCl_2$ solution contains 0.1 millimole of $BaCl_2$

$$\left\{\begin{array}{l}\text{Volume of BaCl}_2\text{ solution required}\\ \text{to have 4 millimoles}\end{array}\right\} = \frac{4}{0.1}\ \text{cm}^3$$

$$= 40\ \text{cm}^3$$

5) See Subsec. 20.6.3.

6) $\overline{M}_n = 6.33$ kg

$\overline{M}_w = 8.17$ kg

The polydispersity index $= \dfrac{\overline{M}_w}{\overline{M}_n} = \dfrac{8.17}{6.33} = 1.29$

7) See Subsec. 20.6.5.

8) See Subsec. 20.6.4 for the explanation of the term, electrophoresis. For applications, see Sec. 20.10 under the captions, rubber, sewage disposal and smoke removal.

UNIT 21 SURFACE CHEMISTRY AND CATALYSIS

Structure

21.1 INTRODUCTION

In Unit 18, we discussed the dependence of the rates of reactions on the concentration of the reactants and temperature. In Unit 20, we explained the characteristics of the colloids which include surface activity also. In this unit, we shall discuss the effect of surface on chemical reactivity.

Surface, in the chemical sense, is a phase boundary. Geometrically a surface has an area but no thickness. Surface is an **interface region** where one phase ends and the other begins. Chemically it is a region in which the properties vary from one phase to another. The transition occurs over distance of molecular dimensions. Thus for a chemist, surface has a thickness which shrinks to zero in an ideal condition of a geometrical description. In this unit we shall discuss the properties of an interface which may be liquid/vapour, solid/liquid or solid/gas. We shall discuss adsorption of gases on solid surfaces. Such a discussion is important since many of the chemical reactions in industry or in the biological systems take place on the interface. We shall also explain the different types of catalysts, inhibition of catalysts and catalytic poisoning.

Objectives

After studying this unit, you should be able to :

- define an interface,
- state the relationship between the concentration of a surface active solute and the surface tension of a solution,
- discuss different isotherms for adsorption on solid surfaces,
- state the role of photoelectron spectroscopy in surface chemical analysis,
- describe the functioning of different types of catalysts, and
- explain the inhibition of chemical reactions and poisoning of catalysts.

21.2 SURFACE TENSION OF SOLUTIONS

Liquids assume a shape with minimum surface area. The molecules in the bulk have less energy than the molecules in the surface, since a molecule in the bulk interacts with larger number of molecules as compared to a molecule on the surface. You are aware that any system tries to assume a state in which it has minimum energy. Hence, a liquid tries to take a shape which has the least surface area. The shape assumed is spherical, as a sphere has the smallest surface to volume ratio. The force that opposes the increase in area of a liquid is referred to as surface tension. In Unit 4 of this course, we have defined surface tension as a force per unit length acting on the surface opposing the expansion of surface area. An alternative definition was also suggested that surface tension is the surface energy per unit area of the surface. Normally the surface tension values reported are for the liquid-vapour interface in presence of air.

When we dissolve a solute in a solvent, the surface tension of the solution changes. A relationship could be derived to establish the fact that the concentration of the solute that lowers the surface tension would tend to be more on the surface of a solvent as compared to that in the bulk. This is the basis of **Gibbs adsorption isotherm**, about which we do not intend giving a detailed discussion. Substances which produce a remarkable lowering of interfacial tension are called 'surface active agents or surfactants'. We have seen one of the applications of the surfactants in Sec. 20.7 of Unit 20 where we dealt with the cleansing action of soaps and detergents. Another application of surfactants is in the formation of surface films. Some insoluble substances such as long-chain fatty acids and alcohols could spread on water surface to form a thin film. The formation of such surface films using long-chain alcohols has been helpful in retarding the evaporation of water from reservoirs.

SAQ 1

What is the essential characteristic of a surface active agent ?

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21.3 ADSORPTION ON SOLIDS

In Sec. 21.2, we studied that the molecules on the surface of a liquid experiences an inward pull. The liquid surface is thus in a state of unsaturation. The surface of a solid also behaves in a similar manner. In a solid, the ions or the molecules at the surface of a crystal do not have all their valencies satisfied by union with other particles. Such forces also arise due to the fact that when a new solid surface is created by breaking a solid, some interatomic bonds are broken and some of the valencies of surface atoms are left unsatisfied. As a result of these residual forces, the surface of the solid has a tendency to attract and retain available molecules and other particles towards itself; such a condition is helpful in decreasing the surface energy of a solid. The molecules so attracted are retained on the surface of the solid and do not go deeper into the bulk. Their concentration is more on the surface than in the bulk of the solid. This phenomenon of higher concentration of a substance on the surface of a solid is called **adsorption**. The substance attracted to the surface is called **adsorbate** while the substance to which it is attached is called **adsorbent**. For example, charcoal adsorbs acetic acid when kept in contact with it; here, acetic acid is adsorbate and charcoal is adsorbent.

Adsorption should be clearly distinguished from absorption. In absorption, the substance is not only retained on the surface but passes through the surface and is distributed throughout the bulk of the solid. Thus, anhydrous calcium chloride absorbs water to form a hydrate while acetic acid is adsorbed from its solution by charcoal. Sometimes the word 'sorption' is used when there is a doubt whether a process is true adsorption or absorption.

Adsorption of Gases by Solids

The studies of the adsorption of gases by solids are similar to those of the adsorption of liquids by solids. In this unit, we shall mainly study the adsorption of gases by solids.

Although all solids adsorb gases, the effects are not evident unless the adsorbent is porous and has a very large area for a given mass. That is why silica gel and charcoal, which have porous structure, are very effective as adsorbing agents.

Porous substance; A substance having tiny openings through which fluids or air could pass.

The extent of adsorption by charcoal can be increased by subjecting charcoal to a process of activation. It involves heating of wood charcoal between 625 K and 1275 K in vacuum, air, steam, chlorine or carbon dioxide. During activation, hydrocarbons and other impurities are removed from charcoal leading thereby to a large surface area for adsorption. The resulting substance is called activated charcoal.

The amount of a gas adsorbed by a solid depends upon

- the nature of the gas and the adsorbent,
- the surface area of the adsorbent, and
- temperature and pressure of the adsorbent - adsorbate system.

Table 21.1 gives the volume of various gases adsorbed by 1.00 kg of charcoal at 288 K. The volume of gases have all been reduced to 273 K and 1.013×10^5 Pa pressure. It can be seen from Table 21.1 that gases which can be liquefied easily are more readily adsorbed.

Table 21.1 : Adsorption of Gases on Charcoal

Gas	Volume adsorbed / m^3	Critical temperature / K
H_2	4.7×10^{-3}	33
N_2	8.0×10^{-3}	126
CO	9.3×10^{-3}	134
CO_2	4.8×10^{-2}	304
HCl	7.2×10^{-2}	324
H_2S	9.9×10^{-2}	373
NH_3	1.8×10^{-1}	406

The total amount of the gas adsorbed increases with the surface area of the adsorbent. During adsorption an equilibrium is established between the gas in contact with the solid and the gas on the surface. An increase in temperature decreases the amount of the gas adsorbed.

In the next section, we shall discuss quantitative relationships regarding adsorption.

21.4 ADSORPTION ISOTHERMS

The amount of a substance adsorbed by an adsorbent at constant temperature depends upon the concentration or pressure of an adsorbate. For the adsorption of a substance (adsorbate) present in a solution by a solid adsorbent, Freundlich gave an empirical equation. This equation gives the relationship between the mass of the adsorbate (x) adsorbed by a particular mass (m) of the adsorbent and the equilibrium concentration of the adsorbate (c) in the solution at a particular temperature as given below:

$$\frac{x}{m} = Kc^{1/n} \qquad \ldots (21.1)$$

where K and n are constants. Eq. 21.1 is a form of Freundlich adsorption isotherm. By plotting log x/m against log c (Fig. 21.1), we can evaluate K and n. The values of K and n depend on

- nature of the adsorbate,
- nature and particle size of the adsorbent, and
- temperature.

It is worth mentioning that as the particle size becomes smaller, the surface area increases enormously. This increases the adsorbing capacity of an adsorbent.

Eq. 21.1 could be slightly modified to express the adsorption of a gas by a solid as given below:

$$\frac{x}{m} = Kp^{1/n} \qquad \ldots (21.2)$$

In this equation, p stands for the pressure of the gas adsorbate; other terms have the same significance as given in Eq. 21.1.

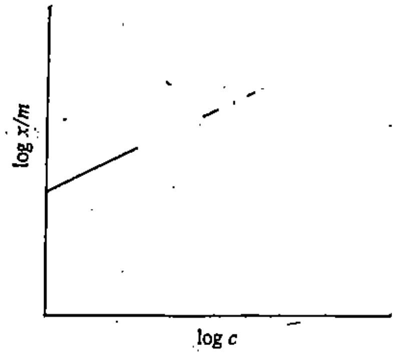

Fig. 21.1: Graphical representation of Freundlich adsorption isotherm.

Freundlich isotherm (Eq. 21.1 or 21.2) is applicable only if the concentration or pressure of the adsorbate is low.

Langmuir Adsorption Isotherm

Langmuir obtained a relationship for the adsorption of a gas by a solid. Langmuir started with the assumptions stated below:

- The adsorbed gas behaves ideally in the vapour phase; there are no attractive or repulsive forces among the gas molecules.

Desorption is the process of release of the adsorbed molecules. Desorption may also be called the evaporation of the adsorbed molecules.

- The surface of a solid is homogeneous and there are a fixed number of adsorption sites. Each site has the same attraction for the gas molecules.
- Each adsorption site can adsorb only one molecule. A solid surface cannot form a layer more than a single molecule in depth. In other words, the adsorption of a gas could lead only to the formation of unimolecular layer on the solid.
- There is an equilibrium between the condensation of gas molecules on the adsorbent and their desorption from it. The initial rate of condensation of gas molecules on the solid surface is high and it decreaseas as the surface available for adsorption decreases. The desorption can occur by thermal agitation and the rate of desorption will depend upon the amount of solid surface covered by gas molecules. It will increase as the surface becomes more and more saturated. At a certain stage, the rates of condensation and desorption become equal and an equilibrium is established.
- Using the above assumptions, Langmuir equation for adsorption can be derived as follows:

  Let the fraction of the total surface covered by gas molecules be θ ; then the surface available for adsorption is $1-\theta$. According to kinetic theory of gases, the rate at which the molecules strike the unit area of surface is proportional to the pressure of the gas. If p is the equilibrium gas pressure, then,

  rate of condensation $\alpha\ (1-\theta)p$

  or rate of condensation $= k_1(1-\theta)p$ . . . (21.3)

  where k_1 is a constant of proportionality.

  Rate of evaporation from the surface will be proportional only to the fraction of the surface which has adsorbed gas molecules on it. Thus,

  rate of evaporation $= k_2\theta$ . . . (21.4)

  k_2 is also a proportionality constant.

  At equilibrium, the rates of condensation and evaporation are equal. Hence,

  $k_1(1-\theta)p = k_2\theta$ . . . (21.5)

Rearranging Eq. 21.5, we can get,

$$\theta = \frac{k_1 p}{k_2 + k_1 p} = \frac{(k_1/k_2)\,p}{1 + (k_1/k_2)\,p} \quad \text{(dividing the numerator and denominator by } k_2\text{)}$$

$$\theta = \frac{Kp}{1 + Kp} \quad \text{(where } k_1/k_2 = K\text{, another constant)} \qquad \ldots (21.6)$$

Eq. 21.6 could be modified to find a relationship between the amount of gas adsorbed and the gas pressure. The amount of gas adsorbed (y) at a pressure p is proportional to the fraction of the total surface covered (θ) by the gas molecules.

i.e., $y \propto \theta$

Hence, $y = y_m\theta$ or $y/y_m = \theta$ ...(21.7)

Where y_m is the proportionality constant and is equal to the amount of the gas molecules required to form a unimolecular layer; i.e., $y = y_m$ when $\theta = 1$.

Using Eqs. 21.6 and 21.7,

$$\frac{y}{y_m} = \frac{Kp}{1 + Kp}$$

$$y = \frac{y_m Kp}{1 + Kp}$$

$$\text{or } \frac{p}{y} = \frac{1 + Kp}{y_m K} = \frac{1}{y_m K} + \frac{p}{y_m} \qquad \ldots (21.8)$$

Eq. 21.8 is known as Langmuir adsorption isotherm.

When the gas pressure is low, p/y_m is small when compared to $\frac{1}{y_m K}$. Hence $\frac{p}{y} = \frac{1}{y_m K}$

or $p/y =$ constant, since y_m and K are constants.

or $p \propto y$

This means that at low pressures, the amount of gas adsorbed is proportional to gas pressure.

When the gas pressure is high, $\frac{p}{y_m}$ is much larger than $1/y_m K$. Hence Eq. 21.8 could be written as,

$$\frac{p}{y} = \frac{p}{y_m}$$

or $y = y_m$ which means that at high pressures, the amount of gas adsorbed is sufficient to form a unimolecular layer. A way to verify Langmuir adsorption isotherm (Eq. 21.8) is to plot p/y against p. A straight line must be obtained. (Fig. 21.2)

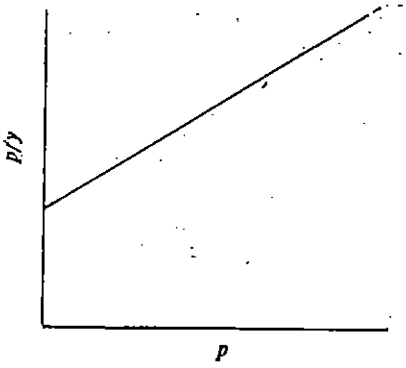

Fig. 21.2 Graphical representation of Langmuir adsorption isotherm.

It is observed that straight line plots are obtained when the surfaces are smooth and nonporous and when the pressures are not too high. Under these conditions, Eq. 21.8 is obeyed. Deviations from Langmuir adsorption isotherm are seen if

- surface is porous (i.e., a good adsorbent) and
- pressure is very high.

Under these conditions, gas molecules give rise to multilayer adsorption on the solid surface which accounts for deviations from Eq. 21.8. For explaining multilayer adsorption, Brunauer, Emmet and Teller have proposed a model which is known as **BET** isotherm which we are not going to discuss in detail.

SAQ 2

Starting from Eq. 21.6, derive the following equation:

$$p = \frac{\theta}{K(1-\theta)}$$

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21.5 PHYSISORPTION AND CHEMISORPTION

Both physisorption and chemisorption are generally exothermic processes. That is why we talk about enthalpy decrease while comparing energies of physisorption and chemisorption.

Depending on the type of interaction between the adsorbate and the adsorbent, adsorption is of two types–physisorption (physical adsorption) and chemisorption (chemical adsorption).

Physisorption

If the adsorbate molecules are weakly bound to the adsorbent, it is classified as physisorption. It is also known as van der Waals adsorption since the forces involved are of van der Waals type and are of the same magnitude as are involved in the liquefaction of gases. The enthalpy decrease $(-\Delta H)$ associated with physisorption is much low (less than 40 kJ mol^{-1}) and is of the same order as the enthalpy of condensation of the adsorbate. Increase of temperature is not favourable to physisorption. Adsorption of gases by charcoal is an example of physisorption. Physisorption is generally independent of the chemical nature of the adsorbate. All gases exhibit van der Waals adsorption.

The unsatisfied valencies of the surface atoms may cause breakage of the bonds in the chemisorbed molecules. The fragments that result in the process are responsible for the increased chemical activity.

Chemisorption

High bond enthalpy of nitrogen (945 kJ mol^{-1}) is mainly responsible for its low reactivity.

If the adsorbed molecules react chemically with the surface, we call it chemisorption. The enthalpy decrease associated with chemisorption is much high (between 40 kJ mol^{-1} and 400 kJ mol^{-1}) and is of the order of bond enthalpies. We shall see in Sec. 21.8 as to how the type of bonding caused by chemisorption between the adsorbent and the adsorbate determines the reactivity pattern. Many chemisorption processes involve activation energy as in a chemical reaction. In such cases, the rates of chemisorption and desorption increase with temperature in contrast with the rate of physisorption.

One of the methods followed in scientific reasoning is to arrive at the same conclusion through more than one method. Take for instance manufacture of ammonia. Based on Le Chatelier principle, we stated in Unit 14 that high pressure (200–300 atm) and optimum temperature (670–870 K) are needed for a good yield of ammonia. These conclusions could be reached from surface studies also. In this section, we have explained that around 770 K, nitrogen is chemisorbed on iron to a large extent and, this facilitates formation of ammonia. As an explanation for the need of high pressure for this reaction, answer SAQ 3.

Let us see how the type of adsorption of nitrogen on iron surface varies with temperature. The studies on the adsorption of nitrogen on iron surface indicate that at about 770 K (the temperature chosen for Haber process), nitrogen is chemisorbed on the iron surface. Chemisorption results in large release of energy. The optimum temperature chosen for the reaction and the energy released during chemisorption are helpful in overcoming the large bond enthalpy of nitrogen. Hence, when nitrogen is chemisorbed at 770 K it is present as nitrogen atoms but not as molecules.

At temperatures less than 770 K, there is not much of chemisorption of nitrogen on iron surface. At room temperature, iron does not adsorb nitrogen at all. But as temperature is lowered and brought near 80 K, the boiling point of liquid nitrogen, iron adsorbs nitrogen gas physically as N_2 molecules! In short, near 770 K, nitrogen is chemisorbed by iron as nitrogen atoms and near 80 K, it is physisorbed as nitrogen molecules.

The dissociation of nitrogen molecule on iron surface at 770 K could facilitate its further reaction such as the formation of ammonia through Haber process. Although the mechanism of iron catalysis in Haber process is not completely understood, the chemisorption of nitorgen on iron certainly plays a role in it.

SAQ 3

Assuming that chemisorption of nitrogen on iron at 770 K follows Langmuir isotherm, could you justify the use of high pressure in Haber process for the manufacture of ammonia?

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21.6 MODERN METHODS OF SURFACE STUDIES

The composition of the adsorbent surface, the nature of binding between the adsorbent and the adsorbate and the extent of surface coverage could be studied by using methods such as X-ray or UV photoelectron spectroscopy, Auger spectroscopy and low energy electron diffraction (LEED). Of these methods, we shall explain the principle of X-ray and UV photoelectron spectroscopy only.

In Unit 1 of Atoms and Molecules course, we have explained the photoelectric effect, according to which photoelectrons could be ejected by irradiating a metal surface with UV rays. The minimum energy that UV rays must possess for photoelectron emission corresponds to the ionisation energy of the valence electrons. If we are interested in the emission of inner electrons, we must use X-rays. The studies on electron emission which is caused by X-ray or UV irradiation are called X-ray or UV photoelectron spectroscopy (X.p.e.s or UV p.e.s). Since such photoelectron spectroscopy studies are useful in obtaining the finger print of the materials present in a surface of a material, these methods are known as **electron spectroscopy for chemical analysis** (ESCA). It is possible to identify the elements present in a given surface using X.p.e.s since each element has characteristic inner shell ionisation energies. The surface study using ESCA is made possible by the fact that the ejected electrons cannot escape except from within a few nanometers from the surface. The nature of chemisorption between a catalyst surface and the reactant molecules could be established by ESCA studies.

Auger effect is the emission of a second electron after high energy radiation has expelled an electron. Auger effect is the basis of Auger Spectroscopy and is much used in microelectronics industry.

Low energy electron diffraction is the diffraction caused by atoms on the surface by using low energy electrons. The LEED pattern depicts the two dimensional structure of a surface. Low energy electrons are used to ensure diffraction by atoms on the surface only, but not by atoms in the bulk.

SAQ 4

What is the basic principle for ESCA studies of the surfaces?

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21.7 TYPES OF CATALYSTS

We have seen in Unit 18, that the rate of a chemical reaction can be increased by raising the temperature. This increases the fraction of molecules having energies in excess of some threshold energy (nearly equal to activation energy). Another way to increase the rate of chemical reaction is to find an alternate path for the reaction that has a lower activation enery. A catalyst produces this alternate path for a chemical reaction. The sole function of the catalyst is to lower the activation energy of a reaction. Thus a small amount of manganese dioxide increases the rate of decomposition of $KClO_3$; the decomposition of nitrous oxide is accelerated by iodine; in presence of Ni, unsaturated hydrocarbons can be hydrogenated to saturated hydrocarbons. The amount of a catalyst remains unchanged at the end of a reacion and, may be used again and again. **A substance which can influence the rate of a chemical reaction but itself remains unchanged chemically is called a catalyst.**

A catalyst cannot start a chemical reaction that could not take place in its absence. A catalyst does not alter the position of equilibrium; in other words, it cannot change the relative amounts of the reactants and products at the equilibrium. Consequently a catalyst must accelerate equally both the forward and the reverse reactions. A catalyst is highly specific in its action, e.g., MnO_2 can catalvse the decomposition of $KClO_3$ but not that of KNO_3. In certain reactions, one of the products could catalyse the reaction. For instance, in the oxidation of oxalic acid by acidified $KMnO_4$, Mn^{2+} ions formed during the reaction, increase the rate of reaction. This type of phenomenon is called **auto-catalysis.**

Catalysis may be of homogeneous or heterogeneous type. In homogeneous catalysis, the catalyst forms a single phase with the reactants and products, whereas in heterogeneous catalysis, it constitutes a seperate phase.

There is another type of catalysis, known as enzyme catalysis. Enzymes have high relative molecular masses and are protein molecules. The enzymes catalyse a variety of chemical reactions in living organisms. The enzyme reaction medium is colloidal in nature and strictly speaking, enzyme catalysis does not fall under homogeneous or heterogeneous catalysis. The enzymes are specific in catalysing only a particular set of reactions. Enzyme activity depends on pH of the medium.

Examples for all the three types of catalysis are provided in Table 21.2.

Table 21.2 : Three Types of Catalysis

Type		Illustrative reaction	Catalyst
Homogeneous catalysis	1)	$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	$NO(g)$
	2)	$CH_3COOC_2H_5(l) + H_2O(l) \rightarrow CH_3COOH(l) + C_2H_5OH(l)$	$H_3O^+(aq)$
Hetero-geneous catalysis	1)	$HCOOH(g) \rightarrow H_2O(g) + CO(g)$	$Al_2O_3(s)$
	2)	$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	$Pt(s)$
Enzyme* catalysis	1)	$NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2$	Urease
	2)	$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$	Zymase

* Note that in enzyme catalysis, we have not specified the states of the substances.

In the next section, we shall discuss the theories of catalysis.

21.8 MECHANISMS OF CATALYTIC REACTIONS

A mechanism offered to explain the specificity of enzymes suggests that the shapes of the reacting molecule and the enzyme must fit together as lock and key. The reactant and the active site of the enzyme get attached through hydrogen bonding, ionic bonding or metal ion-ligand bonding or a combination of these.

In homogeneous or enzyme catalysis, a reaction intermediate is formed between the reactant and the catalyst or the enzyme. The intermediate compound then decomposes to give the product. The reaction sequence can be represented as follows:

Step (i)Formation of the intermediate compound $S + C \rightleftharpoons SC$

Step (ii) Decomposition of the intermediate compound $SC \longrightarrow P + C$

Where S and P are the reactant and the product and C is the catalyst or the enzyme; SC is the intermediate compound. The role of the catalyst or the enzyme is to lower the activation energies of the forward and reverse reactions. In Fig. 21.3, E_c is the activation energy for the conversion of a reactant to a product in the presence of a catalyst and E_{uc} is the activation energy for the same reaction in the absence of catalyst. You can see that $E_c < E_{uc}$. The same is true of the reverse reaction also.

It is interesting to note that many of the biological reactions are catalysed by enzymes. This is facilitated by the fact that the enzyme catalysed reactions have much lower activation energies than systems containing chemical catalysts. Look at Table 21.3 which indicates the activation energies for the decomposition of hydrogen peroxide under different conditions and make your own judgement!

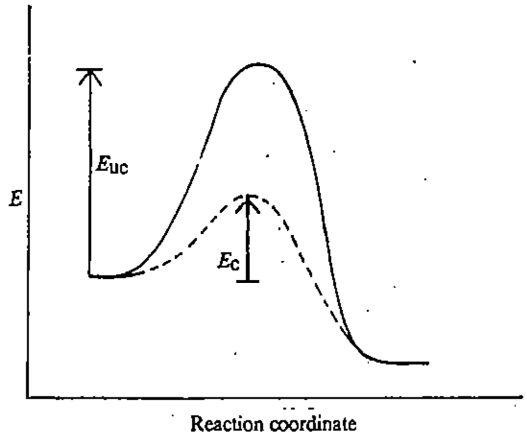

Fig.21.3. Relative activation energies for catalysed and uncatalysed reactions.

Table 21.3 : Activation Energies for the Decomposition of Hydrogen Peroxide Solution

Catalyst	Activation energy/kJ mol^{-1}	Relative rate of reaction
None	75.3	1
I^- (*aq*) (homogeneous)	56.5	2.0×10^3
Pt (*s*) (heterogeneous)	49.0	4.1×10^4
Catalase (enzyme)	8	6.3×10^{11}

In heterogeneous catalysis also, the role of the catalyst surface is to bring down the activation energies of the reactions. This happens due to chemisorption which is similar to intermediate compound formation in homogeneous catalysis. The ability of a surface to have chemisorption of the reactant molecules depends on the chemical nature of surface. ESCA studies (Sec. 21.6) are helpful in deciding the nature of chemisorption between the surface and the reactant molecules. The difference in the nature of chemisorption could lead to different products even from the same reactant. For example, ethyl alcohol is dehydrogenated on Ni, Pd or Pt catalysts to give acetaldehyde.

You can have an idea about the importance of enzyme reactions from the fact that ammonia produced from nitrogen by nitrogenase enzyme is ten times more than that produced by Haber process. Further the enzyme gives good yields of ammonia at room temperature and pressure. Compare this with the experimental conditions needed for Haber process (200-300 atm pressure and 670-870 K temparature).

$$CH_3CH_2OH \xrightarrow{\text{Ni, Pd or Pt}} CH_3CHO + H_2$$

On the other hand, ethyl alcohol undergoes dehydration reaction on alumina.

$$CH_3CH_2OH \xrightarrow{\text{Alumina}} CH_2 = CH_2 + H_2O$$

On Ni, Pd or Pt surfaces, the linkage of ethyl alcohol is through two hydrogen atoms (Fig. 21.4). The strong affinity between Ni and hydrogen accounts for the removal of two hydrogen atoms from ethyl alcohol.

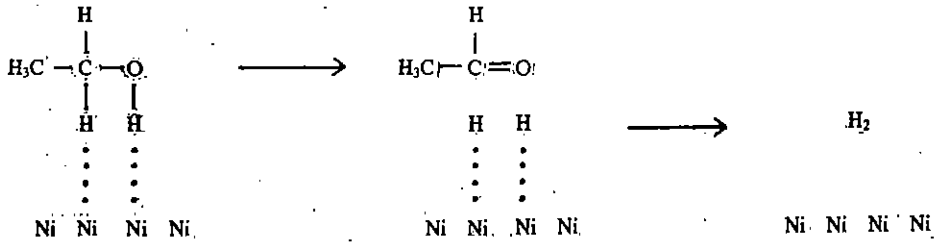

Fig. 21.4 : Dehydrogenation process on Ni

On the other hand, alumina acts differently due to its different structure. Alumina has both oxide groups and hydroxyl groups. The linkage of ethyl alcohol to alumina is through hydrogen and oxygen atoms as shown in Fig. 21.5. The removal of hydrogen and hydroxyl groups from adjacent carbon atoms leads to the dehydration reaction.

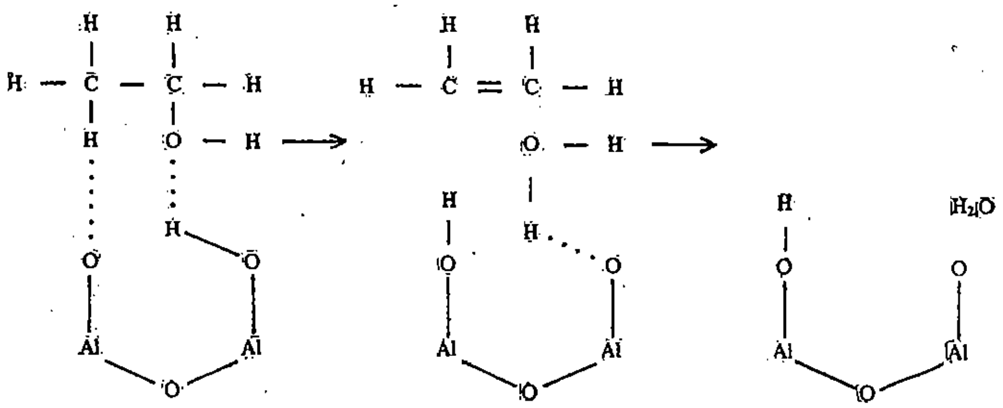

Fig. 21.5: Dehydration process on alumina.

Certain substances improve the activity of a catalyst. Such substances are called **promoters**. These substances may not themselves be effective catalysts. A promoter may increase the number of active sites on a catalyst surface. In the light of this discussion, let us examine the catalysis in Haber process of manufacture of ammonia. A mixture of iron oxide, potassium oxide and aluminium oxide facilitates this reaction. The hydrogen atmosphere reduces iron oxide into porous iron which has large surface area that acts as the catalyst. The mixture of potassium oxide and aluminium oxide acts as promoters.

Let us now see a few applications of catalysts in chemical industries.

- In the preparation of edible fats from vegetable and animal fats, controlled partial hydrogenation with a catalyst such as nickel helps in removing some of the double bonds. In the absence of hydrogenation, these double bonds could be oxidised by air which impart the oil a rancid odour on storage.

- Careful studies of the catalytic surfaces have been helpful in preferential formation of a product starting from a reactant. Thus it is possible to prepare various oxidation products of ethylene such as ethanol, acetaldehyde, vinyl chloride or vinyl acetate by proper choice of catalysts and reaction conditions.

- You may be aware that 'cracking' is the process of producing small organic molecules by the breaking of long-chain hydrocarbon molecules. Usually, silica-alumina catalysts are used for this purpose. Cracking is required to produce branched chain isomeric hydrocarbons which have more fuel efficiency in automobile engines.

SAQ 5

At 310 K (blood temperature), sucrose could be hydrolysed using an enzyme, saccharase or a mineral acid. The reaction rate for one reaction is 10^{12} times higher than the other. Identify the faster reaction.

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SAQ 6

In Unit 18, it has been explained that the rate ~~of a re~~action is proportional to $e^{-E/RT}$. The activation energy of the reaction $H_2(g) + I_2(g)$ $2HI(g)$ is reduced from 184 kJ mol^{-1} to 59 kJ mol^{-1} in the presence of platinum catalyst. By what factor will the reaction rate be increased by platinum at 600 K? Assume that the frequency factor remains unchanged.

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21.9 INHIBITION AND POISONING

We studied that the reactants are to be adsorbed on the surface for the chemical reaction to be influenced by the surface. For the enhancement of the reaction rate, the reactants must be adsorbed more or less to same extent. If one of the reactants is more strongly adsorbed than the other or if a product is adsorbed to a greater extent than the reactants, then the active centres on the catalyst surface would not be available completely for the reaction and the reaction rate decreases. Such a condition is called inhibition of the catalyst. One of the reactants or the products which gets strongly adsorbed and thereby decreases the reaction rate is called the inhibitor. For example, in the decomposition of ammonia on platinum surface, hydrogen (a product) is strongly adsorbed and inhibits the reaction.

It is possible that the reaction could be inhibited by a foreign molecule that does not take part in a reaction. This type of inhibition is called catalytic poisoning. It is observed that even a small amount of the catalytic poison could be effective in stopping a reaction. This phenomenon could be explained by the fact that the active centres constitute only a small fraction of the total surface sites on a catalyst and, the meagre amount of poison could occupy these positions. This prevents the occupation by reactant molecules. For example, in the contact process of sulphuric acid manufacture, even a small amount of arsenic impurity poisons the platinised asbestos catalyst and the reaction almost stops.

SAQ 7

State the conditions under which a catalyst loses its influence over a reaction.

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21.10 SUMMARY

In this unit, we discussed the role of surface in chemical reactions. Here we have

- defined a surface active agent,
- discussed the significance of adsorption isotherms,
- explained physisorption and chemisorption,
- outlined the modern methods of surface studies,
- described the types of catalysts and indicated the mechanisms of their activity, and
- discussed the inhibition and poisoning of catalysts.

21.11 TERMINAL QUESTIONS

1) The activation energies required for the uncatalysed decomposition of ammonia and for its decomposition in presence of tungsten are 350 and 162 kJ mol^{-1} respectively. Explain the reason for this difference in activation energy.

2) The adsorption of a gas follows Langmuir isotherm with $K = 8.50 \times 10^{-4}$ Pa^{-1} at 298 K. Find the pressure at which surface coverage is (a) 15.0% (b) 95%. Comment on your results.

3) The heterogeneous catalyst is often taken in the form of a finely divided powder rather than as a smooth surface. Explain the reason.

4) Based on adsorption studies, justify the temperature choice for Haber process.

5) Copper catalyses the formation of steam from hydrogen and oxygen through the formation of CuO as an intermediate. Suggest a reaction sequence for this condition.

6) Define the terms; (i) adsorption (ii) adsorbate (iii) adsorbent.

7) A particular mass of charcoal adsorbs a larger volume of ammonia than of hydrogen at a given temperature. Explain.

8) Based on energy released during adsorption, how can you distinguish between physisorption and chemisorption?

21.12 ANSWERS

Self-assessment Questions

1) The surface tension of a solution must decrease when a surface active agent is added so that its concentration is more in the surface than in the bulk.

2) According to Eq. 21.6, $\theta = \dfrac{Kp}{1+Kp}$

$$\theta(1+Kp) = Kp$$

$$Kp(\theta-1) = -\theta$$

$$Kp(1-\theta) = \theta$$

Hence, $$p = \frac{\theta}{K(1-\theta)}$$

3) As per Eq. 21.6, at sufficiently high pressure $\theta = 1$. Thus at high pressure, we can expect large coverage of iron surface by nitrogen which could lead to its dissociation and also to its reaction with hydrogen to form ammonia on a large scale.

4) Even though X-rays may penetrate into the bulk sample, the ejected electrons cannot escape except from within a few nanometers from the surface. Hence this technique is mainly limited to the study of surface layers.

5) Enzyme catalysed reaction needs lower activation energy than the mineral acid catalysed reaction. Hence, enzyme catalysed reaction must be faster than the other.

6) Let r_1 and r_2 be the reaction rates in the absence of platinum and in the presence of platinum, respectively. Let E_1 and E_2 be the corresponding activation energies. Assuming frequency factors to be equal,

$$\frac{r_1}{r_2} = e^{-E_1/RT}/e^{-E_2/RT} = e^{(E_2-E_1)/RT}$$

Taking natural logarithms, $$\ln\frac{r_1}{r_2} = \frac{E_2-E_1}{RT}$$

or $$\ln\frac{r_2}{r_1} = \frac{E_1-E_2}{RT}$$

$$2.303\log\frac{r_2}{r_1} = \frac{E_1-E_2}{RT}$$

$$\log\frac{r_2}{r_1} = \frac{E_1-E_2}{2.303\,RT}$$

$$\frac{r_2}{r_1} = \left(\text{Antilog of } \frac{E_1-E_2}{2.303\,RT}\right)$$

$$= \text{Antilog of}\left(\frac{125\times10^3\ \text{J mol}^{-1}}{2.303\times8.314\times600\ \text{J mol}^{-1}}\right)$$

$$\frac{r_2}{r_1} = 7.6\times10^{10}$$

Hence the reaction rate is increased by 7.6×10^{10} times by platinum.

7) When a catalyst surface is strongly adsorbed by reactant or product or foreign gas molecules, the catalyst cannot influence the reaction rate.

Terminal Questions

1) In presence of tungsten catalyst, there is chemisorption of ammonia which is an exothermic process. This helps in bringing down the activation energy of the reaction.

2) a) 208 Pa;

   b) 2.24×10^4 Pa.

   It is seen that if adsorption of a gas follows Langmuir isotherm, then high pressure is required for larger coverage of the surface.

3) For a heterogeneous catalyst to be effective, a large surface area is required. Since a finely divided powder has large surface area, a heterogeneous catalyst is employed in this form.

4) See Sec. 21.5.

5) $Cu(s) + \frac{1}{2} O_2(g) \rightarrow CuO(s)$

   $CuO(s) + H_2(g) \rightarrow H_2O(g) + Cu(s)$

6) See Sec. 21.3.

7) The interaction between charcoal and gases such as ammonia and hydrogen is of van der Waals type. It is a weak interaction. Ammonia which could be liquefied easily is more readily adsorbed than hydrogen since the forces responsible for physical adsorption and liquefaction of gases are the same.

8) Energy released during chemisorption is much larger than that during physisorption.

NOTES