# Chemistry

## Part I

## Textbook for Class XII

12085

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Textbook for Class XII

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# FOREWORD

The National Curriculum Framework (NCF), 2005 recommends that children's life at school must be linked to their life outside the school. This principle marks a departure from the legacy of bookish learning which continues to shape our system and causes a gap between the school, home and community. The syllabi and textbooks developed on the basis of NCF signify an attempt to implement this basic idea. They also attempt to discourage rote learning and the maintenance of sharp boundaries between different subject areas. We hope these measures will take us significantly further in the direction of a child-centred system of education outlined in the National Policy on Education (1986).

The success of this effort depends on the steps that school principals and teachers will take to encourage children to reflect on their own learning and to pursue imaginative activities and questions. We must recognise that, given space, time and freedom, children generate new knowledge by engaging with the information passed on to them by adults. Treating the prescribed textbook as the sole basis of examination is one of the key reasons why other resources and sites of learning are ignored. Inculcating creativity and initiative is possible if we perceive and treat children as participants in learning, not as receivers of a fixed body of knowledge.

These aims imply considerable change in school routines and mode of functioning. Flexibility in the daily time-table is as necessary as rigour in implementing the annual calender so that the required number of teaching days are actually devoted to teaching. The methods used for teaching and evaluation will also determine how effective this textbook proves for making children's life at school a happy experience, rather than a source of stress or boredom. Syllabus designers have tried to address the problem of curricular burden by restructuring and reorienting knowledge at different stages with greater consideration for child psychology and the time available for teaching. The textbook attempts to enhance this endeavour by giving higher priority and space to opportunities for contemplation and wondering, discussion in small groups, and activities requiring hands-on experience.

The National Council of Educational Research and Training (NCERT) appreciates the hard work done by the textbook development committee responsible for this book. We wish to thank the Chairperson of the advisory group in science and mathematics, Professor J.V. Narlikar and the Chief Advisor for this book, Professor B. L. Khandelwal for guiding the work of this committee. Several teachers contributed to the development of this textbook; we are grateful to their principals for making this possible. We are indebted to the institutions and organisations which have generously permitted us to draw upon their resources, material and personnel. As an organisation committed to systemic reform and continuous improvement in the quality of its products, NCERT welcomes comments and suggestions which will enable us to undertake further revision and refinement.

*Director*
National Council of Educational
Research and Training

New Delhi
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# RATIONALISATION OF CONTENT IN THE TEXTBOOKS

In view of the COVID-19 pandemic, it is imperative to reduce content load on students. The National Education Policy 2020, also emphasises reducing the content load and providing opportunities for experiential learning with creative mindset. In this background, the NCERT has undertaken the exercise to rationalise the textbooks across all classes. Learning Outcomes already developed by the NCERT across classes have been taken into consideration in this exercise.

**Contents of the textbooks have been rationalised in view of the following:**

- Overlapping with similar content included in other subject areas in the same class
- Similar content included in the lower or higher class in the same subject
- Difficulty level
- Content, which is easily accessible to students without much interventions from teachers and can be learned by children through self-learning or peer-learning
- Content, which is irrelevant in the present context

**This present edition, is a reformatted version after carrying out the changes given above.**

# PREFACE

Chemistry has made a profound impact on the society. It is intimately linked to the well-being of human kind. The rate of advancements in chemistry is so high that curriculum developers continuously look for strategies to cope with these advancements. Also, the students have to be inspired to be the future leaders who would make fundamental contributions. The present textbook is a sincere effort in this direction.

The structure of the textbook, presented in two parts, comprises of sixteen Units. Although the titles of various Units indicate a sort of compartmentalisation into physical, inorganic and organic chemistry, readers will find that these sub-disciplines have been intermingled, at least to a certain extent, to have a unified approach to the subject. The approach of presentation of the subject matter discourages students from rote memorisation. The subject has in fact, been organised around the laws and principles of chemistry. As students master these laws and principles, they will soon get to the point where they can predict much of what will come.

Efforts have been directed towards making the subject stimulating and exciting by references to the historical developments and its usefulness to our lives, wherever appropriate. The text is well illustrated with examples from surrounding environment to facilitate grasping of the qualitative and quantitative aspects of the concept easily. Physical data are given in SI units throughout the book to make comparison of various properties easier. IUPAC system of nomenclature has been followed along with the common system. Structural formulae of chemical compounds showing functional/coordinating groups in different colours are drawn using electronic system. Each Unit has a good number of examples, as illustrations, with their solutions and some intext questions, the answers of some of which are given at the end of the Unit. The end of Unit exercises are designed to apply important principles and provoke thinking process to solve them. Answers of some of these exercises are given at the end of the book.

A variety of materials, e.g., biographical sketches of some scientists, additional information related to a particular topic, etc., is given in boxes with a deep yellow coloured bar. This boxed material with a 'deep yellow bar' is to bring additional life to the topic. However, it is non-evaluative. The structures of some of the more complex compounds incorporated in the book are for understanding their chemistry. As their reproduction would lead to memorisation, it is also a non-evaluative portion of the text.

The information part has been significantly reduced and, wherever possible, it has been substantiated with facts. However, it is necessary for students to be aware of commercially important chemicals, their process of manufacture and sources of raw materials. This leads to descriptive material in the book. Attempts have been made to make descriptions of such compounds interesting by considering their structures and reactivity. Thermodynamics, kinetics and electrochemical aspects have been applied to chemical reactions which should be beneficial to students for understanding why a particular reaction happened and why a particular property is exhibited by the product. There is currently great awareness of environmental and energy issues which are directly related to chemistry. Such issues have been highlighted and dealt with at appropriate places in the book.

A team of experts constituted by the NCERT has developed the manuscript of the book. It gives me great pleasure to acknowledge the valuable contribution of all the members of this team. I also acknowledge the valuable and relentless contribution of the editors in bringing the book to the present shape. I also acknowledge with thanks the dedicated efforts and valuable contribution of Professor Brahm Parkash, who not only coordinated the entire programme but also actively involved in writing and editing of this book. Thanks are also due to the participating teachers and subject experts of the review workshop for their contribution, which has helped us to make the book learner friendly. Also, I thank the technical and administrative staff of the NCERT for their support in the entire process.

The team of this textbook development programme hopes that the book stimulates its readers and makes them feel the excitement and fascination for this subject. Efforts have been made to bring out this book error-free. Nevertheless, it is recognised that in such a book of complexity, there could inevitably be occasional errors. It will always be a pleasure to hear about them from readers to take necessary steps to rectify them.

B.L. KHANDELWAL

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# THE CONSTITUTION OF INDIA

## PREAMBLE

**WE, THE PEOPLE OF INDIA,** having solemnly resolved to constitute India into a [1]**[SOVEREIGN SOCIALIST SECULAR DEMOCRATIC REPUBLIC]** and to secure to all its citizens :

**JUSTICE,** social, economic and political;

**LIBERTY** of thought, expression, belief, faith and worship;

**EQUALITY** of status and of opportunity; and to promote among them all

**FRATERNITY** assuring the dignity of the individual and the [2][unity and integrity of the Nation];

**IN OUR CONSTITUENT ASSEMBLY** this twenty-sixth day of November, 1949 do **HEREBY ADOPT, ENACT AND GIVE TO OURSELVES THIS CONSTITUTION.**

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1. Subs. by the Constitution (Forty-second Amendment) Act, 1976, Sec.2, for "Sovereign Democratic Republic" (w.e.f. 3.1.1977)
2. Subs. by the Constitution (Forty-second Amendment) Act, 1976, Sec.2, for "Unity of the Nation" (w.e.f. 3.1.1977)

# CONTENTS

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# Unit 1

# Solutions

## Objectives

After studying this Unit, you will be able to

- describe the formation of different types of solutions;
- express concentration of solution in different units;
- state and explain Henry's law and Raoult's law;
- distinguish between ideal and non-ideal solutions;
- explain deviations of real solutions from Raoult's law;
- describe colligative properties of solutions and correlate these with molar masses of the solutes;
- explain abnormal colligative properties exhibited by some solutes in solutions.

*Almost all processes in body occur in some kind of liquid solutions.*

In normal life we rarely come across pure substances. Most of these are mixtures containing two or more pure substances. Their utility or importance in life depends on their composition. For example, the properties of brass (mixture of copper and zinc) are quite different from those of German silver (mixture of copper, zinc and nickel) or bronze (mixture of copper and tin); 1 part per million (ppm) of fluoride ions in water prevents tooth decay, while 1.5 ppm causes the tooth to become mottled and high concentrations of fluoride ions can be poisonous (for example, sodium fluoride is used in rat poison); intravenous injections are always dissolved in water containing salts at particular ionic concentrations that match with blood plasma concentrations and so on.

In this Unit, we will consider mostly liquid solutions and their formation. This will be followed by studying the properties of the solutions, like vapour pressure and colligative properties. We will begin with types of solutions and then various alternatives in which concentrations of a solute can be expressed in liquid solution.

## 1.1 Types of Solutions

Solutions are **homogeneous** mixtures of two or more than two components. By homogenous mixture we mean that its composition and properties are uniform throughout the mixture. Generally, the component that is present in the largest quantity is known as **solvent**. Solvent determines the physical state in which solution exists. One or more components present in the solution other than solvent are called **solutes.** In this Unit we shall consider only **binary solutions** (i.e., consisting of two components). Here each component may be solid, liquid or in gaseous state and are summarised in Table 1.1.

**Table 1.1: Types of Solutions**

| Type of Solution | Solute | Solvent | Common Examples |
|---|---|---|---|
| *Gaseous Solutions* | Gas | Gas | Mixture of oxygen and nitrogen gases |
| | Liquid | Gas | Chloroform mixed with nitrogen gas |
| | Solid | Gas | Camphor in nitrogen gas |
| *Liquid Solutions* | Gas | Liquid | Oxygen dissolved in water |
| | Liquid | Liquid | Ethanol dissolved in water |
| | Solid | Liquid | Glucose dissolved in water |
| *Solid Solutions* | Gas | Solid | Solution of hydrogen in palladium |
| | Liquid | Solid | Amalgam of mercury with sodium |
| | Solid | Solid | Copper dissolved in gold |

## 1.2 Expressing Concentration of Solutions

Composition of a solution can be described by expressing its concentration. The latter can be expressed either qualitatively or quantitatively. For example, qualitatively we can say that the solution is dilute (i.e., relatively very small quantity of solute) or it is concentrated (i.e., relatively very large quantity of solute). But in real life these kinds of description can add to lot of confusion and thus the need for a quantitative description of the solution.

There are several ways by which we can describe the concentration of the solution quantitatively.

(i) *Mass percentage* (w/w): The mass percentage of a component of a solution is defined as:

Mass % of a component

$$= \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100 \qquad (1.1)$$

For example, if a solution is described by 10% glucose in water by mass, it means that 10 g of glucose is dissolved in 90 g of water resulting in a 100 g solution. Concentration described by mass percentage is commonly used in industrial chemical applications. For example, commercial bleaching solution contains 3.62 mass percentage of sodium hypochlorite in water.

(ii) *Volume percentage (V/V)*: The volume percentage is defined as:

$$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of solution}} \times 100 \qquad (1.2)$$

For example, 10% ethanol solution in water means that 10 mL of ethanol is dissolved in water such that the total volume of the solution is 100 mL. Solutions containing liquids are commonly expressed in this unit. For example, a 35% (*v/v*) solution of ethylene glycol, an antifreeze, is used in cars for cooling the engine. At this concentration the antifreeze lowers the freezing point of water to 255.4K (–17.6°C).

(iii) *Mass by volume percentage* (w/V): Another unit which is commonly used in medicine and pharmacy is mass by volume percentage. It is the mass of solute dissolved in 100 mL of the solution.

(iv) *Parts per million*: When a solute is present in **trace** quantities, it is convenient to express concentration in **parts per million (ppm)** and is defined as:

Parts per million =

$$\frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6 \quad (1.3)$$

As in the case of percentage, concentration in parts per million can also be expressed as mass to mass, volume to volume and mass to volume. A litre of sea water (which weighs 1030 g) contains about $6 \times 10^{-3}$ g of dissolved oxygen ($O_2$). Such a small concentration is also expressed as 5.8 g per $10^6$ g (5.8 ppm) of sea water. The concentration of pollutants in water or atmosphere is often expressed in terms of $\mu g\ mL^{-1}$ or ppm.

(v) *Mole fraction*: Commonly used symbol for mole fraction is $x$ and subscript used on the right hand side of $x$ denotes the component. It is defined as:

Mole fraction of a component =

$$\frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}} \quad (1.4)$$

For example, in a binary mixture, if the number of moles of A and B are $n_A$ and $n_B$ respectively, the mole fraction of A will be

$$x_A = \frac{n_A}{n_A + n_B} \quad (1.5)$$

For a solution containing i number of components, we have:

$$x_i = \frac{n_i}{n_1 + n_2 + \ldots\ldots + n_i} = \frac{n_i}{\sum n_i} \quad (1.6)$$

It can be shown that in a given solution sum of all the mole fractions is unity, i.e.

$$x_1 + x_2 + \ldots\ldots\ldots\ldots\ldots + x_i = 1 \quad (1.7)$$

Mole fraction unit is very useful in relating some physical properties of solutions, say vapour pressure with the concentration of the solution and quite useful in describing the calculations involving gas mixtures.

**Example 1.1** Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.

**Solution** Assume that we have 100 g of solution (one can start with any amount of solution because the results obtained will be the same). Solution will contain 20 g of ethylene glycol and 80 g of water.

Molar mass of $C_2H_6O_2$ = 12 × 2 + 1 × 6 + 16 × 2 = 62 g mol$^{-1}$.

$$\text{Moles of } C_2H_6O_2 = \frac{20 \text{ g}}{62 \text{ g mol}^{-1}} = 0.322 \text{ mol}$$

$$\text{Moles of water} = \frac{80 \text{ g}}{18 \text{ g mol}^{-1}} = 4.444 \text{ mol}$$

$$x_{\text{glycol}} = \frac{\text{moles of } C_2H_6O_2}{\text{moles of } C_2H_6O_2 + \text{moles of } H_2O}$$

$$= \frac{0.322 \text{ mol}}{0.322 \text{ mol} + 4.444 \text{ mol}} = 0.068$$

$$\text{Similarly, } x_{\text{water}} = \frac{4.444 \text{ mol}}{0.322 \text{ mol} + 4.444 \text{ mol}} = 0.932$$

Mole fraction of water can also be calculated as: 1 – 0.068 = 0.932

(vi) *Molarity*: Molarity (*M*) is defined as number of moles of solute dissolved in one litre (or one cubic decimetre) of solution,

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}} \tag{1.8}$$

For example, 0.25 mol L$^{-1}$ (or 0.25 M) solution of NaOH means that 0.25 mol of NaOH has been dissolved in one litre (or one cubic decimetre).

**Example 1.2** Calculate the molarity of a solution containing 5 g of NaOH in 450 mL solution.

**Solution** 
$$\text{Moles of NaOH} = \frac{5 \text{ g}}{40 \text{ g mol}^{-1}} = 0.125 \text{ mol}$$

Volume of the solution in litres = 450 mL / 1000 mL L$^{-1}$

Using equation (2.8),

$$\text{Molarity} = \frac{0.125 \text{ mol} \times 1000 \text{ mL L}^{-1}}{450 \text{ mL}} = 0.278 \text{ M}$$

$$= 0.278 \text{ mol L}^{-1}$$

$$= 0.278 \text{ mol dm}^{-3}$$

(vii) *Molality*: Molality (*m*) is defined as the number of moles of the solute per kilogram (kg) of the solvent and is expressed as:

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} \tag{1.9}$$

For example, 1.00 mol $kg^{-1}$ (or 1.00 m) solution of KCl means that 1 mol (74.5 g) of KCl is dissolved in 1 kg of water.

Each method of expressing concentration of the solutions has its own merits and demerits. Mass %, ppm, mole fraction and molality are independent of temperature, whereas molarity is a function of temperature. This is because volume depends on temperature and the mass does not.

**Example 1.3**

Calculate molality of 2.5 g of ethanoic acid ($CH_3COOH$) in 75 g of benzene.

**Solution**

Molar mass of $C_2H_4O_2$: $12 \times 2 + 1 \times 4 + 16 \times 2 = 60 \text{ g mol}^{-1}$

$$\text{Moles of } C_2H_4O_2 = \frac{2.5 \text{ g}}{60 \text{ g mol}^{-1}} = 0.0417 \text{ mol}$$

Mass of benzene in kg = $75 \text{ g}/1000 \text{ g kg}^{-1} = 75 \times 10^{-3}$ kg

$$\text{Molality of } C_2H_4O_2 = \frac{\text{Moles of } C_2H_4O_2}{\text{kg of benzene}} = \frac{0.0417 \text{ mol} \times 1000 \text{ g kg}^{-1}}{75 \text{ g}}$$

$$= 0.556 \text{ mol kg}^{-1}$$

**Intext Questions**

**1.1** Calculate the mass percentage of benzene ($C_6H_6$) and carbon tetrachloride ($CCl_4$) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.

**1.2** Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

**1.3** Calculate the molarity of each of the following solutions: (a) 30 g of $Co(NO_3)_2 . 6H_2O$ in 4.3 L of solution (b) 30 mL of 0.5 M $H_2SO_4$ diluted to 500 mL.

**1.4** Calculate the mass of urea ($NH_2CONH_2$) required in making 2.5 kg of 0.25 molal aqueous solution.

**1.5** Calculate (a) molality (b) molarity and (c) mole fraction of KI if the density of 20% (mass/mass) aqueous KI is 1.202 g $mL^{-1}$.

## 1.3 Solubility

Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature. It depends upon the nature of solute and solvent as well as temperature and pressure. Let us consider the effect of these factors in solution of a solid or a gas in a liquid.

### 1.3.1 Solubility of a Solid in a Liquid

Every solid does not dissolve in a given liquid. While sodium chloride and sugar dissolve readily in water, naphthalene and anthracene do not. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not. It is observed that polar solutes dissolve in polar solvents and non polar solutes in non-polar solvents. In general, a solute dissolves in a solvent if the intermolecular interactions are similar in the two or we may say **like dissolves like**.

When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution. Some solute particles in solution collide with the solid solute particles and get separated out of solution. This process is known as crystallisation. A stage is reached when the two processes occur at the same rate. Under such conditions, number of solute particles going into solution will be equal to the solute particles separating out and a state of dynamic equilibrium is reached.

$$\text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution} \qquad (1.10)$$

At this stage the concentration of solute in solution will remain constant under the given conditions, i.e., temperature and pressure. Similar process is followed when gases are dissolved in liquid solvents. Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a **saturated solution**. An *unsaturated solution* is one in which more solute can be dissolved at the same temperature. The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent. Thus, the concentration of solute in such a solution is its solubility.

Earlier we have observed that solubility of one substance into another depends on the nature of the substances. In addition to these variables, two other parameters, i.e., temperature and pressure also control this phenomenon.

***Effect of temperature***

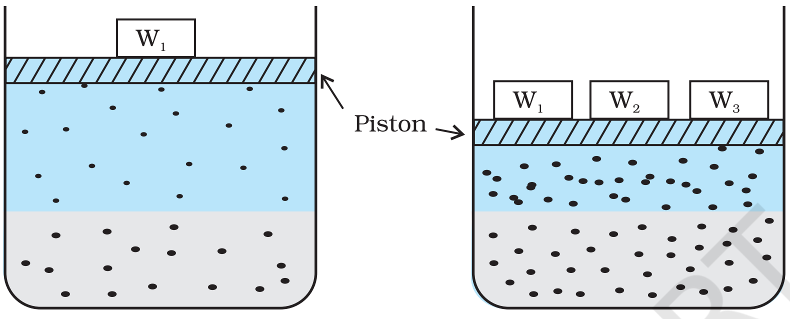
The solubility of a solid in a liquid is significantly affected by temperature changes. Consider the equilibrium represented by equation 1.10. This, being dynamic equilibrium, must follow **Le Chateliers Principle.** In general, if in a *nearly saturated solution*, the dissolution process is endothermic ($\Delta_{sol} H > 0$), the solubility should increase with rise in temperature and if it is exothermic ($\Delta_{sol} H < 0$) the solubility should decrease. These trends are also observed experimentally.

***Effect of pressure***

Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

### 1.3.2 Solubility of a Gas in a Liquid

Many gases dissolve in water. Oxygen dissolves only to a small extent in water. It is this dissolved oxygen which sustains all aquatic life. On the other hand, hydrogen chloride gas (HCl) is highly soluble in water. Solubility of gases in liquids is greatly affected by pressure and temperature. The solubility of gases increase with increase of pressure. For solution of gases in a solvent, consider a system as shown in Fig. 1.1 (a). The lower part is solution and the upper part is gaseous system at pressure $p$ and temperature $T$. Assume this system to be in a state of dynamic equilibrium, i.e., under these conditions rate of gaseous particles entering and leaving the solution phase is the same. Now increase the pressure over the solution phase by compressing the gas to a smaller volume [Fig. 1.1 (b)]. This will increase the number of gaseous particles per unit volume over the solution and also the rate at which the gaseous particles are striking the surface of solution to enter it. The solubility of the gas will increase until a new equilibrium is reached resulting in an increase in the pressure of a gas above the solution and thus its solubility increases.



(a) (b)

***Fig. 1.1:*** *Effect of pressure on the solubility of a gas. The concentration of dissolved gas is proportional to the pressure on the gas above the solution.*

Henry was the first to give a quantitative relation between pressure and solubility of a gas in a solvent which is known as **Henry's law**. The law states that at a constant temperature, **the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.** Dalton, a contemporary of Henry, also concluded independently that the solubility of a gas in a liquid solution is a function of partial pressure of the gas. If we use the mole fraction of a gas in the solution as a measure of its solubility, then it can be said that the **mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.** The most commonly used form of Henry's law states that "**the partial pressure of the gas in vapour phase ($p$) is proportional to the mole fraction of the gas ($x$) in the solution**" and is expressed as:

$$p = K_H \; x \tag{1.11}$$

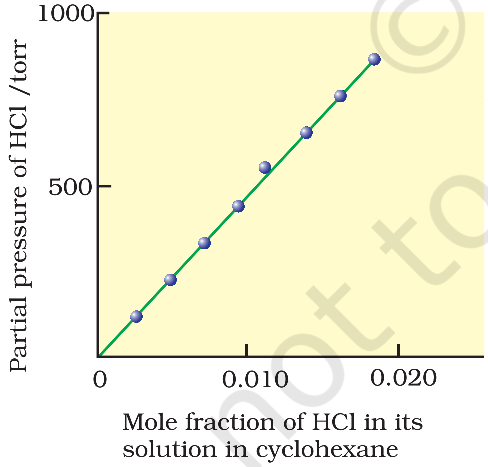


***Fig. 1.2:*** *Experimental results for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's Law constant, $K_H$.*

Here $K_H$ is the Henry's law constant. If we draw a graph between partial pressure of the gas versus mole fraction of the gas in solution, then we should get a plot of the type as shown in Fig. 1.2.

Different gases have different $K_H$ values at the same temperature (Table 1.2). This suggests that $K_H$ is a function of the nature of the gas.

It is obvious from equation (1.11) that higher the value of $K_H$ at a given pressure, the lower is the solubility of the gas in the liquid. It can be seen from Table 1.2 that $K_H$ values for both $N_2$ and $O_2$ increase with increase of temperature indicating that the solubility of gases

**Table 1.2: Values of Henry's Law Constant for Some Selected Gases in Water**

| Gas | Temperature/K | $K_H$ /kbar | Gas | Temperature/K | $K_H$/kbar |
|---|---|---|---|---|---|
| He | 293 | 144.97 | Argon | 298 | 40.3 |
| $H_2$ | 293 | 69.16 | $CO_2$ | 298 | 1.67 |
| $N_2$ | 293 | 76.48 | Formaldehyde | 298 | $1.83\times10^{-5}$ |
| $N_2$ | 303 | 88.84 | Methane | 298 | 0.413 |
| $O_2$ | 293 | 34.86 | Vinyl chloride | 298 | 0.611 |
| $O_2$ | 303 | 46.82 | | | |

increases with decrease of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than in warm waters.

**Example 1.4** If $N_2$ gas is bubbled through water at 293 K, how many millimoles of $N_2$ gas would dissolve in 1 litre of water? Assume that $N_2$ exerts a partial pressure of 0.987 bar. Given that Henry's law constant for $N_2$ at 293 K is 76.48 *k*bar.

**Solution** The solubility of gas is related to the mole fraction in aqueous solution. The mole fraction of the gas in the solution is calculated by applying Henry's law. Thus:

$$x\,(\text{Nitrogen}) = \frac{p\,(\text{nitrogen})}{K_H} = \frac{0.987\text{bar}}{76{,}480\text{ bar}} = 1.29 \times 10^{-5}$$

As 1 litre of water contains 55.5 mol of it, therefore if $n$ represents number of moles of $N_2$ in solution,

$$x\,(\text{Nitrogen}) = \frac{n\text{ mol}}{n\text{ mol} + 55.5\text{ mol}} = \frac{n}{55.5} = 1.29 \times 10^{-5}$$

($n$ in denominator is neglected as it is $<<$ 55.5)

Thus $n = 1.29 \times 10^{-5} \times 55.5\text{ mol} = 7.16 \times 10^{-4}\text{ mol}$

$$= \frac{7.16\times10^{-4}\text{ mol} \times 1000\text{ mmol}}{1\text{ mol}} = 0.716\text{ mmol}$$

Henry's law finds several applications in industry and explains some biological phenomena. Notable among these are:

- To increase the solubility of $CO_2$ in soft drinks and soda water, the bottle is sealed under high pressure.
- Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as *bends*, which are painful and dangerous to life.

To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

- At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as *anoxia*.

### *Effect of Temperature*

Solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. We have learnt in the last Section that dissolution process involves dynamic equilibrium and thus must follow **Le Chatelier's Principle**. As dissolution is an exothermic process, the solubility should decrease with increase of temperature.

### Intext Questions

**1.6** $H_2S$, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of $H_2S$ in water at STP is 0.195 m, calculate Henry's law constant.

**1.7** Henry's law constant for $CO_2$ in water is $1.67 \times 10^8$ Pa at 298 K. Calculate the quantity of $CO_2$ in 500 mL of soda water when packed under 2.5 atm $CO_2$ pressure at 298 K.

## 1.4 Vapour Pressure of Liquid Solutions

Liquid solutions are formed when solvent is a liquid. The solute can be a gas, a liquid or a solid. Solutions of gases in liquids have already been discussed in Section 1.3.2. In this Section, we shall discuss the solutions of liquids and solids in a liquid. Such solutions may contain one or more volatile components. Generally, the liquid solvent is volatile. The solute may or may not be volatile. We shall discuss the properties of only binary solutions, that is, the solutions containing two components, namely, the solutions of (i) liquids in liquids and (ii) solids in liquids.

### 1.4.1 Vapour Pressure of Liquid-Liquid Solutions

Let us consider a binary solution of two volatile liquids and denote the two components as 1 and 2. When taken in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between vapour phase and the liquid phase. Let the total vapour pressure at this stage be $p_{\text{total}}$ and $p_1$ and $p_2$ be the partial vapour pressures of the two components 1 and 2 respectively. These partial pressures are related to the mole fractions $x_1$ and $x_2$ of the two components 1 and 2 respectively.

The French chemist, Francois Marte Raoult (1886) gave the quantitative relationship between them. The relationship is known as the **Raoult's law** which states that **for a solution of volatile liquids,**

**the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution**.

Thus, for component 1

$$p_1 \propto x_1$$

and $$p_1 = p_1^0 \, x_1 \qquad (1.12)$$

where $p_1^0$ is the vapour pressure of pure component 1 at the same temperature.

Similarly, for component 2

$$p_2 = p_2^{\,0} \, x_2 \qquad (1.13)$$

where $p_2^{\,0}$ represents the vapour pressure of the pure component 2.

According to **Dalton's law of partial pressures**, the total pressure $(p_{\text{total}})$ over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as:

$$p_{\text{total}} = p_1 + p_2 \qquad (1.14)$$

Substituting the values of $p_1$ and $p_2$, we get

$$\begin{aligned} p_{\text{total}} &= x_1 \, p_1^{\,0} + x_2 \, p_2^{\,0} \\ &= (1 - x_2) \, p_1^{\,0} + x_2 \, p_2^{\,0} \qquad (1.15) \\ &= p_1^{\,0} + (p_2^{\,0} - p_1^{\,0}) \, x_2 \qquad (1.16) \end{aligned}$$

Following conclusions can be drawn from equation (1.16).

(i) Total vapour pressure over the solution can be related to the mole fraction of any one component.

(ii) Total vapour pressure over the solution varies linearly with the mole fraction of component 2.

(iii) Depending on the vapour pressures of the pure components 1 and 2, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component 1.

A plot of $p_1$ or $p_2$ versus the mole fractions $x_1$ and $x_2$ for a solution gives a linear plot as shown in Fig. 1.3. These lines (I and II) pass through the points for which $x_1$ and $x_2$ are equal to unity. Similarly the plot (line III) of $p_{\text{total}}$ versus $x_2$ is also linear (Fig. 1.3). The minimum value of $p_{\text{total}}$ is $p_1^{\,0}$ and the maximum value is $p_2^{\,0}$, assuming that component 1 is less volatile than component 2, i.e., $p_1^{\,0} < p_2^{\,0}$.

The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components. If $y_1$ and $y_2$ are the mole fractions of the

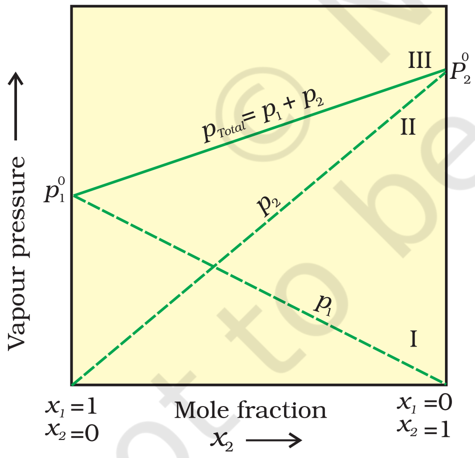


**Fig. 1.3:** *The plot of vapour pressure and mole fraction of an ideal solution at constant temperature. The dashed lines I and II represent the partial pressure of the components. (It can be seen from the plot that $p_1$ and $p_2$ are directly proportional to $x_1$ and $x_2$, respectively). The total vapour pressure is given by line marked III in the figure.*

components 1 and 2 respectively in the vapour phase then, using Dalton's law of partial pressures:

$$p_1 = y_1\ p_{\text{total}} \tag{1.17}$$

$$p_2 = y_2\ p_{\text{total}} \tag{1.18}$$

In general

$$p_i = y_i\ p_{\text{total}} \tag{1.19}$$

**Example 1.5**

Vapour pressure of chloroform ($CHCl_3$) and dichloromethane ($CH_2Cl_2$) at 298 K are 200 mm Hg and 415 mm Hg respectively. (i) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of $CH_2Cl_2$ at 298 K and, (ii) mole fractions of each component in vapour phase.

**Solution**

(i) Molar mass of $CH_2Cl_2 = 12 \times 1 + 1 \times 2 + 35.5 \times 2 = 85\ \text{g mol}^{-1}$

Molar mass of $CHCl_3 = 12 \times 1 + 1 \times 1 + 35.5 \times 3 = 119.5\ \text{g mol}^{-1}$

Moles of $CH_2Cl_2 = \dfrac{40\ \text{g}}{85\ \text{g mol}^{-1}} = 0.47$ mol

Moles of $CHCl_3 = \dfrac{25.5\ \text{g}}{119.5\ \text{g mol}^{-1}} = 0.213$ mol

Total number of moles = 0.47 + 0.213 = 0.683 mol

$x_{CH_2Cl_2} = \dfrac{0.47\ \text{mol}}{0.683\ \text{mol}} = 0.688$

$x_{CHCl_3} = 1.00 - 0.688 = 0.312$

Using equation (2.16),

$$p_{\text{total}} = p_1^0 + (p_2^0 - p_1^0)\,x_2 = 200 + (415 - 200) \times 0.688$$

$$= 200 + 147.9 = 347.9 \text{ mm Hg}$$

(ii) Using the relation (2.19), $y_i = p_i/p_{\text{total}}$, we can calculate the mole fraction of the components in gas phase ($y_i$).

$p_{CH_2Cl_2} = 0.688 \times 415$ mm Hg = 285.5 mm Hg

$p_{CHCl_3} = 0.312 \times 200$ mm Hg = 62.4 mm Hg

$y_{CH_2Cl_2} = 285.5$ mm Hg/347.9 mm Hg = 0.82

$y_{CHCl_3} = 62.4$ mm Hg/347.9 mm Hg = 0.18

**Note:** Since, $CH_2Cl_2$ is a more volatile component than $CHCl_3$, [$p^0_{CH_2Cl_2}$ = 415 mm Hg and $p^0_{CHCl_3}$ = 200 mm Hg] and the vapour phase is also richer in $CH_2Cl_2$ [$y_{CH_2Cl_2}$ = 0.82 and $y_{CHCl_3}$ = 0.18], it may thus be concluded that **at equilibrium, vapour phase will be always rich in the component which is more volatile.**

### 1.4.2 Raoult's Law as a special case of Henry's Law

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by $p_i = x_i\, p_i^0$. In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas and we have already seen that its solubility is given by Henry's law which states that

$$p = K_H\, x.$$

If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution. Only the proportionality constant $K_H$ differs from $p_1^0$. Thus, Raoult's law becomes a special case of Henry's law in which $K_H$ becomes equal to $p_1^0$.

### 1.4.3 Vapour Pressure of Solutions of Solids in Liquids

Another important class of solutions consists of solids dissolved in liquid, for example, sodium chloride, glucose, urea and cane sugar in water and iodine and sulphur dissolved in carbon disulphide. Some physical properties of these solutions are quite different from those of pure solvents. For example, vapour pressure. Liquids at a given temperature vapourise and under equilibrium conditions the pressure exerted by the vapours of the liquid over the liquid phase is called vapour pressure [Fig. 1.4 (a)]. In a pure liquid the entire surface is occupied by the molecules of the liquid. If a non-volatile solute is added to a solvent to give a solution [Fig. 1.4.(b)], the vapour pressure of the solution is solely from the solvent alone. This vapour pressure of the solution at a given temperature is found to be lower than the vapour pressure of the pure solvent at the same temperature. In the solution, the surface has both solute and solvent molecules; thereby the fraction of the surface covered by the solvent molecules gets reduced. Consequently, the number of solvent molecules escaping from the surface is correspondingly reduced, thus, the vapour pressure is also reduced.

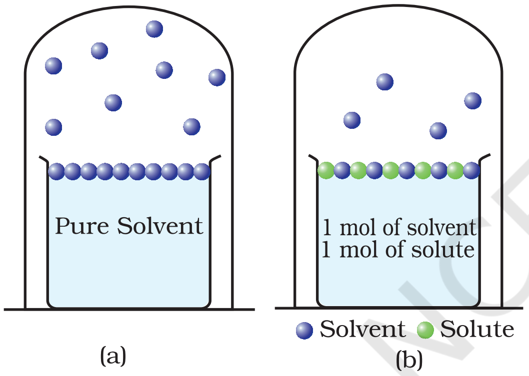


**Fig. 1.4:** *Decrease in the vapour pressure of the solvent on account of the presence of solute in the solvent (a) evaporation of the molecules of the solvent from its surface is denoted by ●, (b) in a solution, solute particles have been denoted by ● and they also occupy part of the surface area.*

The decrease in the vapour pressure of solvent depends on the quantity of non-volatile solute present in the solution, irrespective of its nature. For example, decrease in the vapour pressure of water by adding 1.0 mol of sucrose to one kg of water is nearly similar to that produced by adding 1.0 mol of urea to the same quantity of water at the same temperature.

Raoult's law in its general form can be stated as, **for any solution the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction**.

In a binary solution, let us denote the solvent by 1 and solute by 2. When the solute is non-volatile, only the solvent molecules are present in vapour phase and contribute to vapour pressure. Let $p_1$ be the vapour pressure of the solvent, $x_1$ be its mole fraction, $p_{\mathrm{i}}^0$ be its vapour pressure in the pure state. Then according to Raoult's law

$$p_1 \propto x_1$$

$$\text{and} \quad p_1 = x_1\, p_1^0 \qquad (1.20)$$

The proportionality constant is equal to the vapour pressure of pure solvent, $p_1^0$. A plot between the vapour pressure and the mole fraction of the solvent is linear (Fig. 1.5).

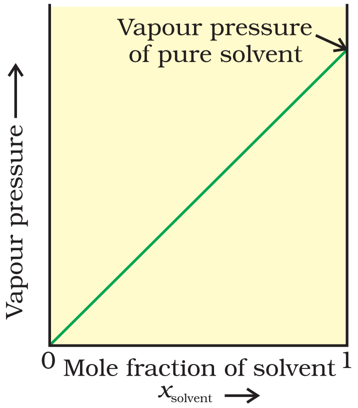


***Fig. 1.5***
*If a solution obeys Raoult's law for all concentrations, its vapour pressure would vary linearly from zero to the vapour pressure of the pure solvent.*

## 1.5 Ideal and Non-ideal Solutions

Liquid-liquid solutions can be classified into ideal and non-ideal solutions on the basis of Raoult's law.

### 1.5.1 Ideal Solutions

The solutions which obey Raoult's law over the entire range of concentration are known as *ideal solutions*. The ideal solutions have two other important properties. The enthalpy of mixing of the pure components to form the solution is zero and the volume of mixing is also zero, i.e.,

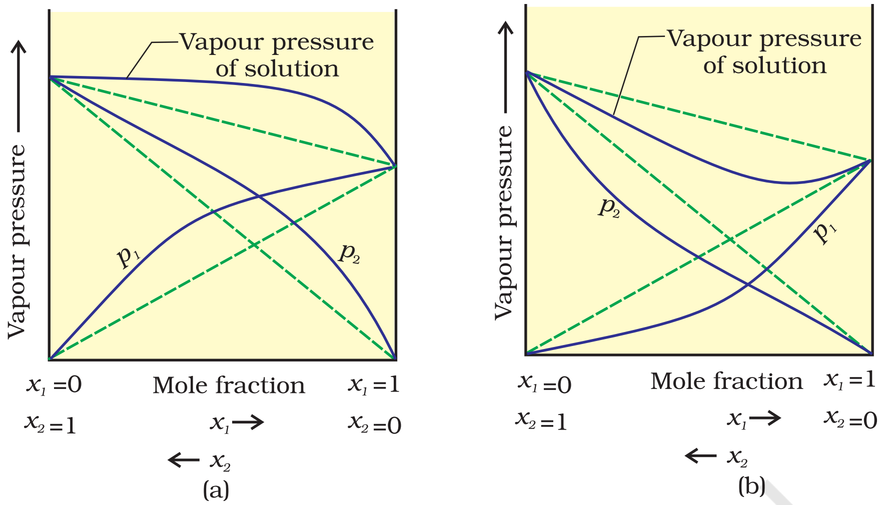
$$\Delta_{\text{mix}}H = 0, \qquad \Delta_{\text{mix}}V = 0 \qquad (1.21)$$

It means that no heat is absorbed or evolved when the components are mixed. Also, the volume of solution would be equal to the sum of volumes of the two components. At molecular level, ideal behaviour of the solutions can be explained by considering two components A and B. In pure components, the intermolecular attractive interactions will be of types A-A and B-B, whereas in the binary solutions in addition to these two interactions, A-B type of interactions will also be present. If the intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B, this leads to the formation of ideal solution. A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Solution of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc. fall into this category.

### 1.5.2 Non-ideal Solutions

When a solution does not obey Raoult's law over the entire range of concentration, then it is called *non-ideal solution*. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law (equation 1.16). If it is higher, the solution exhibits **positive deviation** and if it is lower, it exhibits **negative deviation** from Raoult's law. The plots of vapour pressure as a function of mole fractions for such solutions are shown in Fig. 1.6.

The cause for these deviations lie in the nature of interactions at the molecular level. In case of positive deviation from Raoult's law, A-B interactions are weaker than those between A-A or B-B, i.e., in this case the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules. This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state. This will increase the vapour

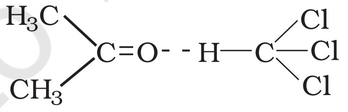


(a) (b)

***Fig.1.6*** *The vapour pressures of two component systems as a function of composition (a) a solution that shows positive deviation from Raoult's law and (b) a solution that shows negative deviation from Raoult's law.*

pressure and result in positive deviation. Mixtures of ethanol and acetone behave in this manner. In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution shows positive deviation from Raoult's law [Fig. 1.6 (a)]. In a solution formed by adding carbon disulphide to acetone, the dipolar interactions between solute-solvent molecules are weaker than the respective interactions among the solute-solute and solvent-solvent molecules. This solution also shows positive deviation.

In case of negative deviations from Raoult's law, the intermolecular attractive forces between A-A and B-B are weaker than those between A-B and leads to decrease in vapour pressure resulting in negative deviations. An example of this type is a mixture of phenol and aniline. In this case the intermolecular hydrogen bonding between phenolic proton and lone pair on nitrogen atom of aniline is stronger than the respective intermolecular hydrogen bonding between similar molecules. Similarly, a mixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown.



This decreases the escaping tendency of molecules for each component and consequently the vapour pressure decreases resulting in negative deviation from Raoult's law [Fig. 1.6. (b)].

Some liquids on mixing, form **azeotropes** which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called **minimum boiling azeotrope and maximum boiling azeotrope**. The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.

For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95% by volume of ethanol. Once this composition, known as azeotrope composition, has been achieved, the liquid and vapour have the same composition, and no further separation occurs.

The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

## Intext Question

**1.8** The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K . Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

## 1.6 Colligative Properties and Determination of Molar Mass

We have learnt in Section 1.4.3 that the vapour pressure of solution decreases when a non-volatile solute is added to a volatile solvent. There are many properties of solutions which are connected with this decrease of vapour pressure. These are: (1) relative lowering of vapour pressure of the solvent (2) depression of freezing point of the solvent (3) elevation of boiling point of the solvent and (4) osmotic pressure of the solution. **All these properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. Such properties are called *colligative properties*** (colligative: from Latin: co means together, ligare means to bind). In the following Sections we will discuss these properties one by one.

### 1.6.1 Relative Lowering of Vapour Pressure

We have learnt in Section 1.4.3 that the vapour pressure of a solvent in solution is less than that of the pure solvent. Raoult established that the lowering of vapour pressure depends only on the concentration of the solute particles and it is independent of their identity. The equation (1.20) given in Section 1.4.3 establishes a relation between vapour pressure of the solution, mole fraction and vapour pressure of the solvent, i.e.,

$$p_1 = x_1\, p_1^0 \tag{1.22}$$

The reduction in the vapour pressure of solvent ($\Delta p_1$) is given as:

$$\begin{aligned}\Delta p_1 &= p_1^0 - p_1 = p_1^0 - p_1^0\, x_1 \\ &= p_1^0\,(1 - x_1) \qquad (1.23)\end{aligned}$$

Knowing that $x_2 = 1 - x_1$, equation (1.23) reduces to

$$\Delta p_1 = x_2\, p_1^0 \tag{1.24}$$

In a solution containing several non-volatile solutes, the lowering of the vapour pressure depends on the sum of the mole fraction of different solutes.

Equation (1.24) can be written as

$$\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x_2 \tag{1.25}$$

The expression on the left hand side of the equation as mentioned earlier is called **relative lowering of vapour pressure and is equal to the mole fraction of the solute**. The above equation can be written as:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2} \quad \left(\text{since } x_2 = \frac{n_2}{n_1 + n_2}\right) \tag{1.26}$$

Here $n_1$ and $n_2$ are the number of moles of solvent and solute respectively present in the solution. For dilute solutions $n_2 << n_1$, hence neglecting $n_2$ in the denominator we have

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1} \tag{1.27}$$

or $$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \tag{1.28}$$

Here $w_1$ and $w_2$ are the masses and $M_1$ and $M_2$ are the molar masses of the solvent and solute respectively.

From this equation (1.28), knowing all other quantities, the molar mass of solute ($M_2$) can be calculated.

**Example 1.6** The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g when added to 39.0 g of benzene (molar mass 78 g $mol^{-1}$). Vapour pressure of the solution, then, is 0.845 bar. What is the molar mass of the solid substance?

**Solution** The various quantities known to us are as follows:

$p_1^0 = 0.850$ bar; $p = 0.845$ bar; $M_1 = 78$ g $mol^{-1}$; $w_2 = 0.5$ g; $w_1 = 39$ g

Substituting these values in equation (2.28), we get

$$\frac{0.850 \text{ bar} - 0.845 \text{ bar}}{0.850 \text{ bar}} = \frac{0.5 \text{ g} \times 78 \text{ g mol}^{-1}}{M_2 \times 39 \text{ g}}$$

Therefore, $M_2 = 170$ g $mol^{-1}$

### 1.6.2 Elevation of Boiling Point

The vapour pressure of a liquid increases with increase of temperature. It boils at the temperature at which its vapour pressure is equal to the atmospheric pressure. For example, water boils at 373.15 K (100° C) because at this temperature the vapour pressure of water is 1.013 bar (1 atmosphere). We have also learnt in the last section that vapour pressure of the solvent decreases in the presence of non-volatile solute. Fig. 1.7 depicts the variation of vapour pressure of the pure solvent and solution as a function of temperature. For example, the vapour pressure of an aqueous solution of sucrose is less than 1.013 bar at 373.15 K. In order to make this solution boil, its vapour pressure must be increased to 1.013 bar by raising the temperature above the boiling temperature of the pure solvent (water). Thus, the boiling point of a solution is

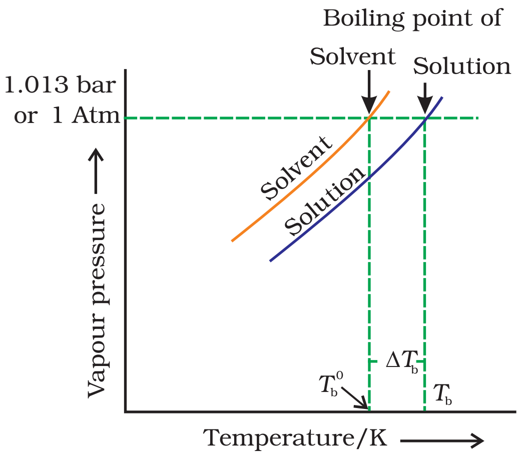


***Fig. 1.7:*** *The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that $\Delta T_b$ denotes the elevation of boiling point of a solvent in solution.*

always higher than that of the boiling point of the pure solvent in which the solution is prepared as shown in Fig. 1.7. Similar to lowering of vapour pressure, the elevation of boiling point also depends on the number of solute molecules rather than their nature. A solution of 1 mol of sucrose in 1000 g of water boils at 373.52 K at one atmospheric pressure.

Let $T_b^0$ be the boiling point of pure solvent and $T_b$ be the boiling point of solution. The increase in the boiling point $\Delta T_b = T_b - T_b^0$ is known as **elevation of boiling point**.

Experiments have shown that for **dilute solutions** the elevation of boiling point ($\Delta T_b$) is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_b \propto m \qquad (1.29)$$

$$\text{or} \quad \Delta T_b = K_b\ m \qquad (1.30)$$

Here *m* (molality) is the number of moles of solute dissolved in 1 kg of solvent and the constant of proportionality, $K_b$ is called **Boiling Point Elevation Constant or Molal Elevation Constant (Ebullioscopic Constant)**. The unit of $K_b$ is K kg mol$^{-1}$. Values of $K_b$ for some common solvents are given in Table 1.3. If $w_2$ gram of solute of molar mass $M_2$ is dissolved in $w_1$ gram of solvent, then molality, m of the solution is given by the expression:

$$m = \frac{w_2/M_2}{w_1/1000} = \frac{1000 \times w_2}{M_2 \times w_1} \qquad (1.31)$$

Substituting the value of molality in equation (1.30) we get

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1} \qquad (1.32)$$

$$M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1} \qquad (1.33)$$

Thus, in order to determine $M_2$, molar mass of the solute, known mass of solute in a known mass of the solvent is taken and $\Delta T_b$ is determined experimentally for a known solvent whose $K_b$ value is known.

**Example 1.7**

18 g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water in a saucepan. At what temperature will water boil at 1.013 bar? $K_b$ for water is 0.52 K kg mol$^{-1}$.

**Solution**

Moles of glucose = 18 g/ 180 g mol$^{-1}$ = 0.1 mol
Number of kilograms of solvent = 1 kg
Thus molality of glucose solution = 0.1 mol kg$^{-1}$
For water, change in boiling point

$\Delta T_b = K_b \times m = 0.52 \text{ K kg mol}^{-1} \times 0.1 \text{ mol kg}^{-1} = 0.052 \text{ K}$

Since water boils at 373.15 K at 1.013 bar pressure, therefore, the boiling point of solution will be 373.15 + 0.052 = 373.202 K.

**Example 1.8** The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. $K_b$ for benzene is 2.53 K kg mol$^{-1}$

**Solution** The elevation ($\Delta T_b$) in the boiling point = 354.11 K – 353. 23 K = 0.88 K

Substituting these values in expression (2.33) we get

$$M_2 = \frac{2.53 \text{ K kg mol}^{-1} \times 1.8 \text{ g} \times 1000 \text{ g kg}^{-1}}{0.88 \text{ K} \times 90 \text{ g}} = 58 \text{ g mol}^{-1}$$

Therefore, molar mass of the solute, $M_2$ = 58 g mol$^{-1}$

### 1.6.3 Depression of Freezing Point

The lowering of vapour pressure of a solution causes a lowering of the freezing point compared to that of the pure solvent (Fig. 1.8). We know that at the freezing point of a substance, the solid phase is in dynamic equilibrium with the liquid phase. Thus, the freezing point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in the solid phase. A solution will freeze when its vapour pressure equals the vapour pressure of the pure solid solvent as is clear from Fig. 1.8. According to Raoult's law, when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at lower temperature. Thus, the freezing point of the solvent decreases.

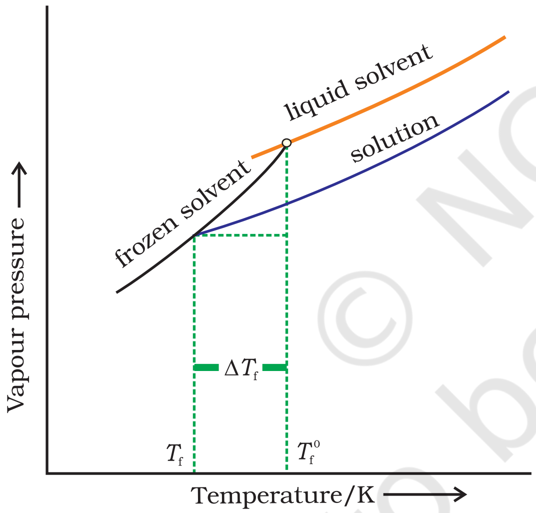


**Fig. 1.8:** *Diagram showing $\Delta T_f$, depression of the freezing point of a solvent in a solution.*

Let $T_f^0$ be the freezing point of pure solvent and $T_f$ be its freezing point when non-volatile solute is dissolved in it. The decrease in freezing point.

$\Delta T_f = T_f^0 - T_f$ is known as depression in freezing point.

Similar to elevation of boiling point, depression of freezing point ($\Delta T_f$) for **dilute solution** (ideal solution) is directly proportional to molality, m of the solution. Thus,

$$\Delta T_f \propto \text{m}$$

or $$\Delta T_f = K_f \text{ m} \qquad (1.34)$$

The proportionality constant, $K_f$, which depends on the nature of the solvent is known as **Freezing Point Depression Constant or Molal**

**Depression Constant or Cryoscopic Constant**. The unit of $K_f$ is K kg mol$^{-1}$. Values of $K_f$ for some common solvents are listed in Table 1.3.

If $w_2$ gram of the solute having molar mass as $M_2$, present in $w_1$ gram of solvent, produces the depression in freezing point $\Delta T_f$ of the solvent then molality of the solute is given by the equation (1.31).

$$\text{m} = \frac{w_2 \;/\; M_2}{w_1/1000} \tag{1.31}$$

Substituting this value of molality in equation (1.34) we get:

$$\Delta T_f = \frac{K_f \times w_2 \,/\, M_2}{w_1 \,/1000}$$

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1} \tag{1.35}$$

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1} \tag{1.36}$$

Thus for determining the molar mass of the solute we should know the quantities $w_1$, $w_2$, $\Delta T_f$, along with the molal freezing point depression constant.

The values of $K_f$ and $K_b$, which depend upon the nature of the solvent, can be ascertained from the following relations.

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus} H} \tag{1.37}$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap} H} \tag{1.38}$$

Here the symbols $R$ and $M_1$ stand for the gas constant and molar mass of the solvent, respectively and $T_f$ and $T_b$ denote the freezing point and the boiling point of the pure solvent respectively in kelvin. Further, $\Delta_{fus}H$ and $\Delta_{vap}H$ represent the enthalpies for the fusion and vapourisation of the solvent, respectively.

### Table 1.3: Molal Boiling Point Elevation and Freezing Point Depression Constants for Some Solvents

| Solvent | b. p./K | $K_b$/K kg mol$^{-1}$ | f. p./K | $K_f$/K kg mol$^{-1}$ |
|---|---|---|---|---|
| Water | 373.15 | 0.52 | 273.0 | 1.86 |
| Ethanol | 351.5 | 1.20 | 155.7 | 1.99 |
| Cyclohexane | 353.74 | 2.79 | 279.55 | 20.00 |
| Benzene | 353.3 | 2.53 | 278.6 | 5.12 |
| Chloroform | 334.4 | 3.63 | 209.6 | 4.79 |
| Carbon tetrachloride | 350.0 | 5.03 | 250.5 | 31.8 |
| Carbon disulphide | 319.4 | 2.34 | 164.2 | 3.83 |
| Diethyl ether | 307.8 | 2.02 | 156.9 | 1.79 |
| Acetic acid | 391.1 | 2.93 | 290.0 | 3.90 |

**Example 1.9** 45 g of ethylene glycol ($C_2H_6O_2$) is mixed with 600 g of water. Calculate (a) the freezing point depression and (b) the freezing point of the solution.

**Solution** Depression in freezing point is related to the molality, therefore, the molality of the solution with respect to ethylene glycol = $\dfrac{\text{moles of ethylene glycol}}{\text{mass of water in kilogram}}$

$$\text{Moles of ethylene glycol} = \frac{45\ \text{g}}{62\ \text{g mol}^{-1}} = 0.73\ \text{mol}$$

$$\text{Mass of water in kg} = \frac{600\text{g}}{1000\text{g kg}^{-1}} = 0.6\ \text{kg}$$

$$\text{Hence molality of ethylene glycol} = \frac{0.73\ \text{mol}}{0.60\ \text{kg}} = 1.2\ \text{mol kg}^{-1}$$

Therefore freezing point depression,

$$\text{Ä}T_f = 1.86\ \text{K kg mol}^{-1} \times 1.2\ \text{mol kg}^{-1} = 2.2\ \text{K}$$

Freezing point of the aqueous solution = 273.15 K – 2.2 K = 270.95 K

**Example 1.10** 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is 5.12 K kg mol$^{-1}$. Find the molar mass of the solute.

**Solution** Substituting the values of various terms involved in equation (1.36) we get,

$$M_2 = \frac{5.12\ \text{K kg mol}^{-1} \times 1.00\ \text{g} \times 1000\ \text{g kg}^{-1}}{0.40 \times 50\ \text{g}} = 256\ \text{g mol}^{-1}$$

Thus, molar mass of the solute = 256 g mol$^{-1}$

### 1.6.4 Osmosis and Osmotic Pressure

There are many phenomena which we observe in nature or at home. For example, raw mangoes shrivel when pickled in brine (salt water); wilted flowers revive when placed in fresh water, blood cells collapse when suspended in saline water, etc. If we look into these processes we find one thing common in all, that is, all these substances are bound by membranes. These membranes can be of animal or vegetable origin and these occur naturally such as pig's bladder or parchment or can be synthetic such as cellophane. These membranes appear to be continuous sheets or films, yet they contain a network of submicroscopic holes or pores. Small solvent

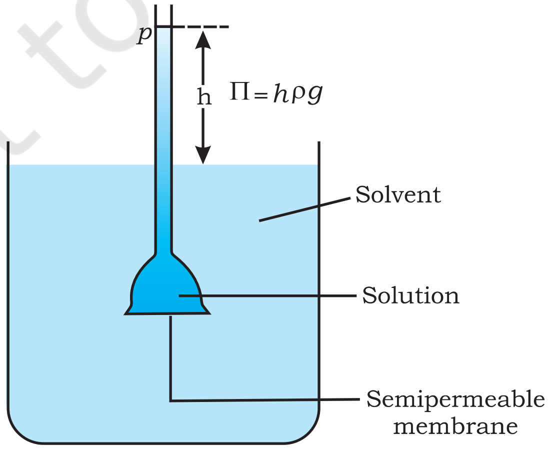


***Fig. 1.9*** *Level of solution rises in the thistle funnel due to osmosis of solvent.*

molecules, like water, can pass through these holes but the passage of bigger molecules like solute is hindered. Membranes having this kind of properties are known as *semipermeable membranes* (SPM).

Assume that only solvent molecules can pass through these semipermeable membranes. If this membrane is placed between the solvent and solution as shown in Fig. 1.9, the solvent molecules will flow through the membrane from pure solvent to the solution. **This process of flow of the solvent is called *osmosis*.**

The flow will continue till the equilibrium is attained. The flow of the solvent from its side to solution side across a semipermeable membrane can be stopped if some extra pressure is applied on the solution. **This pressure that just stops the flow of solvent is called *osmotic pressure* of the solution.** The flow of solvent from dilute solution to the concentrated solution across a semipermeable membrane is due to osmosis. The important point to be kept in mind is that solvent molecules always flow from lower concentration to higher concentration of solution. The osmotic pressure has been found to depend on the concentration of the solution.

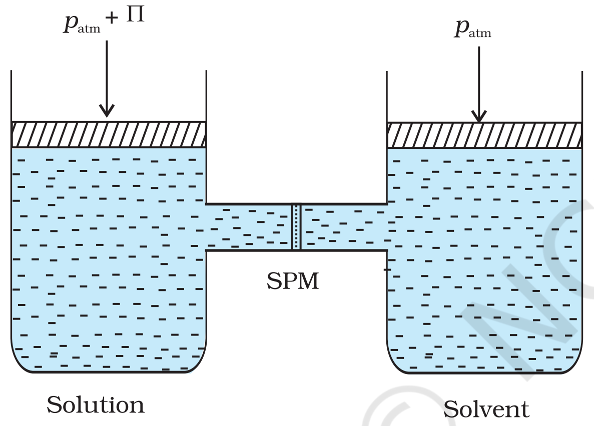


***Fig. 1.10:*** *The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis.*

The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis, i.e., to stop the passage of solvent molecules through a semipermeable membrane into the solution. This is illustrated in Fig. 1.10. Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity. For dilute solutions, it has been found experimentally that **osmotic pressure is proportional to the molarity, *C* of the solution at a given temperature *T*.** Thus:

$$\Pi = C\,R\,T \tag{1.39}$$

Here Π is the osmotic pressure and R is the gas constant.

$$\Pi = (n_2\ /V)\ R\ T \tag{1.40}$$

Here $V$ is volume of a solution in litres containing $n_2$ moles of solute. If $w_2$ grams of solute, of molar mass, $M_2$ is present in the solution, then $n_2 = w_2\ /\ M_2$ and we can write,

$$\Pi\ V = \frac{w_2\ R\,T}{M_2} \tag{1.41}$$

$$\text{or}\quad M_2 = \frac{w_2\ R\ T}{\Pi\ V} \tag{1.42}$$

Thus, knowing the quantities $w_2$, $T$, Π and $V$ we can calculate the molar mass of the solute.

Measurement of osmotic pressure provides another method of determining molar masses of solutes. This method is widely used to determine molar masses of proteins, polymers and other macromolecules. The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and the molarity of the solution is used instead of molality. As compared to other colligative properties, its magnitude is large even for very dilute solutions. The technique of osmotic pressure for determination of molar mass of solutes is particularly useful for biomolecules as they are generally not stable at higher temperatures and polymers have poor solubility.

**Two solutions having same osmotic pressure at a given temperature are called isotonic solutions**. When such solutions are separated by semipermeable membrane no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously. On the other hand, if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called **hypertonic**. If the salt concentration is less than 0.9% (mass/volume), the solution is said to be **hypotonic**. In this case, water will flow into the cells if placed in this solution and they would swell.

**Example 1.11** 200 $cm^3$ of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be $2.57 \times 10^{-3}$ bar. Calculate the molar mass of the protein.

**Solution** The various quantities known to us are as follows: $\Pi = 2.57 \times 10^{-3}$ bar,

$V = 200\ cm^3 = 0.200$ litre

$T = 300$ K

$R = 0.083$ L bar $mol^{-1}$ $K^{-1}$

Substituting these values in equation (2.42) we get

$$M_2 = \frac{1.26\ g \times 0.083\ L\ bar\ K^{-1}\ mol^{-1} \times 300\ K}{2.57 \times 10^{-3} bar \times 0.200\ L} = 61{,}022\ g\ mol^{-1}$$

The phenomena mentioned in the beginning of this section can be explained on the basis of osmosis. A raw mango placed in concentrated salt solution loses water via osmosis and shrivel into pickle. Wilted flowers revive when placed in fresh water. A carrot that has become limp because of water loss into the atmosphere can be placed into the water making it firm once again. Water will move into its cells through osmosis. When placed in water containing less than 0.9% (mass/volume) salt, blood cells swell due to flow of water in them by osmosis. People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The resulting puffiness or swelling is called **edema**. Water movement from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis. The preservation of meat by salting and of fruits by adding sugar protects against bacterial action. Through the process of osmosis, a bacterium on salted meat or candid fruit loses water, shrivels and dies.

### 1.6.5 Reverse Osmosis and Water Purification

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called **reverse osmosis** and is of great practical utility. Reverse osmosis is used in desalination of sea water. A schematic set up for the process is shown in Fig. 1.11. When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane. A variety of polymer membranes are available for this purpose.

The pressure required for the reverse osmosis is quite high. A workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water. These days many countries use desalination plants to meet their potable water requirements.

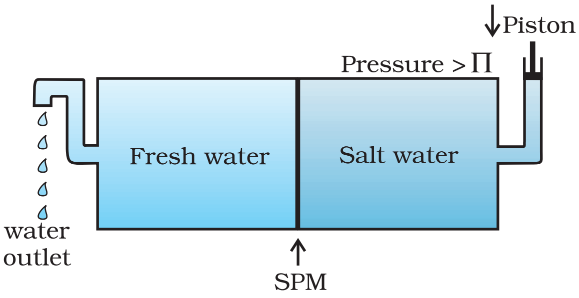


***Fig. 1.11:*** *Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.*

### Intext Questions

**1.9** Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea ($NH_2CONH_2$) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.

**1.10** Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C.

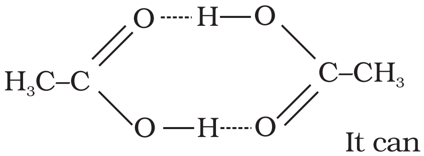
**1.11** Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C. $K_f = 3.9$ K kg mol$^{-1}$.

**1.12** Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.

## 1.7 Abnormal Molar Masses

We know that ionic compounds when dissolved in water dissociate into cations and anions. For example, if we dissolve one mole of KCl (74.5 g) in water, we expect one mole each of $K^+$ and $Cl^-$ ions to be released in the solution. If this happens, there would be two moles of particles in the solution. If we ignore interionic attractions, one mole of KCl in one kg of water would be expected to increase the boiling point by 2 × 0.52 K = 1.04 K. Now if we did not know about the degree of dissociation, we could be led to conclude that the mass of 2 mol particles is 74.5 g and the mass of one mole of KCl would be 37.25 g. This brings into light the rule that, when there is dissociation of solute into ions, the experimentally determined molar mass is always lower than the true value.

$$2\ CH_3COOH \rightleftharpoons (CH_3COOH)_2$$



Molecules of ethanoic acid (acetic acid) dimerise in benzene due to hydrogen bonding. This normally happens in solvents of low dielectric constant. In this case the number of particles is reduced due to dimerisation. Association of molecules is depicted as follows:

It can be undoubtedly stated here that if all the molecules of ethanoic acid associate in benzene, then $\Delta T_b$ or $\Delta T_f$ for ethanoic acid will be half of the normal value. The molar mass calculated on the basis of this $\Delta T_b$ or $\Delta T_f$ will, therefore, be twice the expected value. Such a molar mass that is either lower or higher than the expected or normal value is called as **abnormal molar mass.**

In 1880 van't Hoff introduced a factor *i*, known as the van't Hoff factor, to account for the extent of dissociation or association. This factor *i* is defined as:

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}$$

Here abnormal molar mass is the experimentally determined molar mass and calculated **colligative properties** are obtained by assuming that the non-volatile solute is neither associated nor dissociated. In case of association, value of *i* is less than unity while for dissociation it is greater than unity. For example, the value of *i* for aqueous KCl solution is close to 2, while the value for ethanoic acid in benzene is nearly 0.5.

Inclusion of van't Hoff factor modifies the equations for colligative properties as follows:

Relative lowering of vapour pressure of solvent,

$$\frac{p_1^o - p_1}{p_1^o} = i.\frac{n_2}{n_1}$$

Elevation of Boiling point, $\Delta T_b = i\ K_b\ m$

Depression of Freezing point, $\Delta T_f = i\ K_f\ m$

Osmotic pressure of solution, $\Pi = i\ n_2\ R\ T\ /\ V$

Table 1.4 depicts values of the factor, *i* for several strong electrolytes. For KCl, NaCl and $MgSO_4$, *i* values approach 2 as the solution becomes very dilute. As expected, the value of *i* gets close to 3 for $K_2SO_4$.

**Table 1.4: Values of van't Hoff factor, *i*, at Various Concentrations for NaCl, KCl, $MgSO_4$ and $K_2SO_4$.**

| Salt | *Values of *i* | | | van't Hoff Factor *i* for complete dissociation of solute |
|---|---|---|---|---|
| | 0.1 m | 0.01 m | 0.001 m | |
| NaCl | 1.87 | 1.94 | 1.97 | 2.00 |
| KCl | 1.85 | 1.94 | 1.98 | 2.00 |
| $MgSO_4$ | 1.21 | 1.53 | 1.82 | 2.00 |
| $K_2SO_4$ | 2.32 | 2.70 | 2.84 | 3.00 |

* *represent i values for incomplete dissociation.*

*Example 1.12*

2 g of benzoic acid ($C_6H_5COOH$) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol$^{-1}$. What is the percentage association of acid if it forms dimer in solution?

*Solution*

The given quantities are: $w_2 = 2$ g; $K_f = 4.9$ K kg mol$^{-1}$; $w_1 = 25$ g,

$\Delta T_f = 1.62$ K

Substituting these values in equation (1.36) we get:

$$M_2 = \frac{4.9 \text{ K kg mol}^{-1} \times 2 \text{ g} \times 1000 \text{ g kg}^{-1}}{25 \text{ g} \times 1.62 \text{ K}} = 241.98 \text{ g mol}^{-1}$$

Thus, experimental molar mass of benzoic acid in benzene is

$= 241.98$ g mol$^{-1}$

Now consider the following equilibrium for the acid:

$$2\,C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

If *x* represents the degree of association of the solute then we would have (1 – *x*) mol of benzoic acid left in unassociated form and correspondingly $\frac{x}{2}$ as associated moles of benzoic acid at equilibrium. Therefore, total number of moles of particles at equilibrium is:

$$1 - x + \frac{x}{2} = 1 - \frac{x}{2}$$

Thus, total number of moles of particles at equilibrium equals van't Hoff factor *i*.

$$\text{But } i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$= \frac{122 \text{ g mol}^{-1}}{241.98 \text{ g mol}^{-1}}$$

or $\quad \frac{x}{2} = 1 - \frac{122}{241.98} = 1 - 0.504 = 0.496$

or $\quad x = 2 \times 0 .496 = 0.992$

Therefore, degree of association of benzoic acid in benzene is 99.2 %.

**Example 1.13**

0.6 mL of acetic acid ($CH_3COOH$), having density 1.06 g $mL^{-1}$, is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was 0.0205°C. Calculate the van't Hoff factor and the dissociation constant of acid.

**Solution**

Number of moles of acetic acid $= \frac{0.6 \text{ mL} \times 1.06 \text{ g mL}^{-1}}{60 \text{ g mol}^{-1}}$

$= 0.0106 \text{ mol} = n$

$$\text{Molality} = \frac{0.0106 \text{ mol}}{1000 \text{ mL} \times 1 \text{ g mL}^{-1}} = 0.0106 \text{ mol kg}^{-1}$$

Using equation (1.35)

$$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 0.0106 \text{ mol kg}^{-1} = 0.0197 \text{ K}$$

$$\text{van't Hoff Factor } (i) = \frac{\text{Observed freezing point}}{\text{Calculated freezing point}} = \frac{0.0205 \text{ K}}{0.0197 \text{ K}} = 1.041$$

Acetic acid is a weak electrolyte and will dissociate into two ions: acetate and hydrogen ions per molecule of acetic acid. If $x$ is the degree of dissociation of acetic acid, then we would have $n\,(1 – x)$ moles of undissociated acetic acid, $nx$ moles of $CH_3COO^-$ and $nx$ moles of $H^+$ ions,

$$\begin{array}{lcc} CH_3COOH \rightleftharpoons & H^+ & + \; CH_3COO^- \\ n \text{ mol} & 0 & 0 \\ n(1-x) & nx \text{ mol} & nx \text{ mol} \end{array}$$

Thus total moles of particles are: $n(1 – x + x + x) = n(1 + x)$

$$i = \frac{n(1+x)}{n} = 1 + x = 1.041$$

Thus degree of dissociation of acetic acid = $x$ = 1.041– 1.000 = 0.041

Then $\quad [CH_3COOH] = n(1 – x) = 0.0106\,(1 – 0.041)$,

$[CH_3COO^-] = nx = 0.0106 \times 0.041$, $[H^+] = nx = 0.0106 \times 0.041$.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{0.0106 \times 0.041 \times 0.0106 \times 0.041}{0.0106\,(1.00 - 0.041)}$$

$$= 1.86 \times 10^{-5}$$

## Summary

A solution is a homogeneous mixture of two or more substances. Solutions are classified as solid, liquid and gaseous solutions. The concentration of a solution is expressed in terms of mole fraction, molarity, molality and in percentages. The dissolution of a gas in a liquid is governed by **Henry's law**, according to which, at a given temperature, the **solubility of a gas in a liquid is directly proportional to the partial pressure of the gas**. The vapour pressure of the solvent is lowered by the presence of a non-volatile solute in the solution and this lowering of vapour pressure of the solvent is governed by Raoult's law, according to which the **relative lowering of vapour pressure of the solvent over a solution is equal to the mole fraction of a non-volatile solute present in the solution**. However, in a binary liquid solution, if both the components of the solution are volatile then another form of Raoult's law is used. Mathematically, this form of the Raoult's law is stated as: $p_{\text{total}} = p_1^0 x_1 + p_2^0 x_2$ . **Solutions which obey Raoult's law over the entire range of concentration are called ideal solutions**. Two types of deviations from Raoult's law, called positive and negative deviations are observed. Azeotropes arise due to very large deviations from Raoult's law.

The properties of solutions which depend on the number of solute particles and are independent of their chemical identity are called colligative properties. These are lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. The process of osmosis can be reversed if a pressure higher than the osmotic pressure is applied to the solution. Colligative properties have been used to determine the molar mass of solutes. Solutes which dissociate in solution exhibit molar mass lower than the actual molar mass and those which associate show higher molar mass than their actual values.

Quantitatively, the extent to which a solute is dissociated or associated can be expressed by van't Hoff factor *i*. This factor has been defined as ratio of normal molar mass to experimentally determined molar mass or as the ratio of observed colligative property to the calculated colligative property.

## Exercises

**1.1** Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.

**1.2** Give an example of a solid solution in which the solute is a gas.

**1.3** Define the following terms:

(i) Mole fraction (ii) Molality (iii) Molarity (iv) Mass percentage.

**1.4** Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g $mL^{-1}$?

**1.5** A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole fraction of each component in the solution? If the density of solution is 1.2 g $mL^{-1}$, then what shall be the molarity of the solution?

**1.6** How many mL of 0.1 M HCl are required to react completely with 1 g mixture of $Na_2CO_3$ and $NaHCO_3$ containing equimolar amounts of both?

**1.7** A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

**1.8** An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g $mL^{-1}$, then what shall be the molarity of the solution?

**1.9** A sample of drinking water was found to be severely contaminated with chloroform ($CHCl_3$) supposed to be a carcinogen. The level of contamination was 15 ppm (by mass):

(i) express this in percent by mass

(ii) determine the molality of chloroform in the water sample.

**1.10** What role does the molecular interaction play in a solution of alcohol and water?

**1.11** Why do gases always tend to be less soluble in liquids as the temperature is raised?

**1.12** State Henry's law and mention some important applications.

**1.13** The partial pressure of ethane over a solution containing $6.56 \times 10^{-3}$ g of ethane is 1 bar. If the solution contains $5.00 \times 10^{-2}$ g of ethane, then what shall be the partial pressure of the gas?

**1.14** What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{mix}H$ related to positive and negative deviations from Raoult's law?

**1.15** An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?

**1.16** Heptane and octane form an ideal solution. At 373 *K*, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35 g of octane?

**1.17** The vapour pressure of water is 12.3 kPa at 300 *K*. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.

**1.18** Calculate the mass of a non-volatile solute (molar mass 40 g $mol^{-1}$) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

**1.19** A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 *K*. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 *K*. Calculate:

(i) molar mass of the solute (ii) vapour pressure of water at 298 *K*.

**1.20** A 5% solution (by mass) of cane sugar in water has freezing point of 271*K*. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 *K*.

**1.21** Two elements A and B form compounds having formula $AB_2$ and $AB_4$. When dissolved in 20 g of benzene ($C_6H_6$), 1 g of $AB_2$ lowers the freezing point by 2.3 *K* whereas 1.0 g of $AB_4$ lowers it by 1.3 *K*. The molar depression constant for benzene is 5.1 *K* kg $mol^{-1}$. Calculate atomic masses of A and B.

**1.22** At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bars at the same temperature, what would be its concentration?

**1.23** Suggest the most important type of intermolecular attractive interaction in the following pairs.

(i) n-hexane and n-octane
(ii) $I_2$ and $CCl_4$
(iii) $NaClO_4$ and water
(iv) methanol and acetone
(v) acetonitrile ($CH_3CN$) and acetone ($C_3H_6O$).

**1.24** Based on solute-solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane, KCl, $CH_3OH$, $CH_3CN$.

**1.25** Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?

(i) phenol
(ii) toluene
(iii) formic acid
(iv) ethylene glycol
(v) chloroform
(vi) pentanol.

**1.26** If the density of some lake water is 1.25g $mL^{-1}$ and contains 92 g of $Na^+$ ions per kg of water, calculate the molarity of $Na^+$ ions in the lake.

**1.27** If the solubility product of CuS is $6 \times 10^{-16}$, calculate the maximum molarity of CuS in aqueous solution.

**1.28** Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile ($CH_3CN$) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of $CH_3CN$.

**1.29** Nalorphene ($C_{19}H_{21}NO_3$), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of $1.5 \times 10^{-3}$ m aqueous solution required for the above dose.

**1.30** Calculate the amount of benzoic acid ($C_6H_5COOH$) required for preparing 250 mL of 0.15 M solution in methanol.

**1.31** The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.

**1.32** Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86$ K kg $mol^{-1}$.

**1.33** 19.5 g of $CH_2FCOOH$ is dissolved in 500 g of water. The depression in the freezing point of water observed is $1.0^0$ C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

**1.34** Vapour pressure of water at 293 $K$ is 17.535 mm Hg. Calculate the vapour pressure of water at 293 $K$ when 25 g of glucose is dissolved in 450 g of water.

**1.35** Henry's law constant for the molality of methane in benzene at 298 $K$ is $4.27 \times 10^5$ mm Hg. Calculate the solubility of methane in benzene at 298 $K$ under 760 mm Hg.

**1.36** 100 g of liquid A (molar mass 140 g $mol^{-1}$) was dissolved in 1000 g of liquid B (molar mass 180 g $mol^{-1}$). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 Torr.

**1.37** Vapour pressures of pure acetone and chloroform at 328 *K* are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot $p_{total}$, $p_{chloroform}$, and $p_{acetone}$ as a function of $x_{acetone}$. The experimental data observed for different compositions of mixture is:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 100 x $x_{acetone}$ | 0 | 11.8 | 23.4 | 36.0 | 50.8 | 58.2 | 64.5 | 72.1 |
| $p_{acetone}$ /mm Hg | 0 | 54.9 | 110.1 | 202.4 | 322.7 | 405.9 | 454.1 | 521.1 |
| $p_{chloroform}$ /mm Hg | 632.8 | 548.1 | 469.4 | 359.7 | 257.7 | 193.6 | 161.2 | 120.7 |

Plot this data also on the same graph paper. Indicate whether it has positive deviation or negative deviation from the ideal solution.

**1.38** Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and toluene at 300 *K* are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of toluene.

**1.39** The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 *K*. The water is in equilibrium with air at a pressure of 10 atm. At 298 *K* if the Henry's law constants for oxygen and nitrogen at 298 *K* are $3.30 \times 10^7$ mm and $6.51 \times 10^7$ mm respectively, calculate the composition of these gases in water.

**1.40** Determine the amount of $CaCl_2$ ($i = 2.47$) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27° C.

**1.41** Determine the osmotic pressure of a solution prepared by dissolving 25 mg of $K_2SO_4$ in 2 litre of water at 25° C, assuming that it is completely dissociated.

## Answers to Some Intext Questions

**1.1** $C_6H_6$ = 15.28%, $CCl_4$ = 84.72%

**1.2** 0.459, 0.541

**1.3** 0.024 M, 0.03 M

**1.4** 36.946 g

**1.5** 1.5 mol $kg^{-1}$ , 1.45 mol $L^{-1}$ 0.0263

**1.9** 23.4 mm Hg

**1.10** 121.67 g

**1.11** 5.077 g

**1.12** 30.96 Pa

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# Unit 2

# Electrochemistry

## Objectives

After studying this Unit, you will be able to

- describe an electrochemical cell and differentiate between galvanic and electrolytic cells;
- apply Nernst equation for calculating the emf of galvanic cell and define standard potential of the cell;
- derive relation between standard potential of the cell, Gibbs energy of cell reaction and its equilibrium constant;
- define resistivity (ρ), conductivity (κ) and molar conductivity ($\Lambda_m$) of ionic solutions;
- differentiate between ionic (electrolytic) and electronic conductivity;
- describe the method for measurement of conductivity of electrolytic solutions and calculation of their molar conductivity;
- justify the variation of conductivity and molar conductivity of solutions with change in their concentration and define $\Lambda_m^\circ$ (molar conductivity at zero concentration or infinite dilution);
- enunciate Kohlrausch law and learn its applications;
- understand quantitative aspects of electrolysis;
- describe the construction of some primary and secondary batteries and fuel cells;
- explain corrosion as an electrochemical process.

*Chemical reactions can be used to produce electrical energy, conversely, electrical energy can be used to carry out chemical reactions that do not proceed spontaneously.*

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations. The subject is of importance both for theoretical and practical considerations. A large number of metals, sodium hydroxide, chlorine, fluorine and many other chemicals are produced by electrochemical methods. Batteries and fuel cells convert chemical energy into electrical energy and are used on a large scale in various instruments and devices. The reactions carried out electrochemically can be energy efficient and less polluting. Therefore, study of electrochemistry is important for creating new technologies that are ecofriendly. The transmission of sensory signals through cells to brain and vice versa and communication between the cells are known to have electrochemical origin. Electrochemistry, is therefore, a very vast and interdisciplinary subject. In this Unit, we will cover only some of its important elementary aspects.

## 2.1 Electrochemical Cells

We had studied the construction and functioning of **Daniell cell** (Fig. 2.1). This cell converts the chemical energy liberated during the redox reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \tag{2.1}$$

to electrical energy and has an electrical potential equal to 1.1 V when concentration of $Zn^{2+}$ and $Cu^{2+}$ ions is unity (1 mol $dm^{-3}$)*. Such a device is called a **galvanic** or a **voltaic** cell.

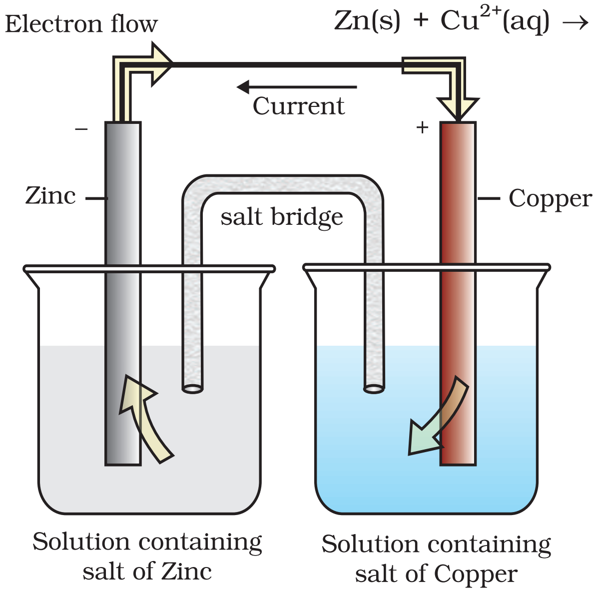
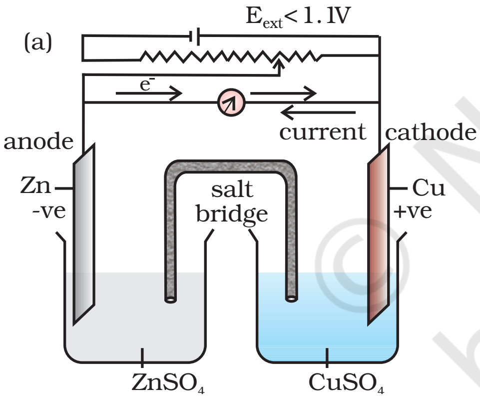
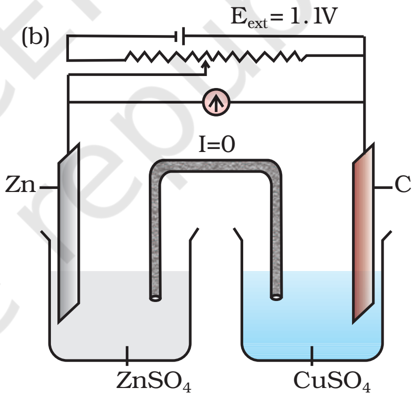


***Fig. 2.1:*** *Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.*

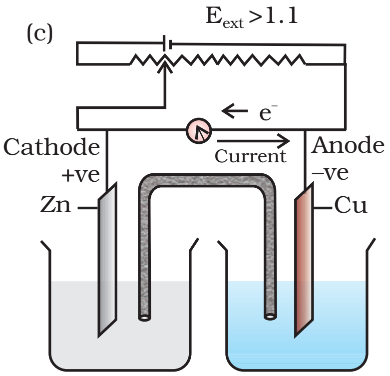
If an external opposite potential is applied in the galvanic cell [Fig. 2.2(a)] and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V [Fig. 2.2(b)] when, the reaction stops altogether and no current flows through the cell. Any further increase in the external potential again starts the reaction but in the opposite direction [Fig. 2.2(c)]. It now functions as an **electrolytic cell**, a device for using electrical energy to carry non-spontaneous chemical reactions. Both types of cells are quite important and we shall study some of their salient features in the following pages.



When $E_{ext} < 1.1$ V
- (i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.
- (ii) Zn dissolves at anode and copper deposits at cathode.



When $E_{ext}$ = 1.1 V
- (i) No flow of electrons or current.
- (ii) No chemical reaction.



When $E_{ext} > 1.1$ V
- (i) Electrons flow from Cu to Zn and current flows from Zn to Cu.
- (ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

***Fig. 2.2***
*Functioning of Daniell cell when external voltage $E_{ext}$ opposing the cell potential is applied.*

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* *Strictly speaking activity should be used instead of concentration. It is directly proportional to concentration. In dilute solutions, it is equal to concentration. You will study more about it in higher classes.*

## 2.2 Galvanic Cells

As mentioned earlier a galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the **Gibbs energy** of the spontaneous redox reaction is converted into electrical work which may be used for running a motor or other electrical gadgets like heater, fan, geyser, etc.

Daniell cell discussed earlier is one such cell in which the following redox reaction occurs.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

This reaction is a combination of two half reactions whose addition gives the overall cell reaction:

(i) $Cu^{2+} + 2e^- \rightarrow Cu(s)$ (reduction half reaction) (2.2)

(ii) $Zn(s) \rightarrow Zn^{2+} + 2e^-$ (oxidation half reaction) (2.3)

These reactions occur in two different portions of the Daniell cell. The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called **half-cells** or **redox couples**. The copper electrode may be called the reduction half cell and the zinc electrode, the oxidation half-cell.

We can construct innumerable number of galvanic cells on the pattern of Daniell cell by taking combinations of different half-cells. Each half-cell consists of a metallic electrode dipped into an electrolyte. The two half-cells are connected by a metallic wire through a voltmeter and a switch externally. The electrolytes of the two half-cells are connected internally through a salt bridge as shown in Fig. 2.1. Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we do not require a salt bridge.

At each electrode-electrolyte interface there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions and leave behind the electrons at the electrode trying to make it negatively charged. At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged with respect to the solution. A potential difference develops between the electrode and the electrolyte which is called **electrode potential**. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**. According to IUPAC convention, standard reduction potentials are now called standard electrode potentials. In a galvanic cell, the half-cell in which oxidation takes place is called **anode** and it has a negative potential with respect to the solution. The other half-cell in which reduction takes place is called **cathode** and it has a positive potential with respect to the solution. Thus, there exists a potential difference between the two electrodes and as soon as the switch is in the *on* position the electrons flow from negative electrode to positive electrode. The direction of current flow is opposite to that of electron flow.

The potential difference between the two electrodes of a galvanic cell is called the *cell potential* and is measured in volts. The **cell potential** is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the **cell electromotive force (emf)** of the cell when no current is drawn through the cell. It is now an accepted convention that we keep the anode on the left and the cathode on the right while representing the galvanic cell. A galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge. Under this convention the emf of the cell is positive and is given by the potential of the half-cell on the right hand side minus the potential of the half-cell on the left hand side i.e.,

$$E_{cell} = E_{right} - E_{left}$$

This is illustrated by the following example:

Cell reaction:

$$Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2\ Ag(s) \qquad (2.4)$$

Half-cell reactions:

$$\text{Cathode } (\textit{reduction}): \quad 2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s) \qquad (2.5)$$

$$\text{Anode } (\textit{oxidation}): \quad Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-} \qquad (2.6)$$

It can be seen that the sum of (3.5) and (3.6) leads to overall reaction (2.4) in the cell and that silver electrode acts as a cathode and copper electrode acts as an anode. The cell can be represented as:

$$Cu(s)|Cu^{2+}(aq)||Ag^{+}(aq)|Ag(s)$$

and we have $E_{cell} = E_{right} - E_{left} = E_{Ag^{+}|Ag} - E_{Cu^{2+}|Cu}$ (2.7)

### 2.2.1 Measurement of Electrode Potential

The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. If we arbitrarily choose the potential of one electrode (half-cell) then that of the other can be determined with respect to this. According to convention, a half-cell called standard hydrogen electrode (Fig.3.3) represented by $Pt(s)|H_2(g)|H^{+}(aq)$, is assigned a zero potential at all temperatures corresponding to the reaction

$$H^{+}(aq) + e^{-} \rightarrow \frac{1}{2}H_2(g)$$

The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity (Fig. 2.3). This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.

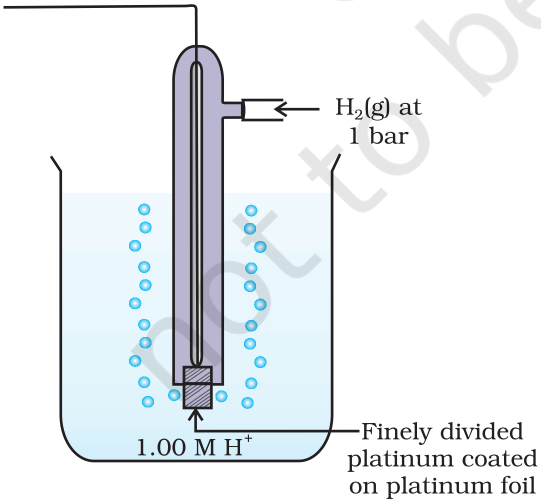


***Fig. 2.3:*** *Standard Hydrogen Electrode (SHE).*

At 298 K the emf of the cell, standard hydrogen electrode || second half-cell constructed by taking standard hydrogen electrode as anode (reference half-cell) and the other half-cell as cathode, gives the reduction potential of the other half-cell. If the concentrations of the oxidised and the reduced forms of the species in the right hand half-cell are unity, then the cell potential is equal to standard electrode potential, $E^o_R$ of the given half-cell.

$$E^o = E^o_R - E^o_L$$

As $E^o_L$ for standard hydrogen electrode is zero.

$$E^o = E^o_R - 0 = E^o_R$$

The measured emf of the cell:

$$\text{Pt(s)} \mid \text{H}_2\text{(g, 1 bar)} \mid \text{H}^+\text{(aq, 1 M)} \parallel \text{Cu}^{2+}\text{ (aq, 1 M)} \mid \text{Cu}$$

is 0.34 V and it is also the value for the standard electrode potential of the half-cell corresponding to the reaction:

$$\text{Cu}^{2+}\text{ (aq, 1M)} + 2\text{ e}^- \rightarrow \text{Cu(s)}$$

Similarly, the measured emf of the cell:

$$\text{Pt(s)} \mid \text{H}_2\text{(g, 1 bar)} \mid \text{H}^+\text{(aq, 1 M)} \parallel \text{Zn}^{2+}\text{ (aq, 1M)} \mid \text{Zn}$$

is -0.76 V corresponding to the standard electrode potential of the half-cell reaction:

$$\text{Zn}^{2+}\text{ (aq, 1 M)} + 2\text{e}^- \rightarrow \text{Zn(s)}$$

The positive value of the standard electrode potential in the first case indicates that $Cu^{2+}$ ions get reduced more easily than $H^+$ ions. The reverse process cannot occur, that is, hydrogen ions cannot oxidise Cu (or alternatively we can say that hydrogen gas can reduce copper ion) under the standard conditions described above. Thus, Cu does not dissolve in HCl. In nitric acid it is oxidised by nitrate ion and not by hydrogen ion. The negative value of the standard electrode potential in the second case indicates that hydrogen ions can oxidise zinc (or zinc can reduce hydrogen ions).

In view of this convention, the half reaction for the Daniell cell in Fig. 2.1 can be written as:

Left electrode: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}\text{ (aq, 1 M)} + 2\text{ e}^-$

Right electrode: $\text{Cu}^{2+}\text{ (aq, 1 M)} + 2\text{ e}^- \rightarrow \text{Cu(s)}$

The overall reaction of the cell is the sum of above two reactions and we obtain the equation:

$$\text{Zn(s)} + \text{Cu}^{2+}\text{ (aq)} \rightarrow \text{Zn}^{2+}\text{ (aq)} + \text{Cu(s)}$$

$$\text{emf of the cell} = E^o_{\text{cell}} = E^o_R - E^o_L$$

$$= 0.34\text{V} - (-0.76)\text{V} = 1.10\text{ V}$$

Sometimes metals like platinum or gold are used as inert electrodes. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for the conduction of electrons. For example, Pt is used in the following half-cells:

Hydrogen electrode: $\text{Pt(s)} \mid \text{H}_2\text{(g)} \mid \text{H}^+\text{(aq)}$

With half-cell reaction: $\text{H}^+\text{ (aq)} + \text{e}^- \rightarrow \frac{1}{2}\text{ H}_2\text{(g)}$

Bromine electrode: $\text{Pt(s)} \mid \text{Br}_2\text{(aq)} \mid \text{Br}^-\text{(aq)}$

With half-cell reaction: $\frac{1}{2}\,Br_2(aq) + e^- \rightarrow Br^-(aq)$

The standard electrode potentials are very important and we can extract a lot of useful information from them. The values of standard electrode potentials for some selected half-cell reduction reactions are given in Table 2.1. If the standard electrode potential of an electrode is greater than zero then its reduced form is more stable compared to hydrogen gas. Similarly, if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of the species. It can be seen that the standard electrode potential for fluorine is the highest in the Table indicating that fluorine gas ($F_2$) has the maximum tendency to get reduced to fluoride ions ($F^-$) and therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent. Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution. It may be seen that as we go from top to bottom in Table 2.1 the standard electrode potential decreases and with this, decreases the oxidising power of the species on the left and increases the reducing power of the species on the right hand side of the reaction. Electrochemical cells are extensively used for determining the pH of solutions, solubility product, equilibrium constant and other thermodynamic properties and for potentiometric titrations.

### Intext Questions

**2.1** How would you determine the standard electrode potential of the system $Mg^{2+}|Mg$?

**2.2** Can you store copper sulphate solutions in a zinc pot?

**2.3** Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.

## 2.3 Nernst Equation

We have assumed in the previous section that the concentration of all the species involved in the electrode reaction is unity. This need not be always true. Nernst showed that for the electrode reaction:

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

the electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{(M^{n+}/M)} = E^{o}_{(M^{n+}/M)} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

but concentration of solid M is taken as unity and we have

$$E_{(M^{n+}/M)} = E^{o}_{(M^{n+}/M)} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]} \qquad (2.8)$$

$E^{o}_{(M^{n+}/M)}$ has already been defined, $R$ is gas constant (8.314 $JK^{-1}\,mol^{-1}$), $F$ is Faraday constant (96487 C $mol^{-1}$), $T$ is temperature in kelvin and $[M^{n+}]$ is the concentration of the species, $M^{n+}$.

### Table 2.1: Standard Electrode Potentials at 298 K

Ions are present as aqueous species and $H_2O$ as liquid; gases and solids are shown by g and s.

Increasing strength of oxidising agent ↑

Increasing strength of reducing agent ↓

| Reaction (Oxidised form + $ne^-$ | → Reduced form) | $E^o$/V |
|---|---|---|
| $F_2(g) + 2e^-$ | $\rightarrow 2F^-$ | 2.87 |
| $Co^{3+} + e^-$ | $\rightarrow Co^{2+}$ | 1.81 |
| $H_2O_2 + 2H^+ + 2e^-$ | $\rightarrow 2H_2O$ | 1.78 |
| $MnO_4^- + 8H^+ + 5e^-$ | $\rightarrow Mn^{2+} + 4H_2O$ | 1.51 |
| $Au^{3+} + 3e^-$ | $\rightarrow Au(s)$ | 1.40 |
| $Cl_2(g) + 2e^-$ | $\rightarrow 2Cl^-$ | 1.36 |
| $Cr_2O_7^{2-} + 14H^+ + 6e^-$ | $\rightarrow 2Cr^{3+} + 7H_2O$ | 1.33 |
| $O_2(g) + 4H^+ + 4e^-$ | $\rightarrow 2H_2O$ | 1.23 |
| $MnO_2(s) + 4H^+ + 2e^-$ | $\rightarrow Mn^{2+} + 2H_2O$ | 1.23 |
| $Br_2 + 2e^-$ | $\rightarrow 2Br^-$ | 1.09 |
| $NO_3^- + 4H^+ + 3e^-$ | $\rightarrow NO(g) + 2H_2O$ | 0.97 |
| $2Hg^{2+} + 2e^-$ | $\rightarrow Hg_2^{2+}$ | 0.92 |
| $Ag^+ + e^-$ | $\rightarrow Ag(s)$ | 0.80 |
| $Fe^{3+} + e^-$ | $\rightarrow Fe^{2+}$ | 0.77 |
| $O_2(g) + 2H^+ + 2e^-$ | $\rightarrow H_2O_2$ | 0.68 |
| $I_2 + 2e^-$ | $\rightarrow 2I^-$ | 0.54 |
| $Cu^+ + e^-$ | $\rightarrow Cu(s)$ | 0.52 |
| $Cu^{2+} + 2e^-$ | $\rightarrow Cu(s)$ | 0.34 |
| $AgCl(s) + e^-$ | $\rightarrow Ag(s) + Cl^-$ | 0.22 |
| $AgBr(s) + e^-$ | $\rightarrow Ag(s) + Br^-$ | 0.10 |
| $\mathbf{2H^+ + 2e^-}$ | $\mathbf{\rightarrow H_2(g)}$ | **0.00** |
| $Pb^{2+} + 2e^-$ | $\rightarrow Pb(s)$ | –0.13 |
| $Sn^{2+} + 2e^-$ | $\rightarrow Sn(s)$ | –0.14 |
| $Ni^{2+} + 2e^-$ | $\rightarrow Ni(s)$ | –0.25 |
| $Fe^{2+} + 2e^-$ | $\rightarrow Fe(s)$ | –0.44 |
| $Cr^{3+} + 3e^-$ | $\rightarrow Cr(s)$ | –0.74 |
| $Zn^{2+} + 2e^-$ | $\rightarrow Zn(s)$ | –0.76 |
| $2H_2O + 2e^-$ | $\rightarrow H_2(g) + 2OH^-(aq)$ | –0.83 |
| $Al^{3+} + 3e^-$ | $\rightarrow Al(s)$ | –1.66 |
| $Mg^{2+} + 2e^-$ | $\rightarrow Mg(s)$ | –2.36 |
| $Na^+ + e^-$ | $\rightarrow Na(s)$ | –2.71 |
| $Ca^{2+} + 2e^-$ | $\rightarrow Ca(s)$ | –2.87 |
| $K^+ + e^-$ | $\rightarrow K(s)$ | –2.93 |
| $Li^+ + e^-$ | $\rightarrow Li(s)$ | –3.05 |

1. A negative $E^o$ means that the redox couple is a stronger reducing agent than the $H^+/H_2$ couple.
2. A positive $E^o$ means that the redox couple is a weaker reducing agent than the $H^+/H_2$ couple.

In Daniell cell, the electrode potential for any given concentration of $Cu^{2+}$ and $Zn^{2+}$ ions, we write

For Cathode:

$$E_{(Cu^{2+}/Cu)} = E^{o}_{(Cu^{2+}/Cu)} - \frac{RT}{2F} \ln \frac{1}{\left[Cu^{2+}(aq)\right]} \qquad (2.9)$$

For Anode:

$$E_{(Zn^{2+}/Zn)} = E^{o}_{(Zn^{2+}/Zn)} - \frac{RT}{2F} \ln \frac{1}{\left[Zn^{2+}(aq)\right]} \qquad (2.10)$$

The cell potential, $E_{(cell)} = E_{(Cu^{2+}/Cu)} - E_{(Zn^{2+}/Zn)}$

$$= E^{o}_{(Cu^{2+}/Cu)} - \frac{RT}{2F} \ln \frac{1}{\left[Cu^{2+}(aq)\right]} - E^{o}_{(Zn^{2+}/Zn)} + \frac{RT}{2F} \ln \frac{1}{\left[Zn^{2+}(aq)\right]}$$

$$= E^{o}_{(Cu^{2+}/Cu)} - E^{o}_{(Zn^{2+}/Zn)} - \frac{RT}{2F} \ln \frac{1}{\left[Cu^{2+}(aq)\right]} - \ln \frac{1}{\left[Zn^{2+}(aq)\right]}$$

$$E_{(cell)} = E^{o}_{(cell)} - \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad (2.11)$$

It can be seen that $E_{(cell)}$ depends on the concentration of both $Cu^{2+}$ and $Zn^{2+}$ ions. It increases with increase in the concentration of $Cu^{2+}$ ions and decrease in the concentration of $Zn^{2+}$ ions.

By converting the natural logarithm in Eq. (2.11) to the base 10 and substituting the values of $R$, $F$ and $T$ = 298 K, it reduces to

$$E_{(cell)} = E^{o}_{(cell)} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad (2.12)$$

We should use the same number of electrons ($n$) for both the electrodes and thus for the following cell

$Ni(s) | Ni^{2+}(aq) || Ag^{+}(aq) | Ag$

The cell reaction is $Ni(s) + 2Ag^{+}(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$

The **Nernst equation** can be written as

$$E_{(cell)} = E^{o}_{(cell)} - \frac{RT}{2F} \ln \frac{[Ni^{2+}]}{[Ag^{+}]^{2}}$$

and for a general electrochemical reaction of the type:

$$a\,A + bB \xrightarrow{ne^{-}} cC + dD$$

Nernst equation can be written as:

$$E_{(cell)} = E^{o}_{(cell)} - \frac{RT}{nF} \ln Q$$

$$= E^{o}_{(cell)} - \frac{RT}{nF} \ln \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \qquad (2.13)$$

**Example 2.1**

Represent the cell in which the following reaction takes place

$$\text{Mg(s)} + 2\text{Ag}^{+}(0.0001\text{M}) \rightarrow \text{Mg}^{2+}(0.130\text{M}) + 2\text{Ag(s)}$$

Calculate its $E_{(\text{cell})}$ if $E^{\text{o}}_{(\text{cell})} = 3.17$ V.

**Solution**

The cell can be written as $\text{Mg}\,|\,\text{Mg}^{2+}(0.130\text{M})\,||\,\text{Ag}^{+}(0.0001\text{M})\,|\,\text{Ag}$

$$E_{(\text{cell})} = E^{\text{o}}_{(\text{cell})} - \frac{\text{RT}}{2\text{F}}\ln\frac{\text{Mg}^{2+}}{{\text{Ag}^{+}}^{\;2}}$$

$$= 3.17\text{ V} - \frac{0.059V}{2}\log\frac{0.130}{(0.0001)^2} = 3.17\text{ V} - 0.21\text{V} = 2.96\text{ V}.$$

### 2.3.1 Equilibrium Constant from Nernst Equation

If the circuit in Daniell cell (Fig. 2.1) is closed then we note that the reaction

$$\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)} \qquad (2.1)$$

takes place and as time passes, the concentration of $\text{Zn}^{2+}$ keeps on increasing while the concentration of $\text{Cu}^{2+}$ keeps on decreasing. At the same time voltage of the cell as read on the voltmeter keeps on decreasing. After some time, we shall note that there is no change in the concentration of $\text{Cu}^{2+}$ and $\text{Zn}^{2+}$ ions and at the same time, voltmeter gives zero reading. This indicates that equilibrium has been attained. In this situation the Nernst equation may be written as:

$$E_{(\text{cell})} = 0 = E^{\text{o}}_{(\text{cell})} - \frac{2.303RT}{2F}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\text{or}\quad E^{\text{o}}_{(\text{cell})} = \frac{2.303RT}{2F}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

But at equilibrium,

$$\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = K_c \text{ for the reaction 2.1}$$

and at T = 298K the above equation can be written as

$$E^{\text{o}}_{(\text{cell})} = \frac{0.059\text{ V}}{2}\log K_C = 1.1\text{ V} \qquad (E^{\text{o}}_{(\text{cell})} = 1.1\text{V})$$

$$\log K_C = \frac{(1.1\text{V} \times 2)}{0.059\text{ V}} = 37.288$$

$$K_C = 2 \times 10^{37} \text{ at 298K.}$$

In general,

$$E^{\text{o}}_{(\text{cell})} = \frac{2.303RT}{nF}\log K_C \qquad (2.14)$$

Thus, Eq. (2.14) gives a relationship between equilibrium constant of the reaction and standard potential of the cell in which that reaction takes place. Thus, equilibrium constants of the reaction, difficult to measure otherwise, can be calculated from the corresponding $E^{\text{o}}$ value of the cell.

**Example 2.2** Calculate the equilibrium constant of the reaction:

$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

$$E^o_{(cell)} = 0.46 \text{ V}$$

**Solution**
$$E^o_{(cell)} = \frac{0.059 \text{ V}}{2} \log K_C = 0.46 \text{ V or}$$

$$\log K_C = \frac{0.46 \text{ V} \times 2}{0.059 \text{ V}} = 15.6$$

$$K_C = 3.92 \times 10^{15}$$

### 2.3.2 Electrochemical Cell and Gibbs Energy of the Reaction

Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf of the cell is $E$ and $nF$ is the amount of charge passed and $\Delta_r G$ is the Gibbs energy of the reaction, then

$$\Delta_r G = -\ nFE_{(cell)} \qquad (2.15)$$

It may be remembered that $E_{(cell)}$ is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on $n$. Thus, if we write the reaction

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \qquad (2.1)$$

$$\Delta_r G = -\ 2FE_{(cell)}$$

but when we write the reaction

$$2\ Zn\ (s) + 2\ Cu^{2+}(aq) \longrightarrow 2\ Zn^{2+}(aq) + 2Cu(s)$$

$$\Delta_r G = -\ 4FE_{(cell)}$$

If the concentration of all the reacting species is unity, then $E_{(cell)} = E^o_{(cell)}$ and we have

$$\Delta_r G^o = -\ nFE^o_{(cell)} \qquad (2.16)$$

Thus, from the measurement of $E^o_{(cell)}$ we can obtain an important thermodynamic quantity, $\Delta_r G^o$, standard Gibbs energy of the reaction. From the latter we can calculate equilibrium constant by the equation:

$$\Delta_r G^o = -RT \ln K.$$

**Example 2.3** The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

**Solution** $\Delta_r G^o = -\ nFE^o_{(cell)}$

$n$ in the above equation is 2, F = 96487 C $mol^{-1}$ and $E^o_{(cell)} = 1.1$ V

$$\begin{aligned}\text{Therefore, } \Delta_r G^o &= -\ 2 \times 1.1\text{V} \times 96487 \text{ C mol}^{-1}\\ &= -\ 21227 \text{ J mol}^{-1}\\ &= -\ 212.27 \text{ kJ mol}^{-1}\end{aligned}$$

## Intext Questions

**2.4** Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

**2.5** Calculate the emf of the cell in which the following reaction takes place:

$Ni(s) + 2Ag^{+}\ (0.002\ M) \rightarrow Ni^{2+}\ (0.160\ M) + 2Ag(s)$

Given that $E^{o}_{cell} = 1.05\ V$

**2.6** The cell in which the following reaction occurs:

$2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$ has $E^{o}_{cell} = 0.236\ V$ at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

## 2.4 Conductance of Electrolytic Solutions

It is necessary to define a few terms before we consider the subject of conductance of electricity through electrolytic solutions. The electrical resistance is represented by the symbol *'R'* and it is measured in ohm (Ω) which in terms of SI base units is equal to (kg m$^2$)/($S^3$ $A^2$). It can be measured with the help of a **Wheatstone bridge** with which you are familiar from your study of physics. The electrical resistance of any object is directly proportional to its length, *l*, and inversely proportional to its area of cross section, *A*. That is,

$$R \propto \frac{l}{A} \text{ or } R = \rho \frac{l}{A} \tag{2.17}$$

The constant of proportionality, ρ (Greek, rho), is called **resistivity** (specific resistance). Its SI units are ohm metre (Ω m) and quite often its submultiple, ohm centimetre (Ω cm) is also used. IUPAC recommends the use of the term resistivity over specific resistance and hence in the rest of the book we shall use the term resistivity. Physically, the resistivity for a substance is its resistance when it is one metre long and its area of cross section is one m$^2$. It can be seen that:

$$1\ \Omega\ m = 100\ \Omega\ cm \text{ or } 1\ \Omega\ cm = 0.01\ \Omega\ m$$

The inverse of resistance, *R*, is called **conductance**, *G*, and we have the relation:

$$G = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l} \tag{2.18}$$

The SI unit of conductance is siemens, represented by the symbol 'S' and is equal to ohm$^{-1}$ (also known as mho) or Ω$^{-1}$. The inverse of resistivity, called **conductivity** (specific conductance) is represented by the symbol, κ (Greek, kappa). IUPAC has recommended the use of term conductivity over specific conductance and hence we shall use the term conductivity in the rest of the book. The SI units of conductivity are S m$^{-1}$ but quite often, κ is expressed in S cm$^{-1}$. Conductivity of a material in S m$^{-1}$ is its conductance when it is 1 m long and its area of cross section is 1 m$^2$. It may be noted that 1 S cm$^{-1}$ = 100 S m$^{-1}$.

**Table 2.2: The values of Conductivity of some Selected Materials at 298.15 K**

| Material | Conductivity/ S $m^{-1}$ | Material | Conductivity/ S $m^{-1}$ |
|---|---|---|---|
| ***Conductors*** | | ***Aqueous Solutions*** | |
| Sodium | $2.1\times10^{3}$ | Pure water | $3.5\times10^{-5}$ |
| Copper | $5.9\times10^{3}$ | 0.1 M HCl | 3.91 |
| Silver | $6.2\times10^{3}$ | 0.01M KCl | 0.14 |
| Gold | $4.5\times10^{3}$ | 0.01M NaCl | 0.12 |
| Iron | $1.0\times10^{3}$ | 0.1 M HAc | 0.047 |
| Graphite | $1.2\times10$ | 0.01M HAc | 0.016 |
| ***Insulators*** | | ***Semiconductors*** | |
| Glass | $1.0\times10^{-16}$ | CuO | $1\times10^{-7}$ |
| Teflon | $1.0\times10^{-18}$ | Si | $1.5\times10^{-2}$ |
| | | Ge | 2.0 |

It can be seen from Table 2.2 that the magnitude of conductivity varies a great deal and depends on the nature of the material. It also depends on the temperature and pressure at which the measurements are made. Materials are classified into conductors, insulators and semiconductors depending on the magnitude of their conductivity. Metals and their alloys have very large conductivity and are known as conductors. Certain non-metals like carbon-black, graphite and some organic polymers* are also electronically conducting. Substances like glass, ceramics, etc., having very low conductivity are known as insulators. Substances like silicon, doped silicon and gallium arsenide having conductivity between conductors and insulators are called semiconductors and are important electronic materials. Certain materials called superconductors by definition have zero resistivity or infinite conductivity. Earlier, only metals and their alloys at very low temperatures (0 to 15 K) were known to behave as superconductors, but nowadays a number of ceramic materials and mixed oxides are also known to show superconductivity at temperatures as high as 150 K.

**Electrical conductance** through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on

(i) the nature and structure of the metal
(ii) the number of valence electrons per atom
(iii) temperature (it decreases with increase of temperature).

---

* *Electronically conducting polymers – In 1977 MacDiarmid, Heeger and Shirakawa discovered that acetylene gas can be polymerised to produce a polymer, polyacetylene when exposed to vapours of iodine acquires metallic lustre and conductivity. Since then several organic conducting polymers have been made such as polyaniline, polypyrrole and polythiophene. These organic polymers which have properties like metals, being composed wholly of elements like carbon, hydrogen and occasionally nitrogen, oxygen or sulphur, are much lighter than normal metals and can be used for making light-weight batteries. Besides, they have the mechanical properties of polymers such as flexibility so that one can make electronic devices such as transistors that can bend like a sheet of plastic. For the discovery of conducting polymers, MacDiarmid, Heeger and Shirakawa were awarded the Nobel Prize in Chemistry for the year 2000.*

As the electrons enter at one end and go out through the other end, the composition of the metallic conductor remains unchanged. The mechanism of conductance through semiconductors is more complex.

We already know that even very pure water has small amounts of hydrogen and hydroxyl ions (~$10^{-7}$M) which lend it very low conductivity ($3.5 \times 10^{-5}$ S $m^{-1}$). When electrolytes are dissolved in water, they furnish their own ions in the solution hence its conductivity also increases. The conductance of electricity by ions present in the solutions is called electrolytic or **ionic conductance**. The conductivity of electrolytic (ionic) solutions depends on:

(i) the nature of the electrolyte added
(ii) size of the ions produced and their solvation
(iii) the nature of the solvent and its viscosity
(iv) concentration of the electrolyte
(v) temperature (it increases with the increase of temperature).

Passage of direct current through ionic solution over a prolonged period can lead to change in its composition due to electrochemical reactions (Section 2.4.1).

### 2.4.1 Measurement of the Conductivity of Ionic Solutions

We know that accurate measurement of an unknown resistance can be performed on a Wheatstone bridge. However, for measuring the resistance of an ionic solution we face two problems. Firstly, passing direct current (DC) changes the composition of the solution. Secondly, a solution cannot be connected to the bridge like a metallic wire or other solid conductor. The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called **conductivity cell.** It is available in several designs and two simple ones are shown in Fig. 2.4.

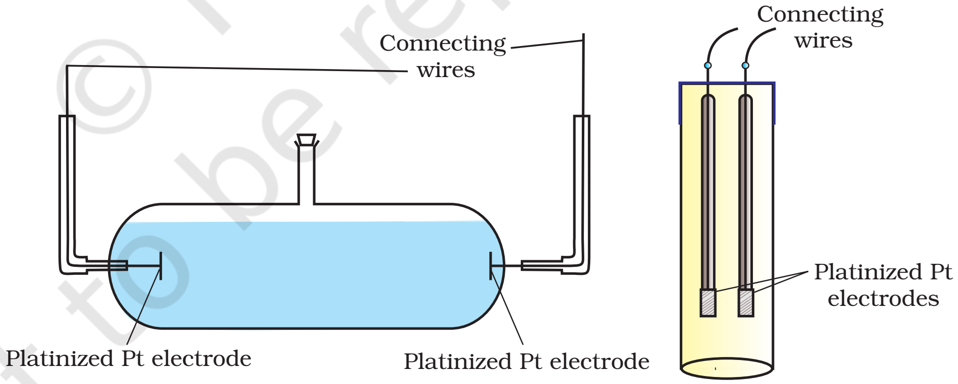


***Fig. 2.4***
*Two different types of conductivity cells.*

Basically it consists of two platinum electrodes coated with platinum black (finely divided metallic Pt is deposited on the electrodes electrochemically). These have area of cross section equal to '$A$' and are separated by distance '$l$'. Therefore, solution confined between these electrodes is a column of length $l$ and area of cross section $A$. The resistance of such a column of solution is then given by the equation:

$$R = \rho \frac{l}{A} = \frac{l}{\kappa A} \qquad (2.17)$$

The quantity $l/A$ is called cell constant denoted by the symbol, $G^*$. It depends on the distance between the electrodes and their area of cross-section and has the dimension of length$^{-1}$ and can be calculated if we know $l$ and $A$. Measurement of $l$ and $A$ is not only inconvenient but also unreliable. The cell constant is usually determined by measuring the resistance of the cell containing a solution whose conductivity is already known. For this purpose, we generally use KCl solutions whose conductivity is known accurately at various concentrations (Table 2.3) and at different temperatures. The cell constant, $G^*$, is then given by the equation:

$$G^* = \frac{l}{A} = \mathrm{R}\,\kappa \tag{2.18}$$

**Table 2.3: Conductivity and Molar conductivity of KCl solutions at 298.15K**

| Concentration/Molarity | | Conductivity | | Molar Conductivity | |
|---|---|---|---|---|---|
| mol L$^{-1}$ | mol m$^{-3}$ | S cm$^{-1}$ | S m$^{-1}$ | S cm$^2$mol$^{-1}$ | S m$^2$ mol$^{-1}$ |
| 1.000 | 1000 | 0.1113 | 11.13 | 111.3 | $111.3\times10^{-4}$ |
| 0.100 | 100.0 | 0.0129 | 1.29 | 129.0 | $129.0\times10^{-4}$ |
| 0.010 | 10.00 | 0.00141 | 0.141 | 141.0 | $141.0\times10^{-4}$ |

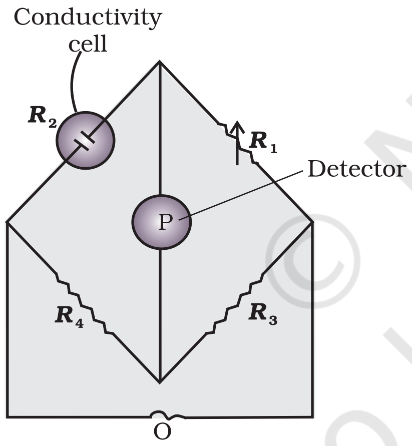


***Fig. 2.5:*** *Arrangement for measurement of resistance of a solution of an electrolyte.*

Once the cell constant is determined, we can use it for measuring the resistance or conductivity of any solution. The set up for the measurement of the resistance is shown in Fig. 2.5.

It consists of two resistances $R_3$ and $R_4$, a variable resistance $R_1$ and the conductivity cell having the unknown resistance $R_2$. The **Wheatstone bridge** is fed by an oscillator O (a source of a.c. power in the audio frequency range 550 to 5000 cycles per second). P is a suitable detector (a headphone or other electronic device) and the bridge is balanced when no current passes through the detector. Under these conditions:

$$\text{Unknown resistance } R_2 = \frac{\mathrm{R}_1\,\mathrm{R}_4}{\mathrm{R}_3} \tag{2.19}$$

These days, inexpensive conductivity meters are available which can directly read the conductance or resistance of the solution in the conductivity cell. Once the cell constant and the resistance of the solution in the cell is determined, the conductivity of the solution is given by the equation:

$$\kappa = \frac{\text{cell constant}}{\mathrm{R}} = \frac{\mathrm{G}^*}{\mathrm{R}} \tag{2.20}$$

The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to charge and size of the ions in which they dissociate, the concentration of ions or ease with which the ions move under a potential gradient. It, therefore, becomes necessary to define a physically more meaningful quantity called **molar conductivity** denoted by the symbol $\Lambda_m$ (Greek, lambda). It is related to the conductivity of the solution by the equation:

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c} \qquad (2.21)$$

In the above equation, if $\kappa$ is expressed in S $m^{-1}$ and the concentration, c in mol $m^{-3}$ then the units of $\Lambda_m$ are in S $m^2$ $mol^{-1}$. It may be noted that:

$1 \text{ mol m}^{-3} = 1000(\text{L/m}^3) \times \text{molarity (mol/L)}$, and hence

$$\Lambda_m(\text{S cm}^2 \text{ mol}^{-1}) = \frac{\kappa \text{ (S cm}^{-1})}{1000 \text{ L m}^{-3} \times \text{molarity (mol L}^{-1})}$$

If we use S $cm^{-1}$ as the units for $\kappa$ and mol $cm^{-3}$, the units of concentration, then the units for $\Lambda_m$ are S $cm^2$ $mol^{-1}$. It can be calculated by using the equation:

$$\Lambda_m(\text{S cm}^2 \text{ mol}^{-1}) = \frac{\kappa \text{ (S cm}^{-1}) \times 1000 \text{ (cm}^3\text{/L)}}{\text{molarity (mol/L)}}$$

Both type of units are used in literature and are related to each other by the equations:

$1 \text{ S m}^2\text{mol}^{-1} = 10^4 \text{ S cm}^2\text{mol}^{-1}$ or

$1 \text{ S cm}^2\text{mol}^{-1} = 10^{-4} \text{ S m}^2\text{mol}^{-1}$.

**Example 2.4**

Resistance of a conductivity cell filled with 0.1 mol $L^{-1}$ KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol $L^{-1}$ KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol $L^{-1}$ KCl solution. The conductivity of 0.1 mol $L^{-1}$ KCl solution is 1.29 S/m.

**Solution**

The cell constant is given by the equation:

Cell constant = $G^*$ = conductivity × resistance

$= 1.29 \text{ S/m} \times 100\ \Omega = 129 \text{ m}^{-1} = 1.29 \text{ cm}^{-1}$

Conductivity of 0.02 mol $L^{-1}$ KCl solution = cell constant / resistance

$$= \frac{G^*}{R} = \frac{129 \text{ m}^{-1}}{520\ \Omega} = 0.248 \text{ S m}^{-1}$$

$$\text{Concentration} = 0.02 \text{ mol L}^{-1}$$

$$= 1000 \times 0.02 \text{ mol m}^{-3} = 20 \text{ mol m}^{-3}$$

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c}$$

$$= \frac{248 \times 10^{-3} \text{ S m}^{-1}}{20 \text{ mol m}^{-3}} = 124 \times 10^{-4} \text{ S m}^2\text{mol}^{-1}$$

$$\text{Alternatively,} \quad \kappa = \frac{1.29 \text{ cm}^{-1}}{520\ \Omega} = 0.248 \times 10^{-2} \text{ S cm}^{-1}$$

and $$\Lambda_m = \kappa \times 1000\ \text{cm}^3\ \text{L}^{-1}\ \text{molarity}^{-1}$$

$$= \frac{0.248\times10^{-2}\ \text{S cm}^{-1}\times 1000\ \text{cm}^3\ \text{L}^{-1}}{0.02\ \text{mol L}^{-1}}$$

$$= 124\ \text{S cm}^2\ \text{mol}^{-1}$$

**Example 2.5** The electrical resistance of a column of 0.05 mol $L^{-1}$ NaOH solution of diameter 1 cm and length 50 cm is 5.55 × $10^3$ ohm. Calculate its resistivity, conductivity and molar conductivity.

**Solution** $A = \pi r^2 = 3.14 \times 0.5^2\ \text{cm}^2 = 0.785\ \text{cm}^2 = 0.785 \times 10^{-4}\ \text{m}^2$

$l = 50\ \text{cm} = 0.5\ \text{m}$

$$R = \frac{\rho\, l}{A} \quad \text{or} \quad \rho = \frac{RA}{l} = \frac{5.55\times10^3\,\Omega\times0.785\,\text{cm}^2}{50\,\text{cm}} = 87.135\ \Omega\ \text{cm}$$

$$\text{Conductivity} = \kappa = \frac{1}{\rho} = \left(\frac{1}{87.135}\right)\ \text{S cm}^{-1}$$

$$= 0.01148\ \text{S cm}^{-1}$$

$$\text{Molar conductivity},\ \Lambda_m = \frac{\kappa \times 1000}{c}\ \text{cm}^3\ \text{L}^{-1}$$

$$= \frac{0.01148\ \text{S cm}^{-1} \times 1000\ \text{cm}^3\ \text{L}^{-1}}{0.05\ \text{mol L}^{-1}}$$

$$= 229.6\ \text{S cm}^2\ \text{mol}^{-1}$$

If we want to calculate the values of different quantities in terms of ‘m’ instead of ‘cm’,

$$\rho = \frac{RA}{l}$$

$$= \frac{5.55\times10^3\ \Omega\times0.785\times10^{-4}\ \text{m}^2}{0.5\ \text{m}} = 87.135\times10^{-2}\ \Omega\ \text{m}$$

$$\kappa = \frac{1}{\rho} = \frac{100}{87.135}\,\Omega\ \text{m} = 1.148\ \text{S m}^{-1}$$

$$\text{and} \quad \Lambda_m = \frac{\kappa}{c} = \frac{1.148\ \text{S m}^{-1}}{50\ \text{mol m}^{-3}} = 229.6\times10^{-4}\ \text{S m}^2\ \text{mol}^{-1}.$$

### 2.4.2 Variation of Conductivity and Molar Conductivity with Concentration

Both conductivity and molar conductivity change with the concentration of the electrolyte. Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution. The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length. This is clear from the equation:

$G = \frac{\kappa A}{l} = \kappa$ (both $A$ and $l$ are unity in their appropriate units in m or cm)

**Molar conductivity** of a solution at a given concentration is the conductance of the volume $V$ of solution containing one mole of electrolyte kept between two electrodes with area of cross section $A$ and distance of unit length. Therefore,

$$\Lambda_m = \frac{\kappa A}{l} = \kappa$$

Since $l = 1$ and $A = V$ ( volume containing 1 mole of electrolyte)

$$\Lambda_m = \kappa \; V \tag{2.22}$$

Molar conductivity increases with decrease in concentration. This is because the total volume, $V$, of solution containing one mole of electrolyte also increases. It has been found that decrease in $\kappa$ on dilution of a solution is more than compensated by increase in its volume. Physically, it means that at a given concentration, $\Lambda_m$ can be defined as the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. When concentration approaches zero, the molar conductivity is known as **limiting molar conductivity** and is represented by the symbol $\Lambda_m^\circ$. The variation in $\Lambda_m$ with concentration is different (Fig. 2.6) for strong and weak electrolytes.

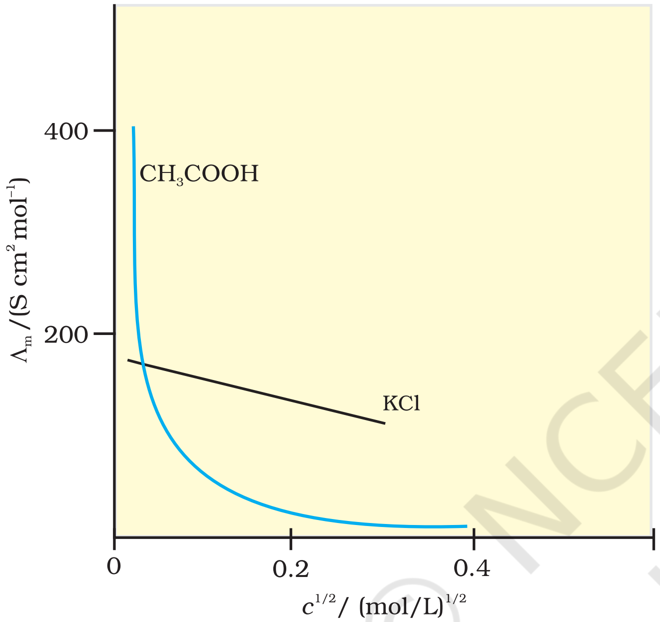


**Fig. 2.6:** *Molar conductivity versus c½ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.*

### *Strong Electrolytes*

For strong electrolytes, $\Lambda_m$ increases slowly with dilution and can be represented by the equation:

$$\Lambda_m = \Lambda_m^\circ - A\, c^{1/2} \tag{2.23}$$

It can be seen that if we plot (Fig. 2.6) $\Lambda_m$ against $c^{1/2}$, we obtain a straight line with intercept equal to $\Lambda_m^\circ$ and slope equal to '–$A$'. The value of the constant '$A$' for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus, NaCl, $CaCl_2$, $MgSO_4$ are known as 1-1, 2-1 and 2-2 electrolytes respectively. All electrolytes of a particular type have the same value for '$A$'.

**Example 2.6** The molar conductivity of KCl solutions at different concentrations at 298 K are given below:

| $c$/mol L$^{-1}$ | $\Lambda_m$/S cm$^2$ mol$^{-1}$ |
|---|---|
| 0.000198 | 148.61 |
| 0.000309 | 148.29 |
| 0.000521 | 147.81 |
| 0.000989 | 147.09 |

Show that a plot between $\Lambda_m$ and $c^{1/2}$ is a straight line. Determine the values of $\Lambda_m^\circ$ and A for KCl.

**Solution** Taking the square root of concentration we obtain:

| $c^{1/2}$/(mol L$^{-1}$ )$^{1/2}$ | $\Lambda_m$/S cm$^2$mol$^{-1}$ |
|---|---|
| 0.01407 | 148.61 |
| 0.01758 | 148.29 |
| 0.02283 | 147.81 |
| 0.03145 | 147.09 |

A plot of $\Lambda_m$ ( y-axis) and $c^{1/2}$ ($x$-axis) is shown in (Fig. 3.7).
It can be seen that it is nearly a straight line. From the intercept ($c^{1/2}$ = 0), we find that

$$\Lambda_m^\circ = 150.0 \text{ S cm}^2 \text{ mol}^{-1} \text{ and}$$

$$A = - \text{slope} = 87.46 \text{ S cm}^2 \text{ mol}^{-1}/(\text{mol/L}^{-1})^{1/2}.$$

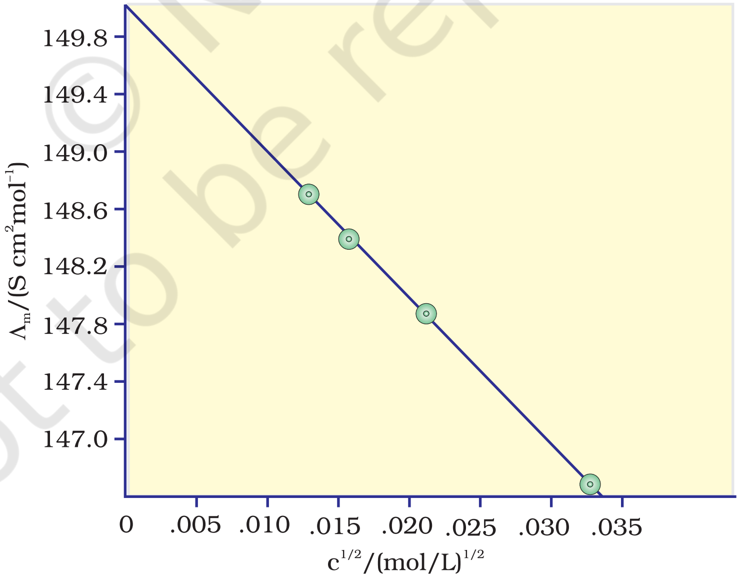


**Fig. 2.7:** *Variation of $\Lambda_m$ against c½.*

Kohlrausch examined $\Lambda_m^\circ$ values for a number of strong electrolytes and observed certain regularities. He noted that the difference in $\Lambda_m^\circ$ of the electrolytes NaX and KX for any X is nearly constant. For example at 298 K:

$$\Lambda_{m\,(\mathrm{KCl})}^\circ - \Lambda_{m\,(\mathrm{NaCl})}^\circ = \Lambda_{m\,(\mathrm{KBr})}^\circ - \Lambda_{m\,(\mathrm{NaBr})}^\circ$$

$$= \Lambda_{m\,(\mathrm{KI})}^\circ - \Lambda_{m\,(\mathrm{NaI})}^\circ \simeq 23.4 \text{ S cm}^2 \text{ mol}^{-1}$$

and similarly it was found that

$$\Lambda_{m\,(\mathrm{NaBr})}^\circ - \Lambda_{m\,(\mathrm{NaCl})}^\circ = \Lambda_{m\,(\mathrm{KBr})}^\circ - \Lambda_{m\,(\mathrm{KCl})}^\circ \simeq 1.8 \text{ S cm}^2 \text{ mol}^{-1}$$

On the basis of the above observations he enunciated **Kohlrausch law of independent migration of ions**. The law states that *limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. Thus, if* $\lambda_{Na^+}^\circ$ *and* $\lambda_{Cl^-}^\circ$ *are limiting molar conductivity* of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:

$$\Lambda_{m\,(\mathrm{NaCl})}^\circ = \lambda_{\mathrm{Na}^+}^\circ + \lambda_{\mathrm{Cl}^-}^\circ \qquad (2.24)$$

In general, if an electrolyte on dissociation gives $\nu_+$ cations and $\nu_-$ anions then its limiting molar conductivity is given by:

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ \qquad (2.25)$$

Here, $\lambda_+^\circ$ and $\lambda_-^\circ$ are the limiting molar conductivities of the cation and anion respectively. The values of $\lambda^\circ$ for some cations and anions at 298 K are given in Table 2.4.

**Table 2.4: Limiting Molar Conductivity for some Ions in Water at 298 K**

| Ion | $\lambda^0$/(S cm$^2$mol$^{-1}$) | Ion | $\lambda^0$/(S cm$^2$ mol$^{-1}$) |
|---|---|---|---|
| $H^+$ | 349.6 | $OH^-$ | 199.1 |
| $Na^+$ | 50.1 | $Cl^-$ | 76.3 |
| $K^+$ | 73.5 | $Br^-$ | 78.1 |
| $Ca^{2+}$ | 119.0 | $CH_3COO^-$ | 40.9 |
| $Mg^{2+}$ | 106.0 | $SO_4^{2-}$ | 160.0 |

### *Weak Electrolytes*

Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations and hence for such electrolytes, the change in $\Lambda_m$ with dilution is due to increase in the degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mol of electrolyte. In such cases $\Lambda_m$ increases steeply (Fig. 2.6) on dilution, especially near lower concentrations. Therefore, $\Lambda_m^\circ$ cannot be obtained by extrapolation of $\Lambda_m$ to zero concentration. At infinite dilution (i.e., concentration $c \to$ zero) electrolyte dissociates completely ($\alpha$ =1), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately. Therefore, $\Lambda_m^\circ$ for weak electrolytes is obtained by using Kohlrausch law of independent migration of ions (Example 2.8). At any concentration $c$, if $\alpha$ is the degree of dissociation then it can be approximated to the ratio of molar conductivity $\Lambda_m$ at the concentration c to limiting molar conductivity, $\Lambda_m^0$. Thus we have:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}} \qquad (2.26)$$

But we know that for a weak electrolyte like acetic acid (Class XI, Unit 7),

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_m^2}{\Lambda_m^{\circ 2}\left(1-\frac{\Lambda_m}{\Lambda_m^{\circ}}\right)} = \frac{c\Lambda_m^2}{\Lambda_m^{\circ}\left(\Lambda_m^{\circ}-\Lambda_m\right)} \qquad (2.27)$$

***Applications of Kohlrausch law***

Using Kohlrausch law of independent migration of ions, it is possible to calculate $\Lambda_m^0$ for any electrolyte from the $\lambda^{\circ}$ of individual ions. Moreover, for weak electrolytes like acetic acid it is possible to determine the value of its dissociation constant once we know the $\Lambda_m^0$ and $\Lambda_m$ at a given concentration *c*.

**Example 2.7** Calculate $\Lambda_m^0$ for $CaCl_2$ and $MgSO_4$ from the data given in Table 3.4.

**Solution** We know from Kohlrausch law that

$$\Lambda^{\circ}_{m(CaCl_2)} = \lambda^{\circ}_{Ca^{2+}} + 2\lambda^{\circ}_{Cl^-} = 119.0 \text{ S cm}^2 \text{ mol}^{-1} + 2(76.3) \text{ S cm}^2 \text{ mol}^{-1}$$

$$= (119.0 + 152.6) \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 271.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^{\circ}_{m(MgSO_4)} = \lambda^{\circ}_{Mg^{2+}} + \lambda^{\circ}_{SO_4^{2-}} = 106.0 \text{ S cm}^2 \text{ mol}^{-1} + 160.0 \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 266 \text{ S cm}^2 \text{ mol}^{-1}\ .$$

**Example 2.8** $\Lambda_m^0$ for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm$^2$ mol$^{-1}$ respectively. Calculate $\Lambda^0$ for HAc.

**Solution**

$$\Lambda^{\circ}_{m(HAc)} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{Ac^-} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{Cl^-} + \lambda^{\circ}_{Ac^-} + \lambda^{\circ}_{Na^+} - \lambda^{\circ}_{Cl^-} - \lambda^{\circ}_{Na^+}$$

$$= \Lambda^{\circ}_{m(HCl)} + \Lambda^{\circ}_{m(NaAc)} - \Lambda^{\circ}_{m(NaCl)}$$

$$= (425.9 + 91.0 - 126.4\ ) \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 390.5 \text{ S cm}^2 \text{ mol}^{-1}\ .$$

**Example 2.9** The conductivity of 0.001028 mol L$^{-1}$ acetic acid is 4.95 × 10$^{-5}$ S cm$^{-1}$. Calculate its dissociation constant if $\Lambda_m^0$ for acetic acid is 390.5 S cm$^2$ mol$^{-1}$.

**Solution**

$$\Lambda_m = \frac{\kappa}{c} = \frac{4.95\times10^{-5}\,\text{S cm}^{-1}}{0.001028\,\text{mol L}^{-1}} \times \frac{1000\,\text{cm}^3}{\text{L}} = 48.15 \text{ S cm}^3 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}} = \frac{48.15 \text{ S cm}^2\text{mol}^{-1}}{390.5 \text{ S cm}^2 \text{mol}^{-1}} = 0.1233$$

$$k = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028\,\text{mol L}^{-1}\times(0.1233)^2}{1-0.1233} = 1.78 \times 10^{-5} \text{ mol L}^{-1}$$

### Intext Questions

**2.7** Why does the conductivity of a solution decrease with dilution?

**2.8** Suggest a way to determine the $\Lambda_m^\circ$ value of water.

**2.9** The molar conductivity of 0.025 mol $L^{-1}$ methanoic acid is 46.1 S $cm^2$ $mol^{-1}$. Calculate its degree of dissociation and dissociation constant. Given $\lambda^0(H^+)$ = 349.6 S $cm^2$ $mol^{-1}$ and $\lambda^0(HCOO^-)$ = 54.6 S $cm^2$ $mol^{-1}$.

## 2.5 Electrolytic Cells and Electrolysis

In an **electrolytic cell** external source of voltage is used to bring about a chemical reaction. The electrochemical processes are of great importance in the laboratory and the chemical industry. One of the simplest electrolytic cell consists of two copper strips dipping in an aqueous solution of copper sulphate. If a DC voltage is applied to the two electrodes, then $Cu^{2+}$ ions discharge at the cathode (negatively charged) and the following reaction takes place:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu\ (s) \qquad (2.28)$$

Copper metal is deposited on the cathode. At the anode, copper is converted into $Cu^{2+}$ ions by the reaction:

$$Cu(s) \rightarrow Cu^{2+}(s) + 2e^- \qquad (2.29)$$

Thus copper is dissolved (oxidised) at anode and deposited (reduced) at cathode. This is the basis for an industrial process in which impure copper is converted into copper of high purity. The impure copper is made an anode that dissolves on passing current and pure copper is deposited at the cathode. Many metals like Na, Mg, Al, etc. are produced on large scale by electrochemical reduction of their respective cations where no suitable chemical reducing agents are available for this purpose.

Sodium and magnesium metals are produced by the electrolysis of their fused chlorides and aluminium is produced by electrolysis of aluminium oxide in presence of cryolite.

### *Quantitative Aspects of Electrolysis*

**Michael Faraday** was the first scientist who described the quantitative aspects of electrolysis. Now Faraday's laws also flow from what has been discussed earlier.

### *Faraday's Laws of Electrolysis*

After his extensive investigations on electrolysis of solutions and melts of electrolytes, Faraday published his results during 1833-34 in the form of the following well known Faraday's two laws of electrolysis:

(i) *First Law*: The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).

(ii) *Second Law*: The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation).

There were no constant current sources available during Faraday's times. The general practice was to put a coulometer (a standard electrolytic cell) for determining the quantity of electricity passed from the amount of metal (generally silver or copper) deposited or consumed. However, coulometers are now obsolete and we now have constant current ($I$) sources available and the quantity of electricity $Q$, passed is given by

$$Q = It$$

$Q$ is in coloumbs when $I$ is in ampere and $t$ is in second.

The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction. For example, in the reaction:

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s) \qquad (2.30)$$

One mole of the electron is required for the reduction of one mole of silver ions.

We know that charge on one electron is equal to $1.6021 \times 10^{-19}$C.

Therefore, the charge on one mole of electrons is equal to:

$$N_A \times 1.6021 \times 10^{-19}\ C = 6.02 \times 10^{23} mol^{-1} \times 1.6021 \times 10^{-19}$$

$$C = 96487\ C\ mol^{-1}$$

This quantity of electricity is called **Faraday** and is represented by the symbol **F**.

For approximate calculations we use $1F \simeq 96500\ C\ mol^{-1}$.

For the electrode reactions:

$$Mg^{2+}(l) + 2e^{-} \longrightarrow Mg(s) \qquad (2.31)$$

$$Al^{3+}(l) + 3e^{-} \longrightarrow Al(s) \qquad (2.32)$$

It is obvious that one mole of $Mg^{2+}$ and $Al^{3+}$ require 2 mol of electrons (2F) and 3 mol of electrons (3F) respectively. The charge passed through the electrolytic cell during electrolysis is equal to the product of current in amperes and time in seconds. In commercial production of metals, current as high as 50,000 amperes are used that amounts to about 0.518 F per second.

*Example 2.10* A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

*Solution* $t$ = 600 s charge = current × time = 1.5 A × 600 s = 900 C

According to the reaction:

$Cu^{2+}(aq) + 2e^{-} = Cu(s)$

We require 2F or 2 × 96487 C to deposit 1 mol or 63 g of Cu.

For 900 C, the mass of Cu deposited

$= (63\ g\ mol^{-1} \times 900\ C)/(2 \times 96487\ C\ mol^{-1}) = 0.2938\ g.$

### 2.5.1 Products of Electrolysis

Products of electrolysis depend on the nature of material being electrolysed and the type of electrodes being used. If the electrode is inert (e.g., platinum or gold), it does not participate in the chemical reaction and acts only as source or sink for electrons. On the other hand, if the electrode is reactive, it participates in the electrode reaction. Thus, the products of electrolysis may be different for reactive and inert electrodes.The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials. Moreover, some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these do not seem to take place and extra potential (called *overpotential*) has to be applied, which makes such process more difficult to occur.

For example, if we use molten NaCl, the products of electrolysis are sodium metal and $Cl_2$ gas. Here we have only one cation ($Na^+$) which is reduced at the cathode ($Na^+ + e^- \rightarrow Na$) and one anion ($Cl^-$) which is oxidised at the anode ($Cl^- \rightarrow ½Cl_2 + e^-$). During the electrolysis of aqueous sodium chloride solution, the products are NaOH, $Cl_2$ and $H_2$. In this case besides $Na^+$ and $Cl^-$ ions we also have $H^+$ and $OH^-$ ions along with the solvent molecules, $H_2O$.

At the cathode there is competition between the following reduction reactions:

$$Na^+ (aq) + e^- \rightarrow Na (s) \qquad E^o_{(cell)} = -2.71 \text{ V}$$

$$H^+ (aq) + e^- \rightarrow ½ H_2 (g) \qquad E^o_{(cell)} = 0.00 \text{ V}$$

The reaction with higher value of $E^o$ is preferred and therefore, the reaction at the cathode during electrolysis is:

$$H^+ (aq) + e^- \rightarrow ½ H_2 (g) \qquad (2.33)$$

but $H^+$ (aq) is produced by the dissociation of $H_2O$, i.e.,

$$H_2O (l) \rightarrow H^+ (aq) + OH^- (aq) \qquad (2.34)$$

Therefore, the net reaction at the cathode may be written as the sum of (2.33) and (2.34) and we have

$$H_2O (l) + e^- \rightarrow ½H_2(g) + OH^- \qquad (2.35)$$

At the anode the following oxidation reactions are possible:

$$Cl^- (aq) \rightarrow ½ Cl_2 (g) + e^- \qquad E^o_{(cell)} = 1.36 \text{ V} \qquad (2.36)$$

$$2H_2O (l) \rightarrow O_2 (g) + 4H^+(aq) + 4e^- \qquad E^o_{(cell)} = 1.23 \text{ V} \qquad (2.37)$$

The reaction at anode with lower value of $E^o$ is preferred and therefore, water should get oxidised in preference to $Cl^-$ (aq). However, on account of overpotential of oxygen, reaction (2.36) is preferred. Thus, the net reactions may be summarised as:

$$NaCl (aq) \xrightarrow{H_2O} Na^+ (aq) + Cl^- (aq)$$

Cathode: $H_2O(l) + e^- \rightarrow ½ H_2(g) + OH^- (aq)$

Anode: $Cl^- (aq) \rightarrow ½ Cl_2(g) + e^-$

Net reaction:

$$NaCl(aq) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + ½H_2(g) + ½Cl_2(g)$$

The standard electrode potentials are replaced by electrode potentials given by Nernst equation (Eq. 2.8) to take into account the concentration effects. During the electrolysis of sulphuric acid, the following processes are possible at the anode:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E^o_{(cell)} = +1.23 \text{ V} \qquad (2.38)$$

$$2SO_4^{2-}\ (aq) \rightarrow S_2O_8^{2-}\ (aq) + 2e^- \qquad E^o_{(cell)} = 1.96\ V \qquad (2.39)$$

For dilute sulphuric acid, reaction (2.38) is preferred but at higher concentrations of $H_2SO_4$, reaction (2.39) is preferred.

## Intext Questions

**2.10** If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

**2.11** Suggest a list of metals that are extracted electrolytically.

**2.12** Consider the reaction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$?

## 2.6 Batteries

Any battery (actually it may have one or more than one cell connected in series) or cell that we use as a source of electrical energy is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries.

### 2.6.1 Primary Batteries

In the primary batteries, the reaction occurs only once and after use over a period of time battery becomes dead and cannot be reused again. The most familiar example of this type is the dry cell (known as Leclanche cell after its discoverer) which is used commonly in our transistors and clocks. The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon (Fig.2.8). The space between the electrodes is filled by a moist paste of ammonium chloride ($NH_4Cl$) and zinc chloride ($ZnCl_2$). The electrode reactions are complex, but they can be written approximately as follows :

Anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

Cathode: $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

In the reaction at cathode, manganese is reduced from the + 4 oxidation state to the +3 state. Ammonia produced in the reaction forms a complex with $Zn^{2+}$ to give $[Zn(NH_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V.

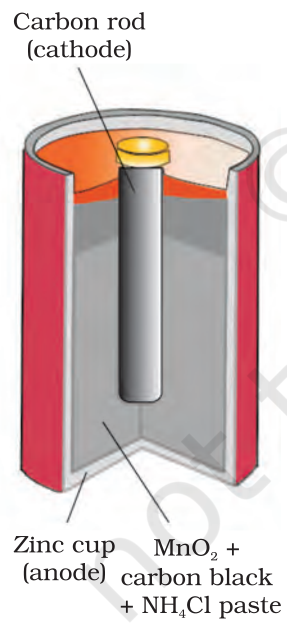


**Fig. 2.8:** *A commercial dry cell consists of a graphite (carbon) cathode in a zinc container; the latter acts as the anode.*

Mercury cell, (Fig. 2.9) suitable for low current devices like hearing aids, watches, etc. consists of zinc – mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions for the cell are given below:

Anode: $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

Cathode: $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

The overall reaction is represented by

$$\mathrm{Zn(Hg)} + \mathrm{HgO(s)} \longrightarrow \mathrm{ZnO(s)} + \mathrm{Hg(l)}$$

The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

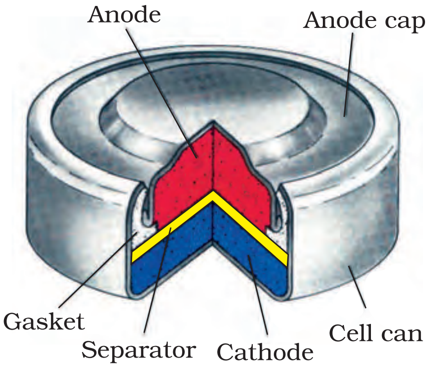


***Fig. 2.9*** *Commonly used mercury cell. The reducing agent is zinc and the oxidising agent is mercury (II) oxide.*

### 2.6.2 Secondary Batteries

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles. The most important secondary cell is the lead storage battery (Fig. 2.10) commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide ($PbO_2$ ) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

The cell reactions when the battery is in use are given below:

Anode: $\mathrm{Pb(s)} + \mathrm{SO_4^{2-}(aq)} \rightarrow \mathrm{PbSO_4(s)} + 2e^-$

Cathode: $\mathrm{PbO_2(s)} + \mathrm{SO_4^{2-}(aq)} + 4\mathrm{H^+(aq)} + 2e^- \rightarrow \mathrm{PbSO_4\,(s)} + 2\mathrm{H_2O\,(l)}$

i.e., overall cell reaction consisting of cathode and anode reactions is:

$$\mathrm{Pb(s)} + \mathrm{PbO_2(s)} + 2\mathrm{H_2SO_4(aq)} \rightarrow 2\mathrm{PbSO_4(s)} + 2\mathrm{H_2O}(l)$$

On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and $PbO_2$, respectively.

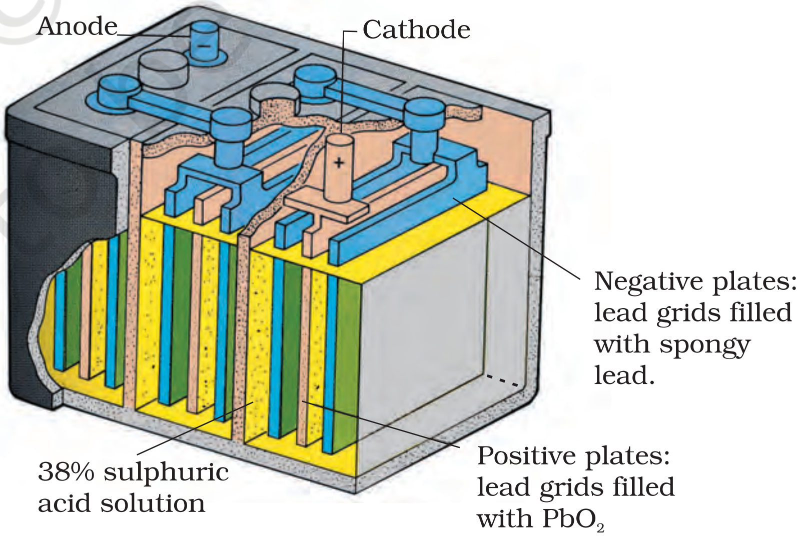


***Fig. 2.10:*** *The Lead storage battery.*

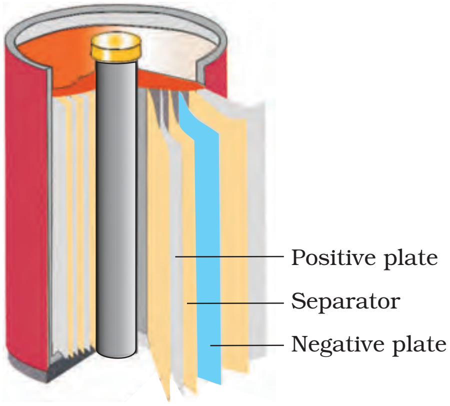


***Fig. 2.11***
*A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.*

Another important secondary cell is the nickel-cadmium cell (Fig. 2.11) which has longer life than the lead storage cell but more expensive to manufacture. We shall not go into details of working of the cell and the electrode reactions during charging and discharging. The overall reaction during discharge is:

$$Cd\ (s) + 2Ni(OH)_3\ (s) \rightarrow CdO\ (s) + 2Ni(OH)_2\ (s) + H_2O\ (l)$$

## 2.7 Fuel Cells

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity. We know that a galvanic cell directly converts chemical energy into electricity and is highly efficient. It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment. **Galvanic cells** that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called **fuel cells**.

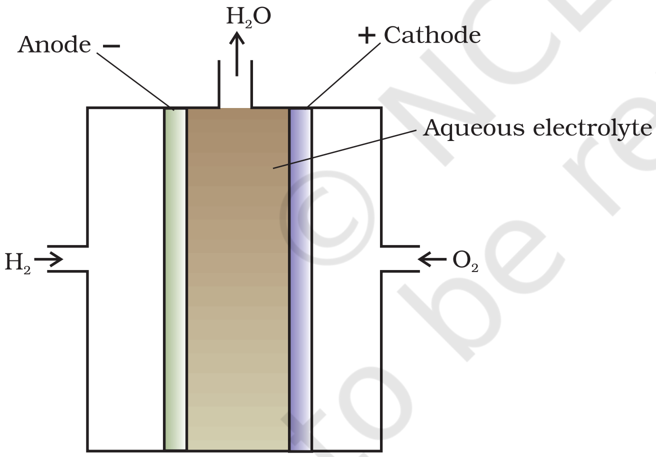


***Fig. 2.12:*** *Fuel cell using $H_2$ and $O_2$ produces electricity.*

One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water (Fig. 2.12). The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
Anode: $2H_2\ (g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

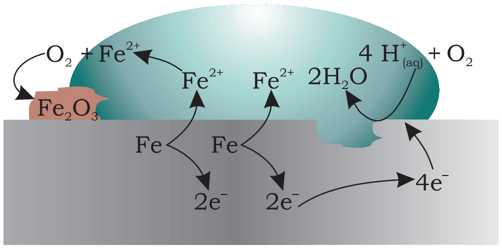
Overall reaction being:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. These have been used in automobiles on an experimental basis. Fuel cells are pollution free and in view of their future importance, a variety of fuel cells have been fabricated and tried.

## 2.8 Corrosion

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion. It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. We lose crores of rupees every year on account of corrosion.



Oxidation: Fe (s)→ $Fe^{2+}$ (aq) +$2e^-$

Reduction: $O_2$ (g) + $4H^+$(aq) +$4e^-$ → $2H_2O$(l)

Atomospheric
oxidation: $2Fe^{2+}$(aq) + $2H_2O$(l) + ½$O_2$(g) → $Fe_2O_3$(s) + $4H^+$(aq)

***Fig. 2.13:*** *Corrosion of iron in atmosphere*

In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. At a particular spot (Fig. 2.13) of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction

$$\text{Anode: } 2\ \text{Fe (s)} \longrightarrow 2\ \text{Fe}^{2+} + 4\ e^- \qquad E^o_{(\text{Fe}^{2+}/\text{Fe})} = -\,0.44\ \text{V}$$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in the presence of $H^+$ (which is believed to be available from $H_2CO_3$ formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction

$$\text{Cathode: } \text{O}_2\text{(g)} + 4\ \text{H}^+\text{(aq)} + 4\ e^- \longrightarrow 2\ \text{H}_2\text{O (l)} \quad E^o_{\text{H}^+|\text{O}_2|\text{H}_2\text{O}} = 1.23\ \text{V}$$

The overall reaction being:

$$2\text{Fe(s)} + \text{O}_2\text{(g)} + 4\text{H}^+\text{(aq)} \longrightarrow 2\text{Fe}^{2+}\text{(aq)} + 2\ \text{H}_2\text{O (l)} \qquad E^o_{(\text{cell})} = 1.67\ \text{V}$$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($Fe_2O_3$. $x\,H_2O$) and with further production of hydrogen ions.

Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion. One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol). Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.

## Intext Questions

**2.13** Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

**2.14** Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

**2.15** Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

## The Hydrogen Economy

At present the main source of energy that is driving our economy is fossil fuels such as coal, oil and gas. As more people on the planet aspire to improve their standard of living, their energy requirement will increase. In fact, the per capita consumption of energy used is a measure of development. Of course, it is assumed that energy is used for productive purpose and not merely wasted. We are already aware that carbon dioxide produced by the combustion of fossil fuels is resulting in the 'Greenhouse Effect'. This is leading to a rise in the temperature of the Earth's surface, causing polar ice to melt and ocean levels to rise. This will flood low-lying areas along the coast and some island nations such as Maldives face total submergence. In order to avoid such a catastrope, we need to limit our use of carbonaceous fuels. Hydrogen provides an ideal alternative as its combustion results in water only. Hydrogen production must come from splitting water using solar energy. Therefore, hydrogen can be used as a renewable and non polluting source of energy. This is the vision of the Hydrogen Economy. Both the production of hydrogen by electrolysis of water and hydrogen combustion in a fuel cell will be important in the future. And both these technologies are based on electrochemical principles.

## Summary

An **electrochemical cell** consists of two metallic electrodes dipping in electrolytic solution(s). Thus an important component of the electrochemical cell is the ionic conductor or electrolyte. Electrochemical cells are of two types. In **galvanic cell**, the **chemical energy** of a **spontaneous redox reaction** is converted into electrical work, whereas in an electrolytic cell, electrical energy is used to carry out a **non-spontaneous redox reaction**. The **standard electrode potential** for any electrode dipping in an appropriate solution is defined with respect to standard electrode potential of **hydrogen electrode** taken as zero. The standard potential of the cell can be obtained by taking the difference of the standard potentials of cathode and anode ($E^o_{(cell)} = E^o$cathode $- E^o$anode). The standard potential of the cells are related to standard Gibbs energy ($\Delta_r G^o = -nFE^o_{(cell)}$) and **equilibrium constant** ($\Delta_r G^o = -RT \ln K$) of the reaction taking place in the cell. Concentration dependence of the potentials of the electrodes and the cells are given by Nernst equation.

The **conductivity**, $\kappa$, of an electrolytic solution depends on the concentration of the electrolyte, nature of solvent and temperature. **Molar conductivity**, $\Lambda_m$, is defined by = $\kappa/c$ where $c$ is the concentration. Conductivity decreases but molar conductivity increases with decrease in concentration. It increases slowly with decrease in concentration for strong electrolytes while the increase is very steep for weak electrolytes in very dilute solutions. Kohlrausch found that molar conductivity at infinite dilution, for an electrolyte is sum of the contribution of the molar conductivity of the ions in which it dissociates. It is known as **law of independent migration of ions** and has many applications. Ions conduct electricity through the solution but oxidation and reduction of the ions take place at the electrodes in an electrochemical cell. **Batteries** and **fuel cells** are very useful forms of galvanic cell. **Corrosion** of metals is essentially an **electrochemical phenomenon**. Electrochemical principles are relevant to the **Hydrogen Economy**.

## Exercises

**2.1** Arrange the following metals in the order in which they displace each other from the solution of their salts.

Al, Cu, Fe, Mg and Zn.

**2.2** Given the standard electrode potentials,

$K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$,

$Hg^{2+}/Hg = 0.79V$

$Mg^{2+}/Mg = -2.37\ V$, $Cr^{3+}/Cr = -\ 0.74V$

Arrange these metals in their increasing order of reducing power.

**2.3** Depict the galvanic cell in which the reaction

$Zn(s)+2Ag^+(aq) \rightarrow Zn^{2+}(aq)+2Ag(s)$ takes place. Further show:

(i) Which of the electrode is negatively charged?

(ii) The carriers of the current in the cell.

(iii) Individual reaction at each electrode.

**2.4** Calculate the standard cell potentials of galvanic cell in which the following reactions take place:

(i) $2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd$

(ii) $Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$

Calculate the $\Delta_r G^\circ$ and equilibrium constant of the reactions.

**2.5** Write the Nernst equation and emf of the following cells at 298 K:

(i) $Mg(s)\,|\,Mg^{2+}(0.001M)\,||\,Cu^{2+}(0.0001\ M)\,|\,Cu(s)$

(ii) $Fe(s)\,|\,Fe^{2+}(0.001M)\,||\,H^+(1M)\,|\,H_2(g)(1bar)\,|\ Pt(s)$

(iii) $Sn(s)\,|\,Sn^{2+}(0.050\ M)\,||\,H^+(0.020\ M)\,|\,H_2(g)\ (1\ bar)\,|\,Pt(s)$

(iv) $Pt(s)\,|\,Br^-(0.010\ M)\,|\,Br_2(l)\,||\,H^+(0.030\ M)\,|\ H_2(g)\ (1\ bar)\,|\,Pt(s)$.

**2.6** In the button cells widely used in watches and other devices the following reaction takes place:

$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

Determine $\Delta_r G^o$ and $E^o$ for the reaction.

**2.7** Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

**2.8** The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S $cm^{-1}$. Calculate its molar conductivity.

**2.9** The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is $0.146 \times 10^{-3}$ S $cm^{-1}$.

**2.10** The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

| Concentration/M | 0.001 | 0.010 | 0.020 | 0.050 | 0.100 |
|---|---|---|---|---|---|
| $10^2 \times \kappa/\text{S m}^{-1}$ | 1.237 | 11.85 | 23.15 | 55.53 | 106.74 |

Calculate $\Lambda_m$ for all concentrations and draw a plot between $\Lambda_m$ and $c^{1/2}$. Find the value of $\Lambda_m^0$.

**2.11** Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5}$ S cm$^{-1}$. Calculate its molar conductivity. If $\Lambda_m^0$ for acetic acid is 390.5 S cm$^2$ mol$^{-1}$, what is its dissociation constant?

**2.12** How much charge is required for the following reductions:

(i) 1 mol of $Al^{3+}$ to Al?
(ii) 1 mol of $Cu^{2+}$ to Cu?
(iii) 1 mol of $MnO_4^-$ to $Mn^{2+}$?

**2.13** How much electricity in terms of Faraday is required to produce

(i) 20.0 g of Ca from molten $CaCl_2$?
(ii) 40.0 g of Al from molten $Al_2O_3$?

**2.14** How much electricity is required in coulomb for the oxidation of

(i) 1 mol of $H_2O$ to $O_2$?
(ii) 1 mol of FeO to $Fe_2O_3$?

**2.15** A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

**2.16** Three electrolytic cells A,B,C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

**2.17** Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:

(i) $Fe^{3+}$(aq) and $I^-$(aq)
(ii) $Ag^+$ (aq) and Cu(s)
(iii) $Fe^{3+}$ (aq) and $Br^-$ (aq)
(iv) Ag(s) and $Fe^{3+}$ (aq)
(v) $Br_2$ (aq) and $Fe^{2+}$ (aq).

**2.18** Predict the products of electrolysis in each of the following:

(i) An aqueous solution of $AgNO_3$ with silver electrodes.
(ii) An aqueous solution of $AgNO_3$ with platinum electrodes.
(iii) A dilute solution of $H_2SO_4$ with platinum electrodes.
(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

## Answers to Some Intext Questions

**2.5** $E_{(cell)} = 0.91$ V

**2.6** $\Delta_r G^o = -45.54 \text{ kJ mol}^{-1}$, $K_c = 9.62 \times 10^7$

**2.9** 0.114, $3.67 \times 10^{-4}$ mol L$^{-1}$

12085CH04

# Unit 3

# Chemical Kinetics

## Objectives

After studying this Unit, you will be able to

- define the average and instantaneous rate of a reaction;
- express the rate of a reaction in terms of change in concentration of either of the reactants or products with time;
- distinguish between elementary and complex reactions;
- differentiate between the molecularity and order of a reaction;
- define rate constant;
- discuss the dependence of rate of reactions on concentration, temperature and catalyst;
- derive integrated rate equations for the zero and first order reactions;
- determine the rate constants for zeroth and first order reactions;
- describe collision theory.

*Chemical Kinetics helps us to understand how chemical reactions occur.*

Chemistry, by its very nature, is concerned with change. Substances with well defined properties are converted by chemical reactions into other substances with different properties. For any chemical reaction, chemists try to find out

(a) the feasibility of a chemical reaction which can be predicted by thermodynamics ( as you know that a reaction with $\Delta G < 0$, at constant temperature and pressure is feasible);

(b) extent to which a reaction will proceed can be determined from chemical equilibrium;

(c) speed of a reaction i.e. time taken by a reaction to reach equilibrium.

Along with feasibility and extent, it is equally important to know the rate and the factors controlling the rate of a chemical reaction for its complete understanding. For example, which parameters determine as to how rapidly food gets spoiled? How to design a rapidly setting material for dental filling? Or what controls the rate at which fuel burns in an auto engine? All these questions can be answered by the branch of chemistry, which deals with the study of reaction rates and their mechanisms, called **chemical kinetics**. The word kinetics is derived from the Greek word 'kinesis' meaning movement. Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction. For example, thermodynamic data indicate that diamond shall convert to graphite but in reality the conversion rate is so slow that the change is not perceptible at all. Therefore, most people think that diamond is forever. Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions by which the reaction rates can be altered. The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction. At the macroscopic level, we are interested in amounts reacted or formed and the rates of their consumption or formation. At the molecular level, the reaction mechanisms involving orientation and energy of molecules undergoing collisions, are discussed.

In this Unit, we shall be dealing with average and instantaneous rate of reaction and the factors affecting these. Some elementary ideas about the collision theory of reaction rates are also given. However, in order to understand all these, let us first learn about the reaction rate.

## 3.1 Rate of a Chemical Reaction

Some reactions such as ionic reactions occur very fast, for example, precipitation of silver chloride occurs instantaneously by mixing of aqueous solutions of silver nitrate and sodium chloride. On the other hand, some reactions are very slow, for example, rusting of iron in the presence of air and moisture. Also there are reactions like inversion of cane sugar and hydrolysis of starch, which proceed with a moderate speed. Can you think of more examples from each category?

You must be knowing that speed of an automobile is expressed in terms of change in the position or distance covered by it in a certain period of time. Similarly, the speed of a reaction or the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. To be more specific, it can be expressed in terms of:

(i) the rate of decrease in concentration of any one of the reactants, or

(ii) the rate of increase in concentration of any one of the products.

Consider a hypothetical reaction, assuming that the volume of the system remains constant.

$$R \rightarrow P$$

One mole of the reactant R produces one mole of the product P. If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time $t_1$ and $[R]_2$ and $[P]_2$ are their concentrations at time $t_2$ then,

$$\Delta t = t_2 - t_1$$

$$\Delta[R] = [R]_2 - [R]_1$$

$$\Delta [P] = [P]_2 - [P]_1$$

The square brackets in the above expressions are used to express molar concentration.

Rate of disappearance of R

$$= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t} \qquad (3.1)$$

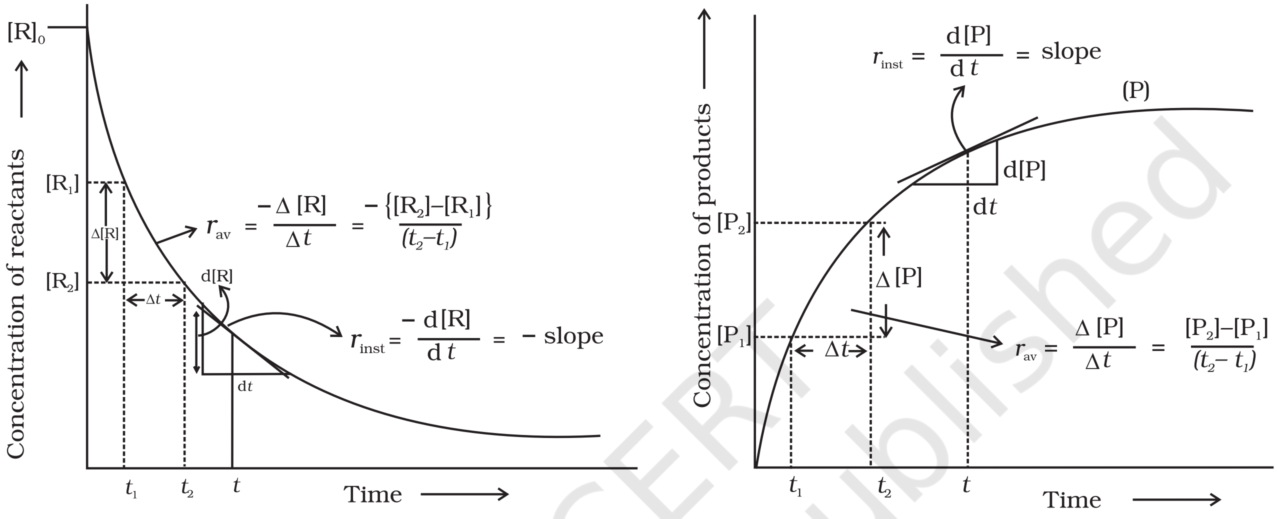
Rate of appearance of P

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = + \frac{\Delta[\text{P}]}{\Delta t} \qquad (3.2)$$

Since, $\Delta$[R] is a negative quantity (as concentration of reactants is decreasing), it is multiplied with –1 to make the rate of the reaction a positive quantity.

Equations (3.1) and (3.2) given above represent the **average rate of a reaction**, $r_{av}$.

Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur (Fig. 3.1).



(a) (b)

***Fig. 3.1:*** *Instantaneous and average rate of a reaction*

***Units of rate of a reaction***

From equations (3.1) and (3.2), it is clear that units of rate are concentration time$^{-1}$. For example, if concentration is in mol L$^{-1}$ and time is in seconds then the units will be mol L$^{-1}$s$^{-1}$. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be atm s$^{-1}$.

**Example 3.1**

From the concentrations of $C_4H_9Cl$ (butyl chloride) at different times given below, calculate the average rate of the reaction:

$$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$$

during different intervals of time.

| $t$/s | 0 | 50 | 100 | 150 | 200 | 300 | 400 | 700 | 800 |
|---|---|---|---|---|---|---|---|---|---|
| $[C_4H_9Cl]$/mol L$^{-1}$ | 0.100 | 0.0905 | 0.0820 | 0.0741 | 0.0671 | 0.0549 | 0.0439 | 0.0210 | 0.017 |

**Solution**

We can determine the difference in concentration over different intervals of time and thus determine the average rate by dividing $\Delta$[R] by $\Delta t$ (Table 3.1).

**Table 3.1: Average rates of hydrolysis of butyl chloride**

| $[C_4H_9Cl]_{t_1}$ / mol $L^{-1}$ | $[C_4H_9Cl]_{t_2}$ / mol $L^{-1}$ | $t_1$/s | $t_2$/s | $r_{av} \times 10^4$/mol $L^{-1}s^{-1}$ $= -\left\{[C_4H_9Cl]_{t_2} - [C_4H_9Cl]_{t_1} / (t_2 - t_1)\right\} \times 10^4$ |
|---|---|---|---|---|
| 0.100 | 0.0905 | 0 | 50 | 1.90 |
| 0.0905 | 0.0820 | 50 | 100 | 1.70 |
| 0.0820 | 0.0741 | 100 | 150 | 1.58 |
| 0.0741 | 0.0671 | 150 | 200 | 1.40 |
| 0.0671 | 0.0549 | 200 | 300 | 1.22 |
| 0.0549 | 0.0439 | 300 | 400 | 1.10 |
| 0.0439 | 0.0335 | 400 | 500 | 1.04 |
| 0.0210 | 0.017 | 700 | 800 | 0.4 |

It can be seen (Table 3.1) that the average rate falls from $1.90 \times 0^{-4}$ mol $L^{-1}s^{-1}$ to $0.4 \times 10^{-4}$ mol $L^{-1}s^{-1}$. However, average rate cannot be used to predict the rate of a reaction at a particular instant as it would be constant for the time interval for which it is calculated. So, to express the rate at a particular moment of time we determine the **instantaneous rate**. It is obtained when we consider the average rate at the smallest time interval say d$t$ ( i.e. when $\Delta t$ approaches zero). Hence, mathematically for an infinitesimally small d$t$ instantaneous rate is given by

$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \tag{3.3}$$

$$\text{As} \quad \Delta t \to 0 \qquad \text{or} \qquad r_{inst} = \frac{-d[R]}{dt} = \frac{d[P]}{dt}$$

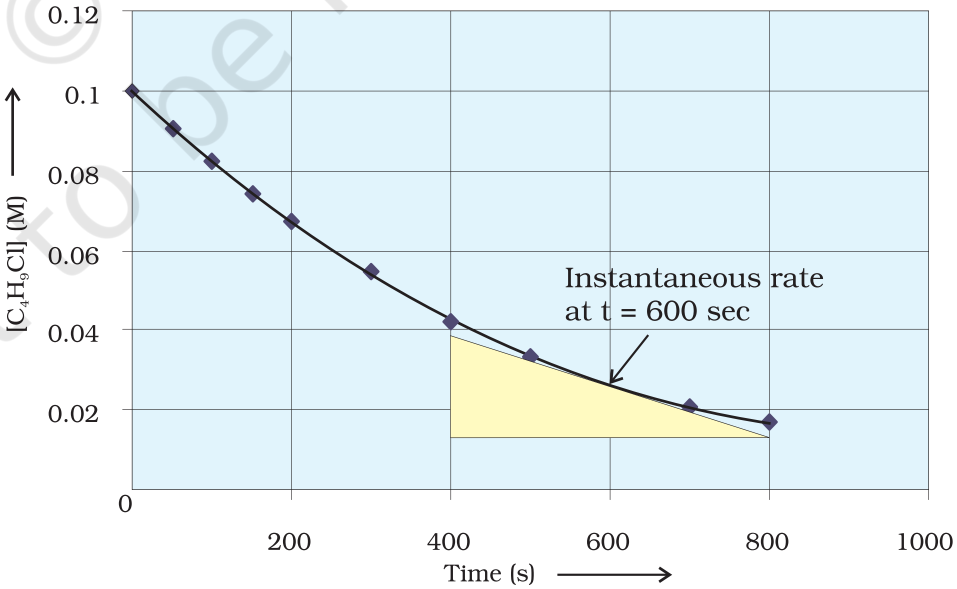


**Fig 3.2**
*Instantaneous rate of hydrolysis of butyl chloride($C_4H_9Cl$)*

It can be determined graphically by drawing a tangent at time t on either of the curves for concentration of R and P vs time t and calculating its slope (Fig. 3.1). So in problem 3.1, $r_{inst}$ at 600s for example, can be calculated by plotting concentration of butyl chloride as a function of time. A tangent is drawn that touches the curve at $t = 600$ s (Fig. 3.2).

The slope of this tangent gives the instantaneous rate.

$$\text{So, } r_{inst} \text{ at } 600 \text{ s} = -\left(\frac{0.0165-0.037}{(800-400)\text{s}}\right) \text{mol L}^{-1} = 5.12 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

At $t = 250$ s  $r_{inst} = 1.22 \times 10^{-4}$ mol $L^{-1}s^{-1}$

$t = 350$ s  $r_{inst} = 1.0 \times 10^{-4}$ mol $L^{-1}s^{-1}$

$t = 450$ s  $r_{inst} = 6.4 \times\times 10^{-5}$ mol $L^{-1}s^{-1}$

Now consider a reaction

$$Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$$

Where stoichiometric coefficients of the reactants and products are same, then rate of the reaction is given as

$$\text{Rate of reaction} = -\frac{\Delta[Hg]}{\Delta t} = -\frac{\Delta[Cl_2]}{\Delta t} = \frac{\Delta[HgCl_2]}{\Delta t}$$

i.e., rate of disappearance of any of the reactants is same as the rate of appearance of the products. But in the following reaction, two moles of HI decompose to produce one mole each of $H_2$ and $I_2$,

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

For expressing the rate of such a reaction where stoichiometric coefficients of reactants or products are not equal to one, rate of disappearance of any of the reactants or the rate of appearance of products is divided by their respective stoichiometric coefficients. Since rate of consumption of HI is twice the rate of formation of $H_2$ or $I_2$, to make them equal, the term Δ[HI] is divided by 2. The rate of this reaction is given by

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

Similarly, for the reaction

$$5\,Br^-(aq) + BrO_3^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(l)$$

$$\text{Rate} = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

For a gaseous reaction at constant temperature, concentration is directly proportional to the partial pressure of a species and hence, rate can also be expressed as rate of change in partial pressure of the reactant or the product.

**Example 3.2** The decomposition of $N_2O_5$ in $CCl_4$ at 318K has been studied by monitoring the concentration of $N_2O_5$ in the solution. Initially the concentration of $N_2O_5$ is 2.33 mol $L^{-1}$ and after 184 minutes, it is reduced to 2.08 mol $L^{-1}$. The reaction takes place according to the equation

$$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$$

Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of $NO_2$ during this period?

**Solution**

$$\text{Average Rate} = \frac{1}{2}\left\{-\frac{\Delta[N_2O_5]}{\Delta t}\right\} = -\frac{1}{2}\left[\frac{(2.08-2.33)\,\text{mol L}^{-1}}{184\ \text{min}}\right]$$

$= \quad 6.79 \times 10^{-4}$ mol $L^{-1}$/min = $(6.79 \times 10^{-4}$ mol $L^{-1}$ $min^{-1}) \times (60$ min/1h)

$= \quad 4.07 \times 10^{-2}$ mol $L^{-1}$/h

$= \quad 6.79 \times 10^{-4}$ mol $L^{-1} \times$ 1min/60s

$= \quad 1.13 \times 10^{-5}$ mol $L^{-1}s^{-1}$

It may be remembered that

$$\text{Rate} = \frac{1}{4}\left\{\frac{\Delta[NO_2]}{\Delta t}\right\}$$

$$\frac{\Delta[NO_2]}{\Delta t} = 6.79 \times 10^{-4} \times 4\ \text{mol L}^{-1}\text{min}^{-1} = 2.72 \times 10^{-3}\ \text{mol L}^{-1}\text{min}^{-1}$$

## Intext Questions

**3.1** For the reaction R → P, the concentration of a reactant changes from 0.03M to 0.02M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

**3.2** In a reaction, 2A → Products, the concentration of A decreases from 0.5 mol $L^{-1}$ to 0.4 mol $L^{-1}$ in 10 minutes. Calculate the rate during this interval?

## 3.2 Factors Influencing Rate of a Reaction

Rate of reaction depends upon the experimental conditions such as concentration of reactants (pressure in case of gases), temperature and catalyst.

### 3.2.1 Dependence of Rate on Concentration

The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products. The representation of rate of reaction in terms of concentration of the reactants is known as **rate law**. It is also called as rate equation or rate expression.

### 3.2.2 Rate Expression and Rate Constant

The results in Table 3.1 clearly show that rate of a reaction decreases with the passage of time as the concentration of reactants decrease. Conversely, rates generally increase when reactant concentrations increase. So, rate of a reaction depends upon the concentration of reactants.

Consider a general reaction

$$aA + bB \rightarrow cC + dD$$

where a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is

$$\text{Rate} \propto [A]^x \; [B]^y \qquad (3.4)$$

where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants. Above equation can also be written as

$$\text{Rate} = k\,[A]^x \; [B]^y \qquad (3.4a)$$

$$-\frac{d[R]}{dt} = k[A]^x [B]^y \qquad (3.4b)$$

This form of equation (3.4 b) is known as differential rate equation, where $k$ is a proportionality constant called **rate constant**. The equation like (3.4), which relates the rate of a reaction to concentration of reactants is called rate law or rate expression. Thus, **rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation**. For example:

$$2NO(g) + O_2(g) \rightarrow 2NO_2\ (g)$$

We can measure the rate of this reaction as a function of initial concentrations either by keeping the concentration of one of the reactants constant and changing the concentration of the other reactant or by changing the concentration of both the reactants. The following results are obtained (Table 3.2).

**Table 3.2: Initial rate of formation of $NO_2$**

| **Experiment** | **Initial [NO]/ mol $L^{-1}$** | **Initial [$O_2$]/ mol $L^{-1}$** | **Initial rate of formation of $NO_2$/ mol $L^{-1}s^{-1}$** |
|---|---|---|---|
| 1. | 0.30 | 0.30 | 0.096 |
| 2. | 0.60 | 0.30 | 0.384 |
| 3. | 0.30 | 0.60 | 0.192 |
| 4. | 0.60 | 0.60 | 0.768 |

It is obvious, after looking at the results, that when the concentration of NO is doubled and that of $O_2$ is kept constant then the initial rate increases by a factor of four from 0.096 to 0.384 mol $L^{-1}s^{-1}$. This indicates that the rate depends upon the square of the concentration of NO. When concentration of NO is kept constant and concentration of $O_2$ is doubled the rate also gets doubled indicating that rate depends on concentration of $O_2$ to the first power. Hence, the rate equation for this reaction will be

$$\text{Rate} = k\,[NO]^2[O_2]$$

The differential form of this rate expression is given as

$$-\frac{d[R]}{dt} = k[NO]^2[O_2]$$

Now, we observe that for this reaction in the rate equation derived from the experimental data, the exponents of the concentration terms are the same as their stoichiometric coefficients in the balanced chemical equation.

Some other examples are given below:

| Reaction | Experimental rate expression |
|---|---|
| 1. $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$ | Rate = $k\,[CHCl_3]\;[Cl_2]^{1/2}$ |
| 2. $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$ | Rate = $k\,[CH_3COOC_2H_5]^1\;[H_2O]^0$ |

In these reactions, the exponents of the concentration terms are not the same as their stoichiometric coefficients. Thus, we can say that:

*Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.*

### 3.2.3 Order of a Reaction

In the rate equation (3.4)

Rate = $k\,[A]^x\;[B]^y$

x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of these exponents, i.e., x + y in (3.4) gives the overall order of a reaction whereas x and y represent the order with respect to the reactants A and B respectively.

Hence, **the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction**.

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.

*Example 3.3* Calculate the overall order of a reaction which has the rate expression

(a) Rate = $k\,[A]^{1/2}\;[B]^{3/2}$

(b) Rate = $k\,[A]^{3/2}\;[B]^{-1}$

*Solution*

(a) Rate = $k\,[A]^x\;[B]^y$

order = x + y

So order = 1/2 + 3/2 = 2, i.e., second order

(b) order = 3/2 + (–1) = 1/2, i.e., half order.

A balanced chemical equation never gives us a true picture of how a reaction takes place since rarely a reaction gets completed in one step. The reactions taking place in one step are called **elementary reactions**. When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called **complex reactions**.

These may be consecutive reactions (e.g., oxidation of ethane to $CO_2$ and $H_2O$ passes through a series of intermediate steps in which alcohol, aldehyde and acid are formed), reverse reactions and side reactions (e.g., nitration of phenol yields *o*-nitrophenol and *p*-nitrophenol).

### *Units of rate constant*

For a general reaction

$$aA + bB \rightarrow cC + dD$$

$$\text{Rate} = k\,[A]^x\,[B]^y$$

Where x + y = n = order of the reaction

$$k = \frac{\text{Rate}}{[A]^x[B]^y}$$

$$= \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n} \qquad \text{(where [A]=[B])}$$

Taking SI units of concentration, mol $L^{-1}$ and time, s, the units of $k$ for different reaction order are listed in Table 3.3

**Table 3.3: Units of rate constant**

| Reaction | Order | Units of rate constant |
|---|---|---|
| Zero order reaction | 0 | $\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1}\text{s}^{-1}$ |
| First order reaction | 1 | $\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$ |
| Second order reaction | 2 | $\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1}\text{L s}^{-1}$ |

**Example 3.4**

Identify the reaction order from each of the following rate constants.

(i) $k = 2.3 \times 10^{-5}$ L $\text{mol}^{-1}$ $\text{s}^{-1}$

(ii) $k = 3 \times 10^{-4}$ $\text{s}^{-1}$

**Solution**

(i) The unit of second order rate constant is L $\text{mol}^{-1}$ $\text{s}^{-1}$, therefore $k = 2.3 \times 10^{-5}$ L $\text{mol}^{-1}$ $\text{s}^{-1}$ represents a second order reaction.

(ii) The unit of a first order rate constant is $\text{s}^{-1}$ therefore $k = 3 \times 10^{-4}$ $\text{s}^{-1}$ represents a first order reaction.

## 3.2.4 Molecularity of a Reaction

Another property of a reaction called molecularity helps in understanding its mechanism. **The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.** The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.

$$2HI \rightarrow H_2 + I_2$$

Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,

$$2NO + O_2 \rightarrow 2NO_2$$

The probability that more than three molecules can collide and react simultaneously is very small. Hence, reactions with the molecularity three are very rare and slow to proceed.

It is, therefore, evident that complex reactions involving more than three molecules in the stoichiometric equation must take place in more than one step.

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 \rightarrow KCl + 3Fe_2(SO_4)_3 + 3H_2O$$

This reaction which apparently seems to be of tenth order is actually a second order reaction. This shows that this reaction takes place in several steps. Which step controls the rate of the overall reaction? The question can be answered if we go through the mechanism of reaction, for example, chances to win the relay race competition by a team depend upon the slowest person in the team. Similarly, the overall rate of the reaction is controlled by the slowest step in a reaction called the **rate determining step**. Consider the decomposition of hydrogen peroxide which is catalysed by iodide ion in an alkaline medium.

$$2H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2H_2O + O_2$$

The rate equation for this reaction is found to be

$$\text{Rate} = \frac{-d[H_2O_2]}{dt} = k[H_2O_2][I^-]$$

This reaction is first order with respect to both $H_2O_2$ and $I^-$. Evidences suggest that this reaction takes place in two steps

(1) $H_2O_2 + I^- \rightarrow H_2O + IO^-$

(2) $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$

Both the steps are bimolecular elementary reactions. Species $IO^-$ is called as an intermediate since it is formed during the course of the reaction but not in the overall balanced equation. The first step, being slow, is the rate determining step. Thus, the rate of formation of intermediate will determine the rate of this reaction.

Thus, from the discussion, till now, we conclude the following:

(i) Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.

(ii) Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning.

(iii) For complex reaction, order is given by the slowest step and molecularity of the slowest step is same as the order of the overall reaction.

## Intext Questions

**3.3** For a reaction, A + B → Product; the rate law is given by, $r = k[A]^{1/2}[B]^2$. What is the order of the reaction?

**3.4** The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y ?

## 3.3 Integrated Rate Equations

We have already noted that the concentration dependence of rate is called differential rate equation. It is not always convenient to determine the instantaneous rate, as it is measured by determination of slope of the tangent at point '*t*' in concentration vs time plot (Fig. 3.1). This makes it difficult to determine the rate law and hence the order of the reaction. In order to avoid this difficulty, we can integrate the differential rate equation to give a relation between directly measured experimental data, i.e., concentrations at different times and rate constant.

The integrated rate equations are different for the reactions of different reaction orders. We shall determine these equations only for zero and first order chemical reactions.

### 3.3.1 Zero Order Reactions

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$$R \rightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0$$

As any quantity raised to power zero is unity

$$\text{Rate} = -\frac{d[R]}{dt} = k \times 1$$

$$d[R] = -k\,dt$$

Integrating both sides

$$[R] = -k\,t + I \qquad (3.5)$$

where, I is the constant of integration.

At $t = 0$, the concentration of the reactant R = $[R]_0$, where $[R]_0$ is initial concentration of the reactant.

Substituting in equation (3.5)

$$[R]_0 = -k \times 0 + I$$

$$[R]_0 = I$$

Substituting the value of I in the equation (3.5)

$$[R] = -kt + [R]_0 \qquad (3.6)$$

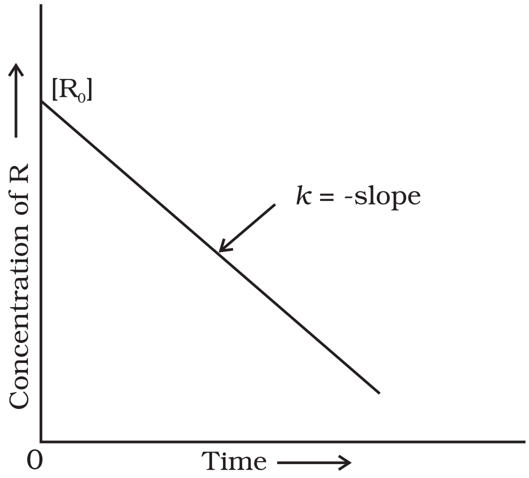


***Fig. 3.3:*** *Variation in the concentration vs time plot for a zero order reaction*

Comparing (3.6) with equation of a straight line, y = mx + c, if we plot [R] against t, we get a straight line (Fig. 3.3) with slope = $-k$ and intercept equal to $[R]_0$.

Further simplifying equation (3.6), we get the rate constant, $k$ as

$$k = \frac{[R]_0 - [R]}{t} \tag{3.7}$$

Zero order reactions are relatively uncommon but they occur under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions. The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.

$$2NH_3(g) \xrightarrow[\text{Pt catalyst}]{\text{1130K}} N_2(g) + 3H_2(g)$$

$$\text{Rate} = k\,[NH_3]^0 = k$$

In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration. The thermal decomposition of HI on gold surface is another example of zero order reaction.

### 3.3.2 First Order Reactions

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant R. For example,

$$R \rightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

$$\text{or} \quad \frac{d[R]}{[R]} = -k\,dt$$

Integrating this equation, we get

$$\ln [R] = -kt + I \tag{3.8}$$

Again, I is the constant of integration and its value can be determined easily.

When $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant.

Therefore, equation (3.8) can be written as

$$\ln [R]_0 = -k \times 0 + I$$

$$\ln [R]_0 = I$$

Substituting the value of I in equation (3.8)

$$\ln[R] = -kt + \ln[R]_0 \tag{3.9}$$

Rearranging this equation

$$\ln \frac{[R]}{[R]_0} = -kt$$

$$\text{or} \quad k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \qquad (3.10)$$

At time $t_1$ from equation (3.8)

$$^*\ln[R]_1 = -kt_1 + {}^*\ln[R]_0 \qquad (3.11)$$

At time $t_2$

$$\ln[R]_2 = -kt_2 + \ln[R]_0 \qquad (3.12)$$

where, $[R]_1$ and $[R]_2$ are the concentrations of the reactants at time $t_1$ and $t_2$ respectively.

Subtracting (3.12) from (3.11)

$$\ln[R]_1 - \ln[R]_2 = -kt_1 - (-kt_2)$$

$$\ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

$$k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2} \qquad (3.13)$$

Equation (3.9) can also be written as

$$\ln \frac{[R]}{[R]_0} = -kt$$

Taking antilog of both sides

$$[R] = [R]_0 \, e^{-kt} \qquad (3.14)$$

Comparing equation (3.9) with y = mx + c, if we plot ln [R] against $t$ (Fig. 3.4) we get a straight line with slope = $-k$ and intercept equal to ln $[R]_0$

The first order rate equation (3.10) can also be written in the form

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \qquad (3.15)$$

$$^*\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

If we plot a graph between log $[R]_0/[R]$ vs $t$, (Fig. 3.5), the slope = $k/2.303$

Hydrogenation of ethene is an example of first order reaction.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Rate = $k\,[C_2H_4]$

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

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* *Refer to Appendix-IV for ln and log (logarithms).*

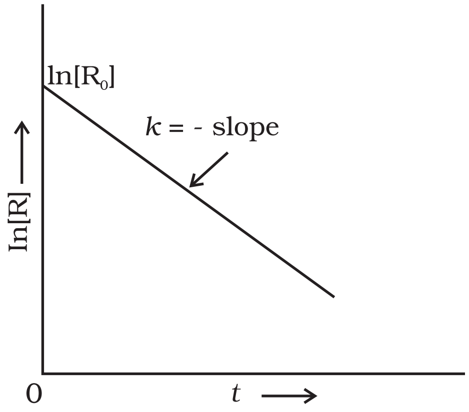

***Fig. 3.4:** A plot between ln[R] and t for a first order reaction*

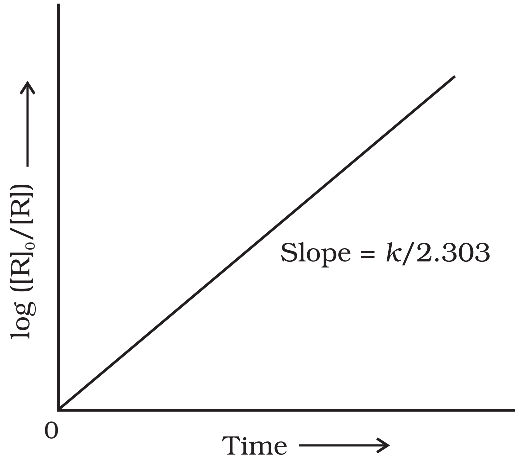

***Fig. 3.5**: Plot of log $[R]_0/[R]$ vs time for a first order reaction*

$$^{226}_{88}\text{Ra} \rightarrow {}^{4}_{2}\text{He} + {}^{222}_{86}\text{Rn}$$

Rate = $k$ [Ra]

Decomposition of $N_2O_5$ and $N_2O$ are some more examples of first order reactions.

**Example 3.5** The initial concentration of $N_2O_5$ in the following first order reaction $N_2O_5(g) \rightarrow 2\ NO_2(g) + 1/2O_2\ (g)$ was $1.24 \times 10^{-2}$ mol $L^{-1}$ at 318 K. The concentration of $N_2O_5$ after 60 minutes was $0.20 \times 10^{-2}$ mol $L^{-1}$. Calculate the rate constant of the reaction at 318 K.

**Solution** For a first order reaction

$$\log\frac{[R]_1}{[R]_2} = \frac{k(t_2 - t_1)}{2.303}$$

$$k = \frac{2.303}{(t_2 - t_1)}\log\frac{[R]_1}{[R]_2}$$

$$= \frac{2.303}{(60\,\text{min} - 0\,\text{min})}\log\frac{1.24\times10^{-2}\ \text{mol L}^{-1}}{0.20\times10^{-2}\ \text{mol L}^{-1}}$$

$$= \frac{2.303}{60}\log 6.2\,\text{min}^{-1}$$

$$k = 0.0304\ \text{min}^{-1}$$

Let us consider a typical first order gas phase reaction

$$A(g) \rightarrow B(g) + C(g)$$

Let $p_i$ be the initial pressure of A and $p_t$ the total pressure at time '$t$'. Integrated rate equation for such a reaction can be derived as

Total pressure $p_t = p_A + p_B + p_C$ (pressure units)

$p_A$, $p_B$ and $p_C$ are the partial pressures of A, B and C, respectively.

If x atm be the decrease in pressure of A at time *t* and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.

| | A(g) | → | B(g) | + | C(g) |
|---|---|---|---|---|---|
| At $t$ = 0 | $p_i$ atm | | 0 atm | | 0 atm |
| At time $t$ | $(p_i–x)$ atm | | x atm | | x atm |

where, $p_i$ is the initial pressure at time $t = 0$.

$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

where, $p_A = p_i - x = p_i - (p_t - p_i)$

$$= 2p_i - p_t$$

$$k = \left(\frac{2.303}{t}\right)\left(\log\frac{p_i}{p_A}\right) \qquad (3.16)$$

$$= \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)}$$

**Example 3.6**

The following data were obtained during the first order thermal decomposition of $N_2O_5$ (g) at constant volume:

$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

| S.No. | Time/s | Total Pressure/(atm) |
|---|---|---|
| 1. | 0 | 0.5 |
| 2. | 100 | 0.512 |

Calculate the rate constant.

**Solution**

Let the pressure of $N_2O_5$(g) decrease by 2x atm. As two moles of $N_2O_5$ decompose to give two moles of $N_2O_4$(g) and one mole of $O_2$ (g), the pressure of $N_2O_4$ (g) increases by 2x atm and that of $O_2$ (g) increases by x atm.

| | $2N_2O_5(g)$ | → | $2N_2O_4(g)$ | + | $O_2(g)$ |
|---|---|---|---|---|---|
| Start $t$ = 0 | 0.5 atm | | 0 atm | | 0 atm |
| At time $t$ | (0.5 – 2x) atm | | 2x atm | | x atm |

$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$

$$= (0.5 - 2x) + 2x + x = 0.5 + x$$

$$x = p_t - 0.5$$

$$p_{N_2O_5} = 0.5 - 2x$$

$$= 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$$

At $t$ = 100 s; $p_t$ = 0.512 atm

$$p_{N_2O_5} = 1.5 - 2 \times 0.512 = 0.476 \text{ atm}$$

Using equation (3.16)

$$k = \frac{2.303}{t}\log\frac{p_i}{p_A} = \frac{2.303}{100\,s}\log\frac{0.5\,atm}{0.476\,atm}$$

$$= \frac{2.303}{100\,s} \times 0.0216 = 4.98 \times 10^{-4}\,s^{-1}$$

### 3.3.3 Half-Life of a Reaction

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.

For a zero order reaction, rate constant is given by equation 3.7.

$$k = \frac{[R]_0 - [R]}{t}$$

$$\text{At } t = t_{1/2}, \quad [R] = \frac{1}{2}[R]_0$$

The rate constant at $t_{1/2}$ becomes

$$k = \frac{[R]_0 - 1/2[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

For the first order reaction,

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} \tag{3.15}$$

$$\text{at } t_{1/2} \quad [R] = \frac{[R]_0}{2} \tag{3.16}$$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]/2}$$

$$\text{or} \quad t_{1/2} = \frac{2.303}{k}\log 2$$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

$$t_{1/2} = \frac{0.693}{k} \tag{3.17}$$

It can be seen that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species. The half-life of a first order equation is readily calculated from the rate constant and vice versa.

**For zero order reaction $t_{1/2} \propto [R]_0$. For first order reaction $t_{1/2}$ is independent of $[R]_0$.**

**Example 3.7**

A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14}\ s^{-1}$. Find the half-life of the reaction.

**Solution**

Half-life for a first order reaction is

$$t_{1/2} = \frac{0.693}{k}$$

$$t_{1/2} = \frac{0.693}{5.5\times10^{-14}s^{-1}} = 1.26 \times 10^{13}s$$

**Example 3.8**

Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ($t_{1/2}$) of the reaction.

**Solution**

When reaction is completed 99.9%, $[R]_n = [R]_0 - 0.999[R]_0$

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

$$= \frac{2.303}{t}\log\frac{[R]_0}{[R]_0 - 0.999[R]_0} = \frac{2.303}{t}\log 10^3$$

$$t = 6.909/k$$

For half-life of the reaction

$$t_{1/2} = 0.693/k$$

$$\frac{t}{t_{1/2}} = \frac{6.909}{k} \times \frac{k}{0.693} = 10$$

Table 3.4 summarises the mathematical features of integrated laws of zero and first order reactions.

**Table 3.4: Integrated Rate Laws for the Reactions of Zero and First Order**

| Order | Reaction type | Differential rate law | Integrated rate law | Straight line plot | Half-life | Units of $k$ |
|---|---|---|---|---|---|---|
| 0 | R→P | $d[R]/dt = -k$ | $kt = [R]_0-[R]$ | [R] vs $t$ | $[R]_0/2k$ | conc time$^{-1}$ or mol $L^{-1}s^{-1}$ |
| 1 | R→P | $d[R]/dt = -k[R]$ | $[R] = [R]_0e^{-kt}$ or $kt = \ln\{[R]_0/[R]\}$ | ln[R] vs $t$ | ln 2/$k$ | time$^{-1}$ or $s^{-1}$ |

The order of a reaction is sometimes altered by conditions. There are many reactions which obey first order rate law although they are higher order reactions. Consider the hydrolysis of ethyl acetate which is a chemical reaction between ethyl acetate and water. In reality, it is a second order reaction and concentration of both ethyl acetate and water affect the rate of the reaction. But water is taken in large excess for hydrolysis, therefore, concentration of water is not altered much during the reaction. Thus, the rate of reaction is affected by concentration of ethyl acetate only. For example, during the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the reactants and products at the beginning (*t* = 0) and completion (*t*) of the reaction are given as under.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

|  | $CH_3COOC_2H_5$ | $H_2O$ | $CH_3COOH$ | $C_2H_5OH$ |
|---|---|---|---|---|
| $t = 0$ | 0.01 mol | 10 mol | 0 mol | 0 mol |
| $t$ | 0 mol | 9.99 mol | 0.01 mol | 0.01 mol |

The concentration of water does not get altered much during the course of the reaction. So, the reaction behaves as first order reaction. Such reactions are called **pseudo first order reactions**.

Inversion of cane sugar is another pseudo first order reaction.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\text{Rate} = k\ [C_{12}H_{22}O_{11}]$$

### Intext Questions

**3.5** A first order reaction has a rate constant $1.15 \times 10^{-3}\ s^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?

**3.6** Time required to decompose $SO_2Cl_2$ to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

## 3.4 Temperature Dependence of the Rate of a Reaction

Most of the chemical reactions are accelerated by increase in temperature. For example, in decomposition of $N_2O_5$, the time taken for half of the original amount of material to decompose is 12 min at 50°C, 5 h at 25°C and 10 days at 0°C. You also know that in a mixture of potassium permanganate ($KMnO_4$) and oxalic acid ($H_2C_2O_4$), potassium permanganate gets decolourised faster at a higher temperature than that at a lower temperature.

It has been found that **for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.**

The temperature dependence of the rate of a chemical reaction can be accurately explained by **Arrhenius equation** (3.18). It was first proposed by Dutch chemist, J.H. van't Hoff but Swedish chemist, Arrhenius provided its physical justification and interpretation.

$$k = A\ e^{-Ea/RT} \tag{3.18}$$

where $A$ is the Arrhenius factor or the **frequency factor**. It is also called pre-exponential factor. It is a constant specific to a particular reaction. $R$ is gas constant and $E_a$ is activation energy measured in joules/mole (J mol $^{-1}$).

It can be understood clearly using the following simple reaction

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate (Fig. 3.6). It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

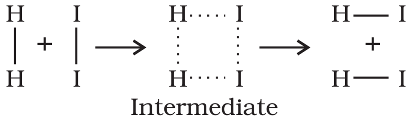

***Fig. 3.6:*** *Formation of HI through the intermediate*

The energy required to form this intermediate, called **activated complex** (C), is known as **activation energy ($E_a$)**. Fig. 3.7 is obtained by plotting potential energy vs reaction coordinate. Reaction coordinate represents the profile of energy change when reactants change into products.

Some energy is released when the complex decomposes to form products. So, the final enthalpy of the reaction depends upon the nature of reactants and products.

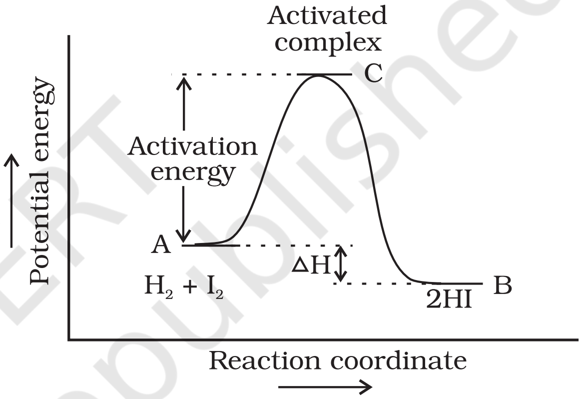

***Fig. 3.7:*** *Diagram showing plot of potential energy vs reaction coordinate*

All the molecules in the reacting species do not have the same kinetic energy. Since it is difficult to predict the behaviour of any one molecule with precision, Ludwig Boltzmann and James Clark Maxwell used statistics to predict the behaviour of large number of molecules. According to them, the distribution of kinetic energy may be described by plotting the fraction of molecules ($N_E/N_T$) with a given kinetic energy (E) vs kinetic energy (Fig. 3.8). Here, $N_E$ is the number of molecules with energy $E$ and $N_T$ is total number of molecules.

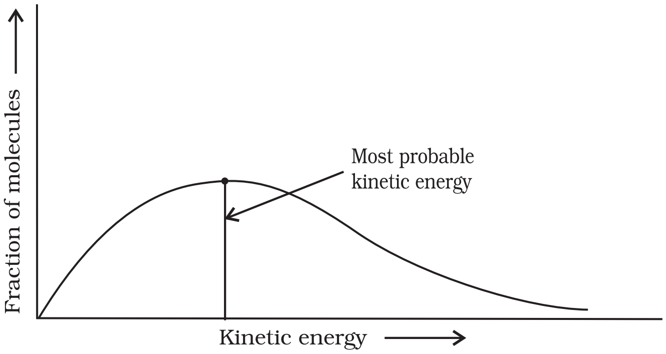

***Fig. 3.8:*** *Distribution curve showing energies among gaseous molecules*

The peak of the curve corresponds to the **most probable kinetic energy,** i.e., kinetic energy of maximum fraction of molecules. There are decreasing number of molecules with energies higher or lower than this value. When the temperature is raised, the maximum of the curve moves to the higher energy value (Fig. 3.9) and the curve broadens out, i.e., spreads to the right such that there is a greater proportion of molecules with much higher energies. The area under the curve must be constant since total probability must be one at all times. We can mark the position of $E_a$ on Maxwell Boltzmann distribution curve (Fig. 3.9).

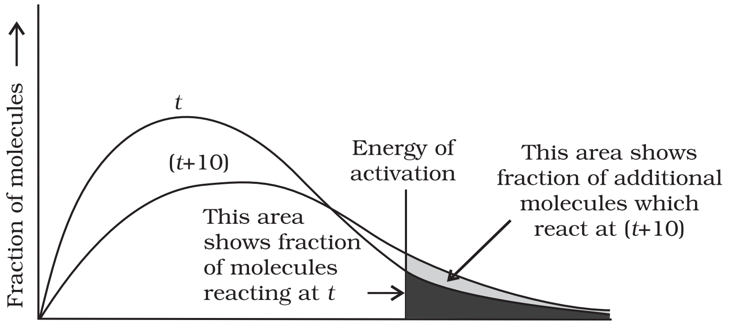

***Fig. 3.9:*** *Distribution curve showing temperature dependence of rate of a reaction*

Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than $E_a$. It is clear from the diagram that in the curve at ($t$ + 10), the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

In the Arrhenius equation (3.18) the factor $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than $E_a$. Taking natural logarithm of both sides of equation (3.18)

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{3.19}$$

The plot of ln $k$ vs 1/T gives a straight line according to the equation (3.19) as shown in Fig. 3.10.

Thus, it has been found from Arrhenius equation (3.18) that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

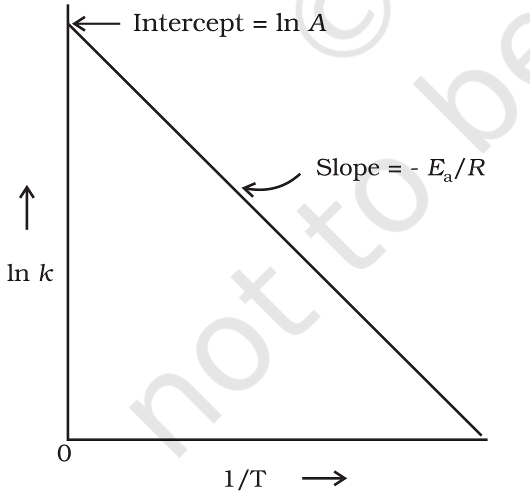

***Fig. 3.10:*** *A plot between ln k and 1/T*

In Fig. 3.10, slope = $-\frac{E_a}{R}$ and intercept = ln $A$. So we can calculate $E_a$ and $A$ using these values.

At temperature $T_1$, equation (3.19) is

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \tag{3.20}$$

At temperature $T_2$, equation (3.19) is

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \tag{3.21}$$

(since $A$ is constant for a given reaction)

$k_1$ and $k_2$ are the values of rate constants at temperatures $T_1$ and $T_2$ respectively.

Subtracting equation (3.20) from (3.21), we obtain

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{3.22}$$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\text{R}}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

**Example 3.9** The rate constants of a reaction at 500K and 700K are $0.02\text{s}^{-1}$ and $0.07\text{s}^{-1}$ respectively. Calculate the values of $E_a$ and $A$.

**Solution**

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log\frac{0.07}{0.02} = \left(\frac{E_a}{2.303 \times 8.314\,\text{J}K^{-1}\text{mol}^{-1}}\right)\left[\frac{700-500}{700 \times 500}\right]$$

$$0.544 = E_a \times 5.714 \times 10^{-4}/19.15$$

$$E_a = 0.544 \times 19.15/5.714 \times 10^{-4} = 18230.8 \text{ J}$$

Since $k = A\text{e}^{-Ea/RT}$

$$0.02 = A\text{e}^{-18230.8/8.314 \times 500}$$

$$A = 0.02/0.012 = 1.61$$

**Example 3.10** The first order rate constant for the decomposition of ethyl iodide by the reaction

$$C_2H_5I(g) \rightarrow C_2H_4\ (g) + HI(g)$$

at 600K is $1.60 \times 10^{-5}\ \text{s}^{-1}$. Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700K.

**Solution** We know that

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log k_2 = \log k_1 + \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \log\left(1.60 \times 10^{-5}\right) + \frac{209000\ \mathrm{J\,mol\,L^{-1}}}{2.303 \times 8.314\ \mathrm{J\,mol\,L^{-1}K^{-1}}}\left[\frac{1}{600\ \mathrm{K}} - \frac{1}{700\ \mathrm{K}}\right]$$

$$\log k_2 = -\ 4.796 + 2.599 = -\ 2.197$$

$$k_2 = 6.36 \times 10^{-3}\ \mathrm{s^{-1}}$$

### 3.4.1 Effect of Catalyst

A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change. For example, $MnO_2$ catalyses the following reaction so as to increase its rate considerably.

$$2KClO_3 \xrightarrow{MnO_2} 2\ KCl + 3O_2$$

The word catalyst should not be used when the added substance reduces the rate of raction. The substance is then called inhibitor. The action of the catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

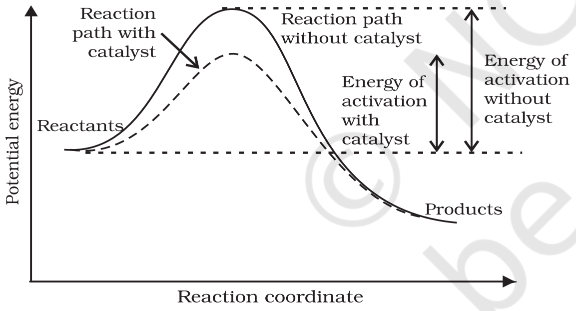

***Fig. 3.11:*** *Effect of catalyst on activation energy*

It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier as shown in Fig. 3.11.

It is clear from Arrhenius equation (3.18) that lower the value of activation energy faster will be the rate of a reaction.

A small amount of the catalyst can catalyse a large amount of reactants. A catalyst does not alter **Gibbs energy**, ΔG of a reaction. It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions. It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

## 3.5 Collision Theory of Chemical Reactions

Though Arrhenius equation is applicable under a wide range of circumstances, collision theory, which was developed by Max Trautz and William Lewis in 1916 -18, provides a greater insight into the energetic and mechanistic aspects of reactions. It is based on kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. **The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z)**. Another factor which affects the rate of chemical reactions is activation energy (as we have already studied). For a bimolecular elementary reaction

$$A + B \rightarrow \text{Products}$$

rate of reaction can be expressed as

$$\text{Rate} = Z_{AB}e^{-E_a/RT} \tag{3.23}$$

where $Z_{AB}$ represents the collision frequency of reactants, A and B and $e^{-Ea/RT}$ represents the fraction of molecules with energies equal to or greater than $E_a$. Comparing (3.23) with Arrhenius equation, we can say that $A$ is related to collision frequency.

Equation (3.23) predicts the value of rate constants fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed. The reason could be that all collisions do not lead to the formation of products. The collisions in which molecules collide with sufficient kinetic energy (called threshold energy*) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as **effective collisions.**

For example, formation of methanol from bromoethane depends upon the orientation of reactant molecules as shown in Fig. 3.12. *The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.*

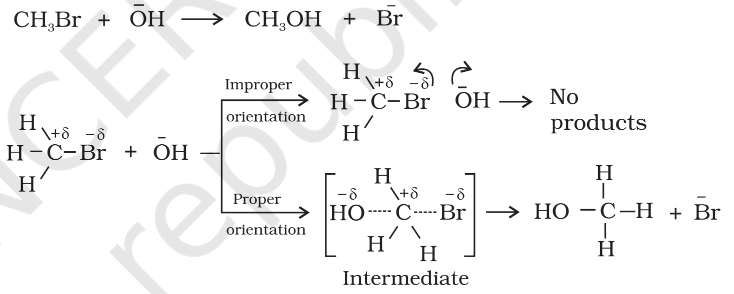

***Fig. 3.12:*** *Diagram showing molecules having proper and improper orientation*

To account for effective collisions, another factor $P$, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

$$\text{Rate} = PZ_{AB}e^{-E_a/RT}$$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

Collision theory also has certain drawbacks as it considers atoms/molecules to be hard spheres and ignores their structural aspect. You will study details about this theory and more on other theories in your higher classes.

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* *Threshold energy = Activation Energy + energy possessed by reacting species.*

## Intext Questions

**3.7** What will be the effect of temperature on rate constant ?

**3.8** The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate $E_a$.

**3.9** The activation energy for the reaction

$$2\,HI(g) \rightarrow H_2 + I_2\,(g)$$

is 209.5 kJ $mol^{-1}$ at 581K.Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

## Summary

**Chemical kinetics** is the study of chemical reactions with respect to reaction rates, effect of various variables, rearrangement of atoms and formation of intermediates. The rate of a reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. A number of factors such as temperature, concentration of reactants, catalyst, affect the rate of a reaction. Mathematical representation of rate of a reaction is given by **rate law**. It has to be determined experimentally and cannot be predicted. **Order of a reaction** with respect to a reactant is the power of its concentration which appears in the rate law equation. The order of a reaction is the sum of all such powers of concentration of terms for different reactants. **Rate constant** is the proportionality factor in the rate law. Rate constant and order of a reaction can be determined from rate law or its integrated rate equation. **Molecularity** is defined only for an elementary reaction. Its values are limited from 1 to 3 whereas order can be 0, 1, 2, 3 or even a fraction. Molecularity and order of an elementary reaction are same.

Temperature dependence of rate constants is described by Arrhenius equation ($k = Ae^{-Ea/RT}$). $E_a$ corresponds to the **activation energy** and is given by the energy difference between activated complex and the reactant molecules, and $A$ (Arrhenius factor or pre-exponential factor) corresponds to the collision frequency. The equation clearly shows that increase of temperature or lowering of $E_a$ will lead to an increase in the rate of reaction and presence of a catalyst lowers the activation energy by providing an alternate path for the reaction. According to collision theory, another factor $P$ called steric factor which refers to the orientation of molecules which collide, is important and contributes to effective collisions, thus, modifying the Arrhenius equation to $k = PZ_{AB}e^{-E_a/RT}$.

# Exercises

**3.1** From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

(i) $3NO(g) \rightarrow N_2O\ (g)$ Rate = $k[NO]^2$

(ii) $H_2O_2\ (aq) + 3I^-\ (aq) + 2H^+ \rightarrow 2H_2O\ (l) + I_3^-$ Rate = $k[H_2O_2][I^-]$

(iii) $CH_3CHO\ (g) \rightarrow CH_4\ (g) + CO(g)$ Rate = $k\,[CH_3CHO]^{3/2}$

(iv) $C_2H_5Cl\ (g) \rightarrow C_2H_4\ (g) + HCl\ (g)$ Rate = $k\,[C_2H_5Cl]$

**3.2** For the reaction:

$$2A + B \rightarrow A_2B$$

the rate = $k[A][B]^2$ with k = $2.0 \times 10^{-6}$ mol$^{-2}$ L$^2$ s$^{-1}$. Calculate the initial rate of the reaction when [A] = 0.1 mol L$^{-1}$, [B] = 0.2 mol L$^{-1}$. Calculate the rate of reaction after [A] is reduced to 0.06 mol L$^{-1}$.

**3.3** The decomposition of $NH_3$ on platinum surface is zero order reaction. What are the rates of production of $N_2$ and $H_2$ if $k = 2.5 \times 10^{-4}$ mol$^{-1}$ L s$^{-1}$?

**3.4** The decomposition of dimethyl ether leads to the formation of $CH_4$, $H_2$ and CO and the reaction rate is given by

$$\text{Rate} = k\ [CH_3OCH_3]^{3/2}$$

The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,

$$\text{Rate} = k\left(p_{CH_3OCH_3}\right)^{3/2}$$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

**3.5** Mention the factors that affect the rate of a chemical reaction.

**3.6** A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is

(i) doubled (ii) reduced to half ?

**3.7** What is the effect of temperature on the rate constant of a reaction? How can this effect of temperature on rate constant be represented quantitatively?

**3.8** In a pseudo first order reaction in water, the following results were obtained:

| t/s | 0 | 30 | 60 | 90 |
|---|---|---|---|---|
| [A]/ mol L$^{-1}$ | 0.55 | 0.31 | 0.17 | 0.085 |

Calculate the average rate of reaction between the time interval 30 to 60 seconds.

**3.9** A reaction is first order in A and second order in B.

(i) Write the differential rate equation.

(ii) How is the rate affected on increasing the concentration of B three times?

(iii) How is the rate affected when the concentrations of both A and B are doubled?

**3.10** In a reaction between A and B, the initial rate of reaction ($r_0$) was measured for different initial concentrations of A and B as given below:

| A/ mol $L^{-1}$ | 0.20 | 0.20 | 0.40 |
|---|---|---|---|
| B/ mol $L^{-1}$ | 0.30 | 0.10 | 0.05 |
| $r_0$/mol $L^{-1}s^{-1}$ | $5.07 \times 10^{-5}$ | $5.07 \times 10^{-5}$ | $1.43 \times 10^{-4}$ |

What is the order of the reaction with respect to A and B?

**3.11** The following results have been obtained during the kinetic studies of the reaction:

$$2A + B \rightarrow C + D$$

| Experiment | [A]/mol $L^{-1}$ | [B]/mol $L^{-1}$ | Initial rate of formation of D/mol $L^{-1}$ $min^{-1}$ |
|---|---|---|---|
| I | 0.1 | 0.1 | $6.0 \times 10^{-3}$ |
| II | 0.3 | 0.2 | $7.2 \times 10^{-2}$ |
| III | 0.3 | 0.4 | $2.88 \times 10^{-1}$ |
| IV | 0.4 | 0.1 | $2.40 \times 10^{-2}$ |

Determine the rate law and the rate constant for the reaction.

**3.12** The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

| Experiment | [A]/ mol $L^{-1}$ | [B]/ mol $L^{-1}$ | Initial rate/ mol $L^{-1}$ $min^{-1}$ |
|---|---|---|---|
| I | 0.1 | 0.1 | $2.0 \times 10^{-2}$ |
| II | – | 0.2 | $4.0 \times 10^{-2}$ |
| III | 0.4 | 0.4 | – |
| IV | – | 0.2 | $2.0 \times 10^{-2}$ |

**3.13** Calculate the half-life of a first order reaction from their rate constants given below:

(i) 200 $s^{-1}$ (ii) 2 $min^{-1}$ (iii) 4 $years^{-1}$

**3.14** The half-life for radioactive decay of $^{14}C$ is 5730 years. An archaeological artifact containing wood had only 80% of the $^{14}C$ found in a living tree. Estimate the age of the sample.

**3.15** The experimental data for decomposition of $N_2O_5$

$$[2N_2O_5 \rightarrow 4NO_2 + O_2]$$

in gas phase at 318K are given below:

| *t*/s | 0 | 400 | 800 | 1200 | 1600 | 2000 | 2400 | 2800 | 3200 |
|---|---|---|---|---|---|---|---|---|---|
| $10^2 \times [N_2O_5]$/ mol $L^{-1}$ | 1.63 | 1.36 | 1.14 | 0.93 | 0.78 | 0.64 | 0.53 | 0.43 | 0.35 |

(i) Plot $[N_2O_5]$ against *t*.
(ii) Find the half-life period for the reaction.
(iii) Draw a graph between $\log[N_2O_5]$ and *t*.
(iv) What is the rate law ?

(v) Calculate the rate constant.

(vi) Calculate the half-life period from $k$ and compare it with (ii).

**3.16** The rate constant for a first order reaction is 60 $s^{-1}$. How much time will it take to reduce the initial concentration of the reactant to its 1/16$^{th}$ value?

**3.17** During nuclear explosion, one of the products is $^{90}Sr$ with half-life of 28.1 years. If 1μg of $^{90}Sr$ was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

**3.18** For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

**3.19** A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

**3.20** For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

| *t* (sec) | P(mm of Hg) |
|---|---|
| 0 | 35.0 |
| 360 | 54.0 |
| 720 | 63.0 |

Calculate the rate constant.

**3.21** The following data were obtained during the first order thermal decomposition of $SO_2Cl_2$ at a constant volume.

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

| Experiment | Time/$s^{-1}$ | Total pressure/atm |
|---|---|---|
| 1 | 0 | 0.5 |
| 2 | 100 | 0.6 |

Calculate the rate of the reaction when total pressure is 0.65 atm.

**3.22** The rate constant for the decomposition of $N_2O_5$ at various temperatures is given below:

| $T$/°C | 0 | 20 | 40 | 60 | 80 |
|---|---|---|---|---|---|
| $10^5 \times k/s^{-1}$ | 0.0787 | 1.70 | 25.7 | 178 | 2140 |

Draw a graph between ln $k$ and $1/T$ and calculate the values of $A$ and $E_a$. Predict the rate constant at 30° and 50°C.

**3.23** The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5} s^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.

**3.24** Consider a certain reaction A → Products with $k = 2.0 \times 10^{-2} s^{-1}$. Calculate the concentration of $A$ remaining after 100 s if the initial concentration of $A$ is 1.0 mol $L^{-1}$.

**3.25** Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2}$ = 3.00 hours. What fraction of sample of sucrose remains after 8 hours ?

**3.26** The decomposition of hydrocarbon follows the equation

$$k = (4.5 \times 10^{11} s^{-1})\ e^{-28000K/T}$$

Calculate $E_a$.

**3.27** The rate constant for the first order decomposition of $H_2O_2$ is given by the following equation:

$$\log k = 14.34 - 1.25 \times 10^4 K/T$$

Calculate $E_a$ for this reaction and at what temperature will its half-period be 256 minutes?

**3.28** The decomposition of A into product has value of $k$ as $4.5 \times 10^3\ s^{-1}$ at 10°C and energy of activation 60 kJ $mol^{-1}$. At what temperature would $k$ be $1.5 \times 10^4 s^{-1}$?

**3.29** The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. If the value of $A$ is $4 \times 10^{10} s^{-1}$. Calculate $k$ at 318K and $E_a$.

**3.30** The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

## Answers to Some Intext Questions

**3.1** $r_{av} = 6.66 \times 10^{-6}\ Ms^{-1}$

**3.2** Rate of reaction = rate of diappearance of A
= 0.005 mol $litre^{-1}min^{-1}$

**3.3** Order of the reaction is 2.5

**3.4** X → Y
Rate = $k[X]^2$
The rate will increase 9 times

**3.5** t = 444 s

**3.6** $1.925 \times 10^{-4}\ s^{-1}$

**3.8** Ea = 52.897 kJ $mol^{-1}$

**3.9** $1.471 \times 10^{-19}$

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# Unit 4

# The *d*- and *f*- Block Elements

## Objectives

After studying this Unit, you will be able to

- learn the positions of the *d*– and *f*-block elements in the periodic table;
- know the electronic configurations of the transition (*d*-block) and the inner transition (*f*-block) elements;
- appreciate the relative stability of various oxidation states in terms of electrode potential values;
- describe the preparation, properties, structures and uses of some important compounds such as $K_2Cr_2O_7$ and $KMnO_4$;
- understand the general characteristics of the *d*– and *f*–block elements and the general horizontal and group trends in them;
- describe the properties of the *f*-block elements and give a comparative account of the lanthanoids and actinoids with respect to their electronic configurations, oxidation states and chemical behaviour.

*Iron, copper, silver and gold are among the transition elements that have played important roles in the development of human civilisation. The inner transition elements such as Th, Pa and U are proving excellent sources of nuclear energy in modern times.*

The *d*-block of the periodic table contains the elements of the groups 3-12 in which the *d* orbitals are progressively filled in each of the four long periods. The *f*-block consists of elements in which 4 *f* and 5 *f* orbitals are progressively filled. They are placed in a separate panel at the bottom of the periodic table. The names *transition metals* and *inner transition* metals are often used to refer to the elements of *d*-and *f*-blocks respectively.

There are mainly four series of the transition metals, 3*d* series (Sc to Zn), 4*d* series (Y to Cd), 5*d* series (La and Hf to Hg) and 6*d* series which has Ac and elements from Rf to Cn. The two series of the inner transition metals; 4*f* (Ce to Lu) and 5*f* (Th to Lr) are known as *lanthanoids* and *actinoids* respectively.

Originally the name transition metals was derived from the fact that their chemical properties were transitional between those of *s* and *p*-block elements. Now according to IUPAC, transition metals are defined as metals which have incomplete *d* subshell either in neutral atom or in their ions. Zinc, cadmium and mercury of group 12 have full $d^{10}$ configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals. However, being the end members of the 3*d*, 4*d* and 5*d* transition series, respectively, their chemistry is studied along with the chemistry of the transition metals.

The presence of partly filled *d* or *f* orbitals in their atoms makes transition elements different from that of the non-transition elements. Hence, transition elements and their compounds are studied separately. However, the usual theory of valence as applicable to the non-transition elements can be applied successfully to the transition elements also.

Various precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium belong to the transition metals series.

In this Unit, we shall first deal with the electronic configuration, occurrence and general characteristics of transition elements with special emphasis on the trends in the properties of the first row (3*d*) transition metals along with the preparation and properties of some important compounds. This will be followed by consideration of certain general aspects such as electronic configurations, oxidation states and chemical reactivity of the inner transition metals.

## THE TRANSITION ELEMENTS (*d*-BLOCK)

### 4.1 Position in the Periodic Table

The *d*–block occupies the large middle section of the periodic table flanked between *s*– and *p*– blocks in the periodic table. The *d*–orbitals of the penultimate energy level of atoms receive electrons giving rise to four rows of the transition metals, i.e., 3*d*, 4*d*, 5*d* and 6*d*. All these series of transition elements are shown in Table 4.1.

### 4.2 Electronic Configurations of the d-Block Elements

In general the electronic configuration of outer orbitals of these elements is $(n\text{-}1)d^{1-10}ns^{1-2}$except for Pd where its electronic configuration is $4d^{10}5s^{0}$. The (n–1) stands for the inner *d* orbitals which may have one to ten electrons and the outermost n*s* orbital may have one or two electrons. However, this generalisation has several exceptions because of very little energy difference between (n-1)*d* and n*s* orbitals. Furthermore, half and completely filled sets of orbitals are relatively more stable. A consequence of this factor is reflected in the electronic configurations of Cr and Cu in the 3*d* series. For example, consider the case of Cr, which has $3d^5\,4s^1$ configuration instead of $3d^44s^2$; the energy gap between the two sets (3*d* and 4*s*) of orbitals is small enough to prevent electron entering the 3*d* orbitals. Similarly in case of Cu, the configuration is $3d^{10}4s^1$ and not $3d^94s^2$. The ground state electronic configurations of the outer orbitals of transition elements are given in Table 4.1.

**Table 4.1: Electronic Configurations of outer orbitals of the Transition Elements (ground state)**

| 1st Series | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| *Z* | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| 4*s* | 2 | 2 | 2 | 1 | 2 | 2 | 2 | 2 | 1 | 2 |
| 3*d* | 1 | 2 | 3 | 5 | 5 | 6 | 7 | 8 | 10 | 10 |

**2nd Series**

| | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
|---|---|---|---|---|---|---|---|---|---|---|
| *Z* | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 |
| 5*s* | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 2 |
| 4*d* | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 10 | 10 |

**3rd Series**

| | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg |
|---|---|---|---|---|---|---|---|---|---|---|
| *Z* | 57 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 |
| 6*s* | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 1 | 1 | 2 |
| 5*d* | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 9 | 10 | 10 |

**4th Series**

| | Ac | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | Cn |
|---|---|---|---|---|---|---|---|---|---|---|
| *Z* | 89 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 |
| 7*s* | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 1 | 2 |
| 6*d* | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 10 |

The electronic configurations of outer orbitals of Zn, Cd, Hg and Cn are represented by the general formula $(n\text{-}1)d^{10}ns^2$. The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements.

The *d* orbitals of the transition elements protrude to the periphery of an atom more than the other orbitals (i.e., *s* and *p*), hence, they are more influenced by the surroundings as well as affect the atoms or molecules surrounding them. In some respects, ions of a given $d^n$ configuration (n = 1 – 9) have similar magnetic and electronic properties. With partly filled *d* orbitals these elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands.

The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour. All these characteristics have been discussed in detail later in this Unit.

There are greater similarities in the properties of the transition elements of a horizontal row in contrast to the non-transition elements. However, some group similarities also exist. We shall first study the general characteristics and their trends in the horizontal rows (particularly 3*d* row) and then consider some group similarities.

**Example 4.1**

On what ground can you say that scandium (*Z* = 21) is a transition element but zinc (*Z* = 30) is not?

**Solution**

On the basis of incompletely filled 3*d* orbitals in case of scandium atom in its ground state ($3d^1$), it is regarded as a transition element. On the other hand, zinc atom has completely filled *d* orbitals ($3d^{10}$) in its ground state as well as in its oxidised state, hence it is not regarded as a transition element.

### Intext Question

**4.1** Silver atom has completely filled $d$ orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?

We will discuss the properties of elements of first transition series only in the following sections.

## 4.3 General Properties of the Transition Elements (d-Block)

### 4.3.1 Physical Properties

Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre. With the exceptions of Zn, Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.

**Lattice Structures of Transition Metals**

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| hcp<br>(bcc) | hcp<br>(bcc) | bcc | bcc | X<br>(bcc, ccp) | bcc<br>(hcp) | ccp<br>(hcp) | ccp | ccp | X<br>(hcp) |
| **Y** | **Zr** | **Nb** | **Mo** | **Tc** | **Ru** | **Rh** | **Pd** | **Ag** | **Cd** |
| hcp<br>(bcc) | hcp<br>(bcc) | bcc | bcc | hcp | hcp | ccp | ccp | ccp | X<br>(hcp) |
| **La** | **Hf** | **Ta** | **W** | **Re** | **Os** | **Ir** | **Pt** | **Au** | **Hg** |
| hcp<br>(ccp,bcc) | hcp<br>(bcc) | bcc | bcc | hcp | hcp | ccp | ccp | ccp | X |

*(bcc = body centred cubic; hcp = hexagonal close packed; ccp = cubic close packed; X = a typical metal structure).*

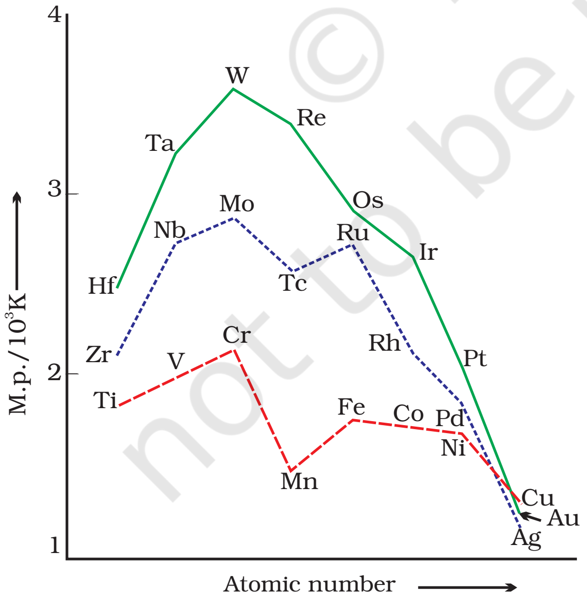


*Fig. 4.1: Trends in melting points of transition elements*

The transition metals (with the exception of Zn, Cd and Hg) are very hard and have low volatility. Their melting and boiling points are high. Fig. 4.1 depicts the melting points of transition metals belonging to 3$d$, 4$d$ and 5$d$ series. The high melting points of these metals are attributed to the involvement of greater number of electrons from (n-1)$d$ in addition to the ns electrons in the interatomic metallic bonding. In any row the melting points of these metals rise to a maximum at $d^5$ except for anomalous values of Mn and Tc and fall regularly as the atomic number increases. They have high enthalpies of atomisation which are shown in Fig. 4.2. The maxima at about the middle of each series indicate that one unpaired electron per $d$ orbital is particularly favourable for strong interatomic interaction. In general, greater the number of valence electrons, stronger is the resultant bonding. Since the enthalpy of atomisation is an important factor in determining the standard electrode potential of a metal, metals with very high enthalpy of atomisation (i.e., very high boiling point) tend to be noble in their reactions (see later for electrode potentials).

Another generalisation that may be drawn from Fig. 4.2 is that the metals of the second and third series have greater enthalpies of atomisation than the corresponding elements of the first series; this is an important factor in accounting for the occurrence of much more frequent metal – metal bonding in compounds of the heavy transition metals.

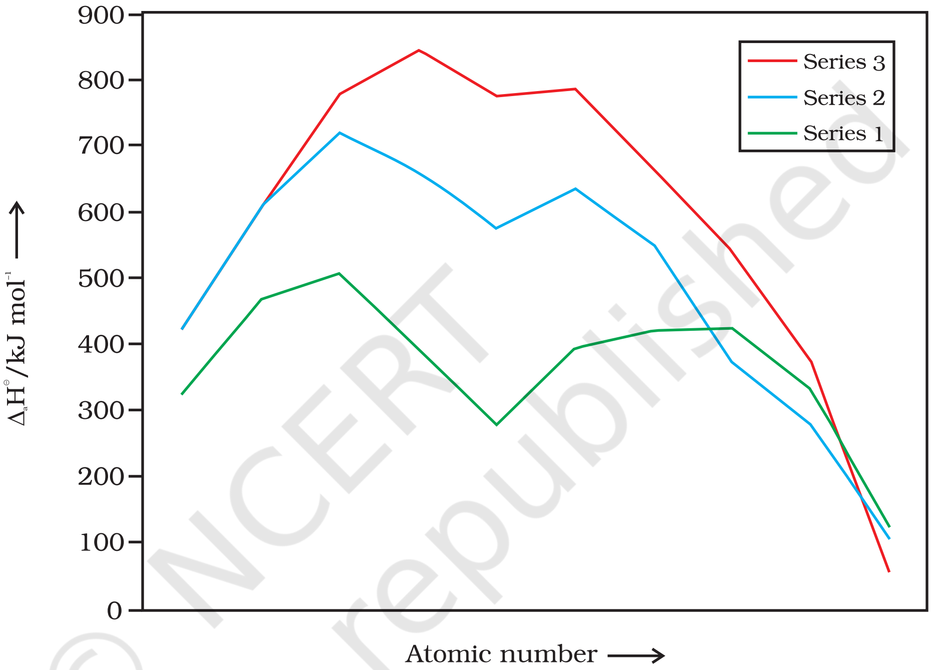


*Fig. 4.2* Trends in enthalpies of atomisation of transition elements

### 4.3.2 Variation in Atomic and Ionic Sizes of Transition Metals

In general, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. This is because the new electron enters a *d* orbital each time the nuclear charge increases by unity. It may be recalled that the shielding effect of a *d* electron is not that effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases. The same trend is observed in the atomic radii of a given series. However, the variation within a series is quite small. An interesting point emerges when atomic sizes of one series are compared with those of the corresponding elements in the other series. The curves in Fig. 4.3 show an increase from the first (3*d*) to the second (4*d*) series of the elements but the radii of the third (5*d*) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4*f* orbitals which must be filled before the 5*d* series of elements begin. The filling of 4*f* before 5*d* orbital results in a regular decrease in atomic radii called **Lanthanoid contraction** which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third *d* series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship.

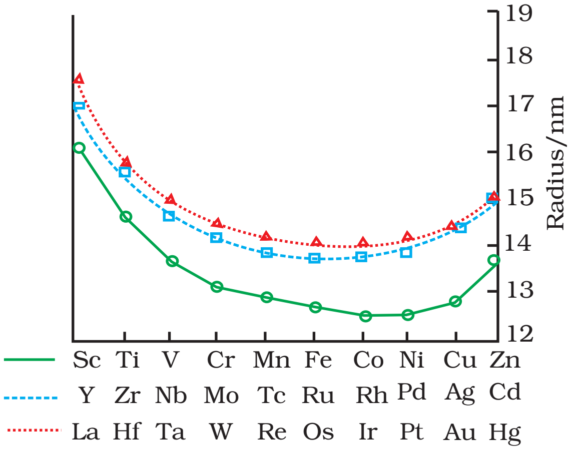


***Fig. 4.3:*** *Trends in atomic radii of transition elements*

The factor responsible for the lanthanoid contraction is somewhat similar to that observed in an ordinary transition series and is attributed to similar cause, i.e., the imperfect shielding of one electron by another in the same set of orbitals. However, the shielding of one $4f$ electron by another is less than that of one $d$ electron by another, and as the nuclear charge increases along the series, there is fairly regular decrease in the size of the entire $4f^n$ orbitals.

The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus, from titanium (Z = 22) to copper (Z = 29) the significant increase in the density may be noted (Table 4.2).

**Table 4.2: Electronic Configurations and some other Properties of the First Series of Transition Elements**

| **Element** | | **Sc** | **Ti** | **V** | **Cr** | **Mn** | **Fe** | **Co** | **Ni** | **Cu** | **Zn** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Atomic number** | | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| **Electronic configuration** | | | | | | | | | | | |
| | M | $3d^1 4s^2$ | $3d^2 4s^2$ | $3d^3 4s^2$ | $3d^5 4s^1$ | $3d^5 4s^2$ | $3d^6 4s^2$ | $3d^7 4s^2$ | $3d^8 4s^2$ | $3d^{10} 4s^1$ | $3d^{10} 4s^2$ |
| | $M^+$ | $3d^1 4s^1$ | $3d^2 4s^1$ | $3d^3 4s^1$ | $3d^5$ | $3d^5 4s^1$ | $3d^6 4s^1$ | $3d^7 4s^1$ | $3d^8 4s^1$ | $3d^{10}$ | $3d^{10} 4s^1$ |
| | $M^{2+}$ | $3d^1$ | $3d^2$ | $3d^3$ | $3d^4$ | $3d^5$ | $3d^6$ | $3d^7$ | $3d^8$ | $3d^9$ | $3d^{10}$ |
| | $M^{3+}$ | [Ar] | $3d^1$ | $3d^2$ | $3d^3$ | $3d^4$ | $3d^5$ | $3d^6$ | $3d^7$ | – | – |
| **Enthalpy of atomisation,** $\Delta_a H^o$**/kJ mol**$^{-1}$ | | | | | | | | | | | |
| | | 326 | 473 | 515 | 397 | 281 | 416 | 425 | 430 | 339 | 126 |
| **Ionisation enthalpy/**$\Delta_i H^o$**/kJ mol**$^{-1}$ | | | | | | | | | | | |
| $\Delta_i H^o$ | I | 631 | 656 | 650 | 653 | 717 | 762 | 758 | 736 | 745 | 906 |
| $\Delta_i H^o$ | II | 1235 | 1309 | 1414 | 1592 | 1509 | 1561 | 1644 | 1752 | 1958 | 1734 |
| $\Delta_i H^o$ | III | 2393 | 2657 | 2833 | 2990 | 3260 | 2962 | 3243 | 3402 | 3556 | 3837 |
| **Metallic/ionic** | M | 164 | 147 | 135 | 129 | 137 | 126 | 125 | 125 | 128 | 137 |
| **radii/pm** | $M^{2+}$ | – | – | 79 | 82 | 82 | 77 | 74 | 70 | 73 | 75 |
| | $M^{3+}$ | 73 | 67 | 64 | 62 | 65 | 65 | 61 | 60 | – | – |
| **Standard** | | | | | | | | | | | |
| **electrode** | $M^{2+}/M$ | – | –1.63 | –1.18 | –0.90 | –1.18 | –0.44 | –0.28 | –0.25 | +0.34 | -0.76 |
| **potential** $E^o$**/V** | $M^{3+}/M^{2+}$ | – | –0.37 | –0.26 | -0.41 | +1.57 | +0.77 | +1.97 | – | – | – |
| **Density/g cm**$^{-3}$ | | 3.43 | 4.1 | 6.07 | 7.19 | 7.21 | 7.8 | 8.7 | 8.9 | 8.9 | 7.1 |

Example 4.2

Why do the transition elements exhibit higher enthalpies of atomisation?

Solution

Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomisation.

### Intext Question

**4.2** In the series Sc ($Z = 21$) to Zn ($Z = 30$), the enthalpy of atomisation of zinc is the lowest, i.e., 126 kJ $mol^{-1}$. Why?

### 4.3.3 Ionisation Enthalpies

There is an increase in ionisation enthalpy along each series of the transition elements from left to right due to an increase in nuclear charge which accompanies the filling of the inner *d* orbitals. Table 4.2 gives the values of the first three ionisation enthalpies of the first series of transition elements. These values show that the successive enthalpies of these elements do not increase as steeply as in the case of non-transition elements. The variation in ionisation enthalpy along a series of transition elements is much less in comparison to the variation along a period of non-transition elements. The first ionisation enthalpy, in general, increases, but the magnitude of the increase in the second and third ionisation enthalpies for the successive elements, is much higher along a series.

The irregular trend in the first ionisation enthalpy of the metals of 3*d* series, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4*s* and 3*d* orbitals. You have learnt that when *d*-block elements form ions, *ns* electrons are lost before $(n – 1)$ *d* electrons. As we move along the period in 3*d* series, we see that nuclear charge increases from scandium to zinc but electrons are added to the orbital of inner subshell, i.e., 3*d* orbitals. These 3*d* electrons shield the 4*s* electrons from the increasing nuclear charge somewhat more effectively than the outer shell electrons can shield one another. Therefore, the atomic radii decrease less rapidly. Thus, ionization energies increase only slightly along the 3*d* series. The doubly or more highly charged ions have $d^n$ configurations with no 4*s* electrons. A general trend of increasing values of second ionisation enthalpy is expected as the effective nuclear charge increases because one *d* electron does not shield another electron from the influence of nuclear charge because *d*-orbitals differ in direction. However, the trend of steady increase in second and third ionisation enthalpy breaks for the formation of $Mn^{2+}$ and $Fe^{3+}$ respectively. In both the cases, ions have $d^5$ configuration. Similar breaks occur at corresponding elements in the later transition series.

The interpretation of variation in ionisation enthalpy for an electronic configuration $d^n$ is as follows:

The three terms responsible for the value of ionisation enthalpy are attraction of each electron towards nucleus, repulsion between the electrons and the exchange energy. Exchange energy is responsible for the stabilisation of energy state. Exchange energy is approximately proportional to the total number of possible pairs of parallel spins in the degenerate orbitals. When several electrons occupy a set of degenerate orbitals, the lowest energy state corresponds to the maximum possible extent of single occupation of orbital and parallel spins (Hunds rule). The loss of exchange energy increases the stability. As the stability increases, the ionisation becomes more difficult. There is no loss of exchange energy at $d^6$ configuration. $Mn^+$ has $3d^5 4s^1$ configuration and configuration of $Cr^+$ is $d^5$, therefore, ionisation enthalpy of $Mn^+$ is lower than $Cr^+$. In the same way, $Fe^{2+}$ has $d^6$ configuration and $Mn^{2+}$ has $3d^5$ configuration. Hence, ionisation enthalpy of $Fe^{2+}$ is lower than the $Mn^{2+}$. In other words, we can say that the third ionisation enthalpy of Fe is lower than that of Mn.

The lowest common oxidation state of these metals is +2. To form the $M^{2+}$ ions from the gaseous atoms, the sum of the first and second ionisation enthalpy is required in addition to the enthalpy of atomisation. The dominant term is the second ionisation enthalpy which shows unusually high values for Cr and Cu where $M^+$ ions have the $d^5$ and $d^{10}$ configurations respectively. The value for Zn is correspondingly low as the ionisation causes the removal of one 4*s* electron which results in the formation of stable $d^{10}$ configuration. The trend in the third ionisation enthalpies is not complicated by the 4*s* orbital factor and shows the greater difficulty of removing an electron from the $d^5$ ($Mn^{2+}$) and $d^{10}$ ($Zn^{2+}$) ions. In general, the third ionisation enthalpies are quite high. Also the high values for third ionisation enthalpies of copper, nickel and zinc indicate why it is difficult to obtain oxidation state greater than two for these elements.

Although ionisation enthalpies give some guidance concerning the relative stabilities of oxidation states, this problem is very complex and not amenable to ready generalisation.

### 4.3.4 Oxidation States

One of the notable features of a transition elements is the great variety of oxidation states these may show in their compounds. Table 4.3 lists the common oxidation states of the first row transition elements.

**Table 4.3: Oxidation States of the first row Transition Metal (the most common ones are in bold types)**

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
|  | +2 | +2 | +2 | **+2** | **+2** | **+2** | **+2** | +1 | **+2** |
| +3 | +3 | +3 | **+3** | +3 | **+3** | **+3** | +3 | **+2** |  |
|  | **+4** | +4 | +4 | +4 | +4 | +4 | +4 |  |  |
|  |  | **+5** | +5 | +5 |  |  |  |  |  |
|  |  |  | **+6** | +6 | +6 |  |  |  |  |
|  |  |  |  | **+7** |  |  |  |  |  |

The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many *d* electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn). Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no *d* electrons are involved). The maximum oxidation states of reasonable stability correspond in value to the sum of the *s* and *d* electrons upto manganese ($Ti^{IV}O_2$, $V^{V}O_2^{+}$, $Cr^{V1}O_4^{2-}$, $Mn^{VII}O_4^{-}$) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are $Fe^{II,III}$, $Co^{II,III}$, $Ni^{II}$, $Cu^{I,II}$, $Zn^{II}$.

The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of *d* orbitals in such a way that their oxidation states differ from each other by unity, e.g., $V^{II}$, $V^{III}$, $V^{IV}$, $V^{V}$. This is in contrast with the variability of oxidation states of non transition elements where oxidation states normally differ by a unit of two.

An interesting feature in the variability of oxidation states of the *d*–block elements is noticed among the groups (groups 4 through 10). Although in the *p*–block the lower oxidation states are favoured by the heavier members (due to inert pair effect), the opposite is true in the groups of *d*-block. For example, in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas $MoO_3$ and $WO_3$ are not.

Low oxidation states are found when a complex compound has ligands capable of π-acceptor character in addition to the σ-bonding. For example, in $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero.

**Example 4.3**

Name a transition element which does not exhibit variable oxidation states.

**Solution**

Scandium ($Z$ = 21) does not exhibit variable oxidation states.

## Intext Question

**4.3** Which of the 3*d* series of the transition metals exhibits the largest number of oxidation states and why?

### 4.3.5 Trends in the $M^{2+}/M$ Standard Electrode Potentials

Table 4.4 contains the thermochemical parameters related to the transformation of the solid metal atoms to $M^{2+}$ ions in solution and their standard electrode potentials. The observed values of $E^{\ominus}$ and those calculated using the data of Table 4.4 are compared in Fig. 4.4.

The unique behaviour of Cu, having a positive $E^{\ominus}$, accounts for its inability to liberate $H_2$ from acids. Only oxidising acids (nitric and hot concentrated sulphuric) react with Cu, the acids being reduced. The high energy to transform Cu(s) to $Cu^{2+}$(aq) is not balanced by its hydration enthalpy. The general trend towards less negative $E^{\ominus}$ values across the series is related to the general increase in the sum of the first and second ionisation enthalpies. It is interesting to note that the value of $E^{\ominus}$ for Mn, Ni and Zn are more negative than expected from the trend.

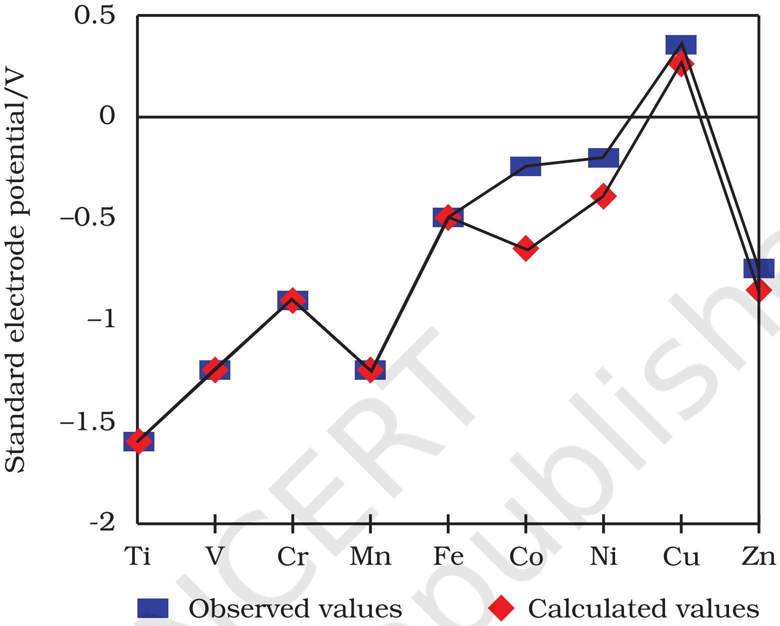


***Fig. 4.4:*** *Observed and calculated values for the standard electrode potentials ($M^{2+} \rightarrow M^{\circ}$) of the elements Ti to Zn*

**Example 4.4**

Why is $Cr^{2+}$ reducing and $Mn^{3+}$ oxidising when both have $d^4$ configuration?

**Solution**

$Cr^{2+}$ is reducing as its configuration changes from $d^4$ to $d^3$, the latter having a half-filled $t_{2g}$ level (see Unit 5). On the other hand, the change from $Mn^{3+}$ to $Mn^{2+}$ results in the half-filled ($d^5$) configuration which has extra stability.

**Intext Question**

**4.4** The $E^{\circ}(M^{2+}/M)$ value for copper is positive (+0.34V). What is possible reason for this? (Hint: consider its high $\Delta_a H^{\circ}$ and low $\Delta_{hyd} H^{\circ}$)

**Table 4.4: Thermochemical data (kJ mol$^{-1}$) for the first row Transition Elements and the Standard Electrode Potentials for the Reduction of M$^{II}$ to M.**

| Element (M) | $\Delta_aH^o$ (M) | $\Delta_iH_1^o$ | $\Delta_iH_2^o$ | $\Delta_{hyd}H^o(M^{2+})$ | $E^o$/V |
|---|---|---|---|---|---|
| Ti | 469 | 656 | 1309 | -1866 | -1.63 |
| V | 515 | 650 | 1414 | -1895 | -1.18 |
| Cr | 398 | 653 | 1592 | -1925 | -0.90 |
| Mn | 279 | 717 | 1509 | -1862 | -1.18 |
| Fe | 418 | 762 | 1561 | -1998 | -0.44 |
| Co | 427 | 758 | 1644 | -2079 | -0.28 |
| Ni | 431 | 736 | 1752 | -2121 | -0.25 |
| Cu | 339 | 745 | 1958 | -2121 | 0.34 |
| Zn | 130 | 906 | 1734 | -2059 | -0.76 |

The stability of the half-filled *d* sub-shell in Mn$^{2+}$ and the completely filled $d^{10}$ configuration in Zn$^{2+}$ are related to their $E^o$ values, whereas $E^o$ for Ni is related to the highest negative $\Delta_{hyd}H^o$.

### 4.3.6 Trends in the $M^{3+}/M^{2+}$ Standard Electrode Potentials

An examination of the $E^o(M^{3+}/M^{2+})$ values (Table 4.2) shows the varying trends. The low value for Sc reflects the stability of Sc$^{3+}$ which has a noble gas configuration. The highest value for Zn is due to the removal of an electron from the stable $d^{10}$ configuration of Zn$^{2+}$. The comparatively high value for Mn shows that Mn$^{2+}$($d^5$) is particularly stable, whereas comparatively low value for Fe shows the extra stability of Fe$^{3+}$ ($d^5$). The comparatively low value for V is related to the stability of V$^{2+}$ (half-filled $t_{2g}$ level, Unit 5).

### 4.3.7 Trends in Stability of Higher Oxidation States

Table 4.5 shows the stable halides of the 3*d* series of transition metals. The highest oxidation numbers are achieved in $TiX_4$ (tetrahalides), $VF_5$ and $CrF_6$. The +7 state for Mn is not represented in simple halides but $MnO_3F$ is known, and beyond Mn no metal has a trihalide except $FeX_3$ and $CoF_3$. The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of $CoF_3$, or higher bond enthalpy terms for the higher covalent compounds, e.g., $VF_5$ and $CrF_6$.

Although V$^{+5}$ is represented only by $VF_5$, the other halides, however, undergo hydrolysis to give oxohalides, $VOX_3$. Another feature of fluorides is their instability in the low oxidation states e.g., $VX_2$ (X = CI, Br or I)

**Table 4.5: Formulas of Halides of 3*d* Metals**

| Oxidation Number | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| + 6 | | | $CrF_6$ | | | | | | |
| + 5 | | $VF_5$ | $CrF_5$ | | | | | | |
| + 4 | $TiX_4$ | $VX^I_4$ | $CrX_4$ | $MnF_4$ | | | | | |
| + 3 | $TiX_3$ | $VX_3$ | $CrX_3$ | $MnF_3$ | $FeX^I_3$ | $CoF_3$ | | | |
| + 2 | $TiX_2^{III}$ | $VX_2$ | $CrX_2$ | $MnX_2$ | $FeX_2$ | $CoX_2$ | $NiX_2$ | $CuX_2^{II}$ | $ZnX_2$ |
| + 1 | | | | | | | | $CuX^{III}$ | |

Key: X = F → I; X$^I$ = F → Br; X$^{II}$ = F, CI; X$^{III}$ = CI → I and the same applies to CuX. On the other hand, all $Cu^{II}$ halides are known except the iodide. In this case, $Cu^{2+}$ oxidises $I^-$ to $I_2$:

$$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2(s) + I_2$$

However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

The stability of $Cu^{2+}$ (aq) rather than $Cu^+$(aq) is due to the much more negative $\Delta_{hyd}H^o$ of $Cu^{2+}$ (aq) than $Cu^+$, which more than compensates for the second ionisation enthalpy of Cu.

The ability of oxygen to stabilise the highest oxidation state is demonstrated in the oxides. The highest oxidation number in the oxides (Table 4.6) coincides with the group number and is attained in $Sc_2O_3$ to $Mn_2O_7$. Beyond Group 7, no higher oxides of Fe above $Fe_2O_3$, are known, although ferrates (VI)$(FeO_4)^{2-}$, are formed in alkaline media but they readily decompose to $Fe_2O_3$ and $O_2$. Besides the oxides, oxocations stabilise $V^V$ as $VO_2^+$, $V^{IV}$ as $VO^{2+}$ and $Ti^{IV}$ as $TiO^{2+}$. The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is $MnF_4$ whereas the highest oxide is $Mn_2O_7$. The ability of oxygen to form multiple bonds to metals explains its superiority. In the covalent oxide $Mn_2O_7$, each Mn is tetrahedrally surrounded by O's including a Mn–O–Mn bridge. The tetrahedral $[MO_4]^{n-}$ ions are known for $V^V$, $Cr^{VI}$, $Mn^V$, $Mn^{VI}$ and $Mn^{VII}$.

**Table 4.6: Oxides of 3d Metals**

| Oxidation Number | Groups |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| + 7 |  |  |  |  | $Mn_2O_7$ |  |  |  |  |  |
| + 6 |  |  |  | $CrO_3$ |  |  |  |  |  |  |
| + 5 |  |  | $V_2O_5$ |  |  |  |  |  |  |  |
| + 4 |  | $TiO_2$ | $V_2O_4$ | $CrO_2$ | $MnO_2$ |  |  |  |  |  |
| + 3 | $Sc_2O_3$ | $Ti_2O_3$ | $V_2O_3$ | $Cr_2O_3$ | $Mn_2O_3$ | $Fe_2O_3$ |  |  |  |  |
|  |  |  |  |  | $Mn_3O_4^*$ | $Fe_3O_4^*$ | $Co_3O_4^*$ |  |  |  |
| + 2 |  | TiO | VO | (CrO) | MnO | FeO | CoO | NiO | CuO | ZnO |
| + 1 |  |  |  |  |  |  |  |  | $Cu_2O$ |  |

* *mixed oxides*

*Example 4.5*

How would you account for the increasing oxidising power in the series $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$?

*Solution*

This is due to the increasing stability of the lower species to which they are reduced.

## *Intext Question*

**4.5** How would you account for the irregular variation of ionisation enthalpies (first and second) in the first series of the transition elements?

### 4.3.8 Chemical Reactivity and E° Values

Transition metals vary widely in their chemical reactivity. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble'—that is, they are unaffected by single acids.

The metals of the first series with the exception of copper are relatively more reactive and are oxidised by 1M $H^+$, though the actual rate at which these metals react with oxidising agents like hydrogen ion ($H^+$) is sometimes slow. For example, titanium and vanadium, in practice, are passive to dilute non oxidising acids at room temperature. The $E^o$ values for $M^{2+}/M$ (Table 4.2) indicate a decreasing tendency to form divalent cations across the series. This general trend towards less negative $E^o$ values is related to the increase in the sum of the first and second ionisation enthalpies. It is interesting to note that the $E^o$ values for Mn, Ni and Zn are more negative than expected from the general trend. Whereas the stabilities of half-filled *d* subshell ($d^5$) in $Mn^{2+}$ and completely filled *d* subshell ($d^{10}$) in zinc are related to their $E^{e}$ values; for nickel, $E^o$ value is related to the highest negative enthalpy of hydration.

An examination of the $E^o$ values for the redox couple $M^{3+}/M^{2+}$ (Table 4.2) shows that $Mn^{3+}$ and $Co^{3+}$ ions are the strongest oxidising agents in aqueous solutions. The ions $Ti^{2+}$, $V^{2+}$ and $Cr^{2+}$ are strong reducing agents and will liberate hydrogen from a dilute acid, e.g.,

$$2\ Cr^{2+}(aq) + 2\ H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + H_2(g)$$

**Example 4.6** For the first row transition metals the $E^o$ values are:

| $E^o$ | V | Cr | Mn | Fe | Co | Ni | Cu |
|---|---|---|---|---|---|---|---|
| $(M^{2+}/M)$ | −1.18 | – 0.91 | −1.18 | – 0.44 | – 0.28 | – 0.25 | +0.34 |

Explain the irregularity in the above values.

**Solution** The $E^o$ $(M^{2+}/M)$ values are not regular which can be explained from the irregular variation of ionisation enthalpies $(\Delta_i H_1 + \Delta_i H_2)$ and also the sublimation enthalpies which are relatively much less for manganese and vanadium.

**Example 4.7** Why is the $E^o$ value for the $Mn^{3+}/Mn^{2+}$ couple much more positive than that for $Cr^{3+}/Cr^{2+}$ or $Fe^{3+}/Fe^{2+}$? Explain.

**Solution** Much larger third ionisation energy of Mn (where the required change is $d^5$ to $d^4$) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.

#### Intext Questions

**4.6** Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

**4.7** Which is a stronger reducing agent $Cr^{2+}$ or $Fe^{2+}$ and why ?

### 4.3.9 Magnetic Properties

When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: *diamagnetism* and *paramagnetism*. Diamagnetic substances are repelled by the applied field while the paramagnetic substances are attracted. Substances which are attracted very strongly are said to be **ferromagnetic**. In fact, ferromagnetism is an extreme form of paramagnetism. Many of the transition metal ions are paramagnetic.

Paramagnetism arises from the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e.,

$$\mu = \sqrt{n(n+2)}$$

where n is the number of unpaired electrons and μ is the magnetic moment in units of **Bohr magneton (BM)**. A single unpaired electron has a magnetic moment of 1.73 Bohr magnetons (BM).

The magnetic moment increases with the increasing number of unpaired electrons. Thus, the observed magnetic moment gives a useful indication about the number of unpaired electrons present in the atom, molecule or ion. The magnetic moments calculated from the 'spin-only' formula and those derived experimentally for some ions of the first row transition elements are given in Table 4.7. The experimental data are mainly for hydrated ions in solution or in the solid state.

**Table 4.7: Calculated and Observed Magnetic Moments (BM)**

| Ion | Configuration | Unpaired electron(s) | Magnetic moment | |
|---|---|---|---|---|
| | | | Calculated | Observed |
| $Sc^{3+}$ | $3d^0$ | 0 | 0 | 0 |
| $Ti^{3+}$ | $3d^1$ | 1 | 1.73 | 1.75 |
| $Tl^{2+}$ | $3d^2$ | 2 | 2.84 | 2.76 |
| $V^{2+}$ | $3d^3$ | 3 | 3.87 | 3.86 |
| $Cr^{2+}$ | $3d^4$ | 4 | 4.90 | 4.80 |
| $Mn^{2+}$ | $3d^5$ | 5 | 5.92 | 5.96 |
| $Fe^{2+}$ | $3d^6$ | 4 | 4.90 | 5.3 – 5.5 |
| $Co^{2+}$ | $3d^7$ | 3 | 3.87 | 4.4 – 5.2 |
| $Ni^{2+}$ | $3d^8$ | 2 | 2.84 | 2.9 – 3, 4 |
| $Cu^{2+}$ | $3d^9$ | 1 | 1.73 | 1.8 – 2.2 |
| $Zn^{2+}$ | $3d^{10}$ | 0 | 0 | |

**Example 4.8**

Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

**Solution**

With atomic number 25, the divalent ion in aqueous solution will have $d^5$ configuration (five unpaired electrons). The magnetic moment, μ is

$$\mu = \sqrt{5(5+2)} = 5.92\,\text{BM}$$

## Intext Question

**4.8** Calculate the 'spin only' magnetic moment of $M^{2+}_{(aq)}$ ion ($Z = 27$).

### 4.3.10 Formation of Coloured Ions

When an electron from a lower energy *d* orbital is excited to a higher energy *d* orbital, the energy of excitation corresponds to the frequency of light absorbed (Unit 5). This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand. In aqueous solutions where water molecules are the ligands, the colours of the ions observed are listed in Table 4.8. A few coloured solutions of *d*–block elements are illustrated in Fig. 4.5.

***Fig. 4.5:*** *Colours of some of the first row transition metal ions in aqueous solutions. From left to right:* $V^{4+}$, $V^{3+}$, $Mn^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$ *and* $Cu^{2+}$ .

**Table 4.8: Colours of Some of the First Row (aquated) Transition Metal Ions**

| Configuration | Example | Colour |
|---|---|---|
| $3d^0$ | $Sc^{3+}$ | colourless |
| $3d^0$ | $Ti^{4+}$ | colourless |
| $3d^1$ | $Ti^{3+}$ | purple |
| $3d^1$ | $V^{4+}$ | blue |
| $3d^2$ | $V^{3+}$ | green |
| $3d^3$ | $V^{2+}$ | violet |
| $3d^3$ | $Cr^{3+}$ | violet |
| $3d^4$ | $Mn^{3+}$ | violet |
| $3d^4$ | $Cr^{2+}$ | blue |
| $3d^5$ | $Mn^{2+}$ | pink |
| $3d^5$ | $Fe^{3+}$ | yellow |
| $3d^6$ | $Fe^{2+}$ | green |
| $3d^6 3d^7$ | $Co^{3+} Co^{2+}$ | bluepink |
| $3d^8$ | $Ni^{2+}$ | green |
| $3d^9$ | $Cu^{2+}$ | blue |
| $3d^{10}$ | $Zn^{2+}$ | colourless |

### 4.3.11 Formation of Complex Compounds

Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species with characteristic properties. A few examples are: $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$. (The chemistry of complex compounds is dealt with in detail in Unit 5). The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of *d* orbitals for bond formation.

### 4.3.12 Catalytic Properties

The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in Catalytic Hydrogenation) are some of the examples. Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3*d* and 4*s* electrons for bonding). This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering). Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions.

$$2\ I^- + S_2O_8^{2-} \rightarrow I_2 + 2\ SO_4^{2-}$$

An explanation of this catalytic action can be given as:

$$2\ Fe^{3+} + 2\ I^- \rightarrow 2\ Fe^{2+} + I_2$$

$$2\ Fe^{2+} + S_2O_8^{2-} \rightarrow 2\ Fe^{3+} + 2SO_4^{2-}$$

### 4.3.13 Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, $Mn_4N$, $Fe_3H$, $VH_{0.56}$ and $TiH_{1.7}$, etc. The formulas quoted do not, of course, correspond to any normal oxidation state of the metal. Because of the nature of their composition, these compounds are referred to as *interstitial* compounds. The principal physical and chemical characteristics of these compounds are as follows:

(i) They have high melting points, higher than those of pure metals.
(ii) They are very hard, some borides approach diamond in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

### 4.3.14 Alloy Formation

An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

**Example 4.9** What is meant by 'disproportionation' of an oxidation state? Give an example.

**Solution** When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation. For example, manganese (VI) becomes unstable relative to manganese(VII) and manganese (IV) in acidic solution.

$$3\ Mn^{VI}O_4^{\ 2-} + 4\ H^+ \rightarrow 2\ Mn^{VII}O^-_4 + Mn^{IV}O_2 + 2H_2O$$

**Intext Question**

**4.9** Explain why $Cu^+$ ion is not stable in aqueous solutions?

## 4.4 Some Important Compounds of Transition Elements

### 4.4.1 Oxides and Oxoanions of Metals

These oxides are generally formed by the reaction of metals with oxygen at high temperatures. All the metals except scandium form MO oxides which are ionic. The highest oxidation number in the oxides, coincides with the group number and is attained in $Sc_2O_3$ to $Mn_2O_7$. Beyond group 7, no higher oxides of iron above $Fe_2O_3$ are known. Besides the oxides, the oxocations stabilise $V^V$ as $VO_2^{\ +}$, $V^{IV}$ as $VO^{2+}$ and $Ti^{IV}$ as $TiO^{2+}$.

As the oxidation number of a metal increases, ionic character decreases. In the case of Mn, $Mn_2O_7$ is a covalent green oil. Even $CrO_3$ and $V_2O_5$ have low melting points. In these higher oxides, the acidic character is predominant.

Thus, $Mn_2O_7$ gives $HMnO_4$ and $CrO_3$ gives $H_2CrO_4$ and $H_2Cr_2O_7$. $V_2O_5$ is, however, amphoteric though mainly acidic and it gives $VO_4^{\ 3-}$ as well as $VO_2^{\ +}$ salts. In vanadium there is gradual change from the basic $V_2O_3$ to less basic $V_2O_4$ and to amphoteric $V_2O_5$. $V_2O_4$ dissolves in acids to give $VO^{2+}$ salts. Similarly, $V_2O_5$ reacts with alkalies as well as acids to give $VO_4^{3-}$ and $VO_4^+$ respectively. The well characterised CrO is basic but $Cr_2O_3$ is amphoteric.

***Potassium dichromate $K_2Cr_2O_7$***

Potassium dichromate is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds. Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore ($FeCr_2O_4$) with sodium or potassium carbonate in free access of air. The reaction with sodium carbonate occurs as follows:

$$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$$

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.\ 2H_2O$ can be crystallised.

$$2Na_2CrO_4 + 2\ H^+ \rightarrow Na_2Cr_2O_7 + 2\ Na^+ + H_2O$$

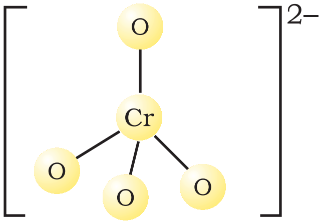
Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

$$Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$$

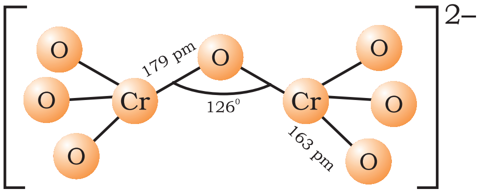
Orange crystals of potassium dichromate crystallise out. The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

$$2\ CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$
$$Cr_2O_7^{2-} + 2\ OH^- \rightarrow 2\ CrO_4^{2-} + H_2O$$

The structures of chromate ion, $CrO_4^{2-}$ and the dichromate ion, $Cr_2O_7^{2-}$ are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126°.



Chromate ion



Dichromate ion

Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O\ (E^\circ = 1.33V)$$

Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:

$6\ I^- \rightarrow 3I_2 + 6\ e^-$ ; $\quad 3\ Sn^{2+} \rightarrow 3Sn^{4+} + 6\ e^-$

$3\ H_2S \rightarrow 6H^+ + 3S + 6e^-$ ; $\quad 6\ Fe^{2+} \rightarrow 6Fe^{3+} + 6\ e^-$

The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ Fe^{2+} \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$$

### *Potassium permanganate $KMnO_4$*

Potassium permanganate is prepared by fusion of $MnO_2$ with an alkali metal hydroxide and an oxidising agent like $KNO_3$. This produces the dark green $K_2MnO_4$ which disproportionates in a neutral or acidic solution to give permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Commercially it is prepared by the alkaline oxidative fusion of $MnO_2$ followed by the electrolytic oxidation of manganate (Vl).

$$MnO_2 \xrightarrow[\text{with air or } KNO_3]{\text{Fused with KOH, oxidised}} \underset{\text{manganate ion}}{MnO_4^{2-}}\ ;\ \underset{\text{manganate}}{MnO_4^{2-}} \xrightarrow[\text{alkaline solution}]{\text{Electrolytic oxidation in}} \underset{\text{permanganate ion}}{MnO_4^-}$$

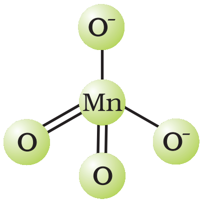
In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^{-} + 10SO_4^{2-} + 16H^{+}$$

Potassium permanganate forms dark purple (almost black) crystals which are isostructural with those of $KClO_4$. The salt is not very soluble in water (6.4 g/100 g of water at 293 K), but when heated it decomposes at 513 K.

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

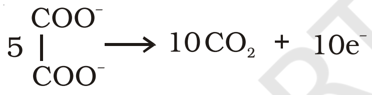
It has two physical properties of considerable interest: its intense colour and its diamagnetism along with temperature-dependent weak paramagnetism. These can be explained by the use of molecular orbital theory which is beyond the present scope.



Tetrahedral manganate ion (green)

The manganate and permanganate ions are tetrahedral; the π-bonding takes place by overlap of *p* orbitals of oxygen with *d* orbitals of manganese. The green manganate is paramagnetic because of one unpaired electron but the permanganate is diamagnetic due to the absence of unpaired electron.

Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine. The half-reactions of reductants are:

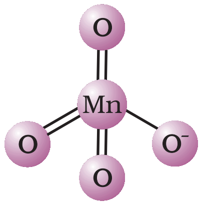


$$5\,\left|\begin{matrix}COO^{-}\\COO^{-}\end{matrix}\right. \longrightarrow 10CO_2 + 10e^{-}$$

$$5\,Fe^{2+} \rightarrow 5\,Fe^{3+} + 5e^{-}$$

$$5NO_2^{-} + 5H_2O \rightarrow 5NO_3^{-} + 10H^{+} + 10e^{-}$$

$$10I^{-} \rightarrow 5I_2 + 10e^{-}$$



Tetrahedral permanganate ion (purple)

The full reaction can be written by adding the half-reaction for $KMnO_4$ to the half-reaction of the reducing agent, balancing wherever necessary.

If we represent the reduction of permanganate to manganate, manganese dioxide and manganese(II) salt by half-reactions,

$$MnO_4^{-} + e^{-} \rightarrow MnO_4^{2-} \qquad (E^{o} = +\,0.56\ V)$$

$$MnO_4^{-} + 4H^{+} + 3e^{-} \rightarrow MnO_2 + 2H_2O \qquad (E^{o} = +\,1.69\ V)$$

$$MnO_4^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_2O \qquad (E^{o} = +\,1.52\ V)$$

We can very well see that the hydrogen ion concentration of the solution plays an important part in influencing the reaction. Although many reactions can be understood by consideration of redox potential, kinetics of the reaction is also an important factor. Permanganate at $[H^{+}] = 1$ should oxidise water but in practice the reaction is extremely slow unless either manganese(II) ions are present or the temperature is raised.

A few important oxidising reactions of $KMnO_4$ are given below:

**1.** In acid solutions:

(a) Iodine is liberated from potassium iodide :

$$10I^{-} + 2MnO_4^{-} + 16H^{+} \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

(b) $Fe^{2+}$ ion (green) is converted to $Fe^{3+}$ (yellow):

$$5Fe^{2+} + MnO_4^{-} + 8H^{+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

(c) Oxalate ion or oxalic acid is oxidised at 333 K:

$$5C_2O_4^{2-} + 2MnO_4^{-} + 16H^{+} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

(d) Hydrogen sulphide is oxidised, sulphur being precipitated:

$$H_2S \longrightarrow 2H^{+} + S^{2-}$$

$$5S^{2-} + 2MnO^{-}_{4} + 16H^{+} \longrightarrow 2Mn^{2+} + 8H_2O + 5S$$

(e) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:

$$5SO_3^{2-} + 2MnO_4^{-} + 6H^{+} \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$$

(f) Nitrite is oxidised to nitrate:

$$5NO_2^{-} + 2MnO_4^{-} + 6H^{+} \longrightarrow 2Mn^{2+} + 5NO_3^{-} + 3H_2O$$

**2.** In neutral or faintly alkaline solutions:

(a) A notable reaction is the oxidation of iodide to iodate:

$$2MnO_4^{-} + H_2O + I^{-} \longrightarrow 2MnO_2 + 2OH^{-} + IO_3^{-}$$

(b) Thiosulphate is oxidised almost quantitatively to sulphate:

$$8MnO_4^{-} + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^{-}$$

(c) Manganous salt is oxidised to $MnO_2$; the presence of zinc sulphate or zinc oxide catalyses the oxidation:

$$2MnO_4^{-} + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^{+}$$

***Note***: Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

*Uses:* Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

## THE INNER TRANSITION ELEMENTS (*f*-BLOCK)

The *f*-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium). Because lanthanum closely resembles the lanthanoids, it is usually included in any discussion of the lanthanoids for which the general symbol Ln is often used. Similarly, a discussion of the actinoids includes actinium besides the fourteen elements constituting the series. The lanthanoids resemble one another more closely than do the members of ordinary transition elements in any series. They have only one stable oxidation state and their chemistry provides an excellent opportunity to examine the effect of small changes in size and nuclear charge along a series of otherwise similar elements. The chemistry of the actinoids is, on the other hand, much more complicated. The complication arises partly owing to the occurrence of a wide range of oxidation states in these elements and partly because their radioactivity creates special problems in their study; the two series will be considered separately here.

## 4.5 The Lanthanoids

The names, symbols, electronic configurations of atomic and some ionic states and atomic and ionic radii of lanthanum and lanthanoids (for which the general symbol Ln is used) are given in Table 4.9.

### 4.5.1 Electronic Configurations

It may be noted that atoms of these elements have electronic configuration with $6s^2$ common but with variable occupancy of $4f$ level (Table 4.9). However, the electronic configurations of all the tripositive ions (the most stable oxidation state of all the lanthanoids) are of the form $4f^n$ (n = 1 to 14 with increasing atomic number).

### 4.5.2 Atomic and Ionic Sizes

The overall decrease in atomic and ionic radii from lanthanum to lutetium (the **lanthanoid contraction**) is a unique feature in the chemistry of the lanthanoids. It has far reaching consequences in the chemistry of the third transition series of the elements. The decrease in atomic radii (derived from the structures of metals) is not quite regular as it is regular in $M^{3+}$ ions (Fig. 4.6). This contraction is, of course, similar to that observed in an ordinary transition series and is attributed to the same cause, the imperfect shielding of one electron by another in the same sub-shell. However, the shielding of one $4f$ electron by another is less than one $d$ electron by another with the increase in nuclear charge along the series. There is fairly regular decrease in the sizes with increasing atomic number.

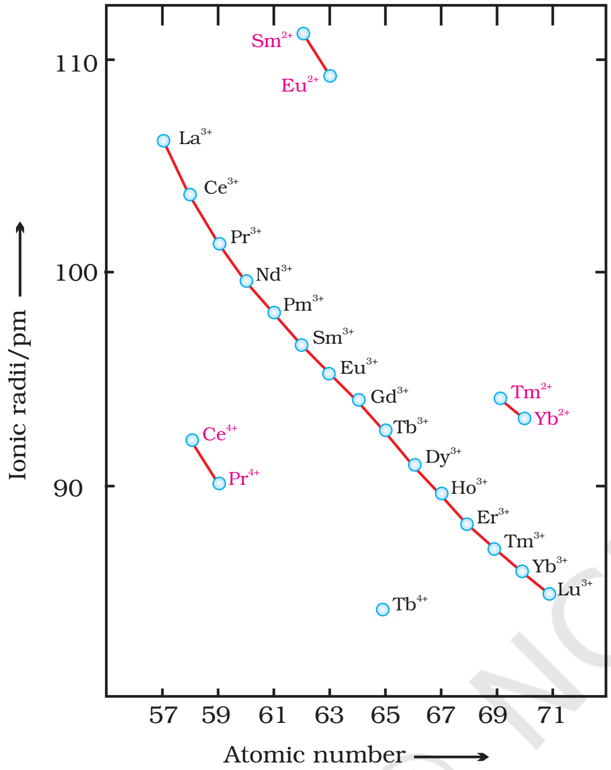


*Fig. 4.6: Trends in ionic radii of lanthanoids*

The cumulative effect of the contraction of the lanthanoid series, known as *lanthanoid contraction*, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

### 4.5.3 Oxidation States

In the lanthanoids, La(II) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled $f$ subshell. Thus, the formation of $Ce^{IV}$ is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The $E^o$ value for $Ce^{4+}/Ce^{3+}$ is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, $MO_2$. $Eu^{2+}$ is formed by losing the two $s$ electrons and its $f^7$ configuration accounts for the formation of this ion. However, $Eu^{2+}$ is a strong reducing agent changing to the common +3 state. Similarly $Yb^{2+}$ which has $f^{14}$ configuration is a reductant. $Tb^{IV}$ has half-filled $f$-orbitals and is an oxidant. The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

Table 4.9: Electronic Configurations and Radii of Lanthanum and Lanthanoids

| Atomic Number | Name | Symbol | Electronic configurations* | | | Radii/pm | | |
|---|---|---|---|---|---|---|---|---|
| | | | Ln | $Ln^{2+}$ | $Ln^{3+}$ | $Ln^{4+}$ | Ln | $Ln^{3+}$ |
| 57 | Lanthanum | La | $5d^1 6s^2$ | $5d^1$ | $4f^0$ | | 187 | 106 |
| 58 | Cerium | Ce | $4f^1 5d^1 6s^2$ | $4f^2$ | $4f^1$ | $4f^0$ | 183 | 103 |
| 59 | Praseodymium | Pr | $4f^3 6s^2$ | $4f^3$ | $4f^2$ | $4f^1$ | 182 | 101 |
| 60 | Neodymium | Nd | $4f^4 6s^2$ | $4f^4$ | $4f^3$ | $4f^2$ | 181 | 99 |
| 61 | Promethium | Pm | $4f^5 6s^2$ | $4f^5$ | $4f^4$ | | 181 | 98 |
| 62 | Samarium | Sm | $4f^6 6s^2$ | $4f^6$ | $4f^5$ | | 180 | 96 |
| 63 | Europium | Eu | $4f^7 6s^2$ | $4f^7$ | $4f^6$ | | 199 | 95 |
| 64 | Gadolinium | Gd | $4f^7 5d^1 6s^2$ | $4f^7 5d^1$ | $4f^7$ | | 180 | 94 |
| 65 | Terbium | Tb | $4f^9 6s^2$ | $4f^9$ | $4f^8$ | $4f^7$ | 178 | 92 |
| 66 | Dysprosium | Dy | $4f^{10} 6s^2$ | $4f^{10}$ | $4f^9$ | $4f^8$ | 177 | 91 |
| 67 | Holmium | Ho | $4f^{11} 6s^2$ | $4f^{11}$ | $4f^{10}$ | | 176 | 89 |
| 68 | Erbium | Er | $4f^{12} 6s^2$ | $4f^{12}$ | $4f^{11}$ | | 175 | 88 |
| 69 | Thulium | Tm | $4f^{13} 6s^2$ | $4f^{13}$ | $4f^{12}$ | | 174 | 87 |
| 70 | Ytterbium | Yb | $4f^{14} 6s^2$ | $4f^{14}$ | $4f^{13}$ | | 173 | 86 |
| 71 | Lutetium | Lu | $4f^{14} 5d^1 6s^2$ | $4f^{14} 5d^1$ | $4f^{14}$ | – | – | – |

* *Only electrons outside [Xe] core are indicated*

### 4.5.4 General Characteristics

All the lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number, samarium being steel hard. Their melting points range between 1000 to 1200 K but samarium melts at 1623 K. They have typical metallic structure and are good conductors of heat and electricity. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of *f* electrons. Neither $La^{3+}$ nor $Lu^{3+}$ ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within *f* level. The lanthanoid ions other than the $f^0$ type ($La^{3+}$ and $Ce^{4+}$) and the $f^{14}$ type ($Yb^{2+}$ and $Lu^{3+}$) are all paramagnetic.

The first ionisation enthalpies of the lanthanoids are around 600 kJ $mol^{-1}$, the second about 1200 kJ $mol^{-1}$ comparable with those of calcium. A detailed discussion of the variation of the third ionisation enthalpies indicates that the exchange enthalpy considerations (as in 3*d* orbitals of the first transition series), appear to impart a certain degree of stability to empty, half-filled and completely filled orbitals *f* level. This is indicated from the abnormally low value of the third ionisation enthalpy of lanthanum, gadolinium and lutetium.

In their chemical behaviour, in general, the earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they behave more like aluminium. Values for $E^{o}$ for the half-reaction:

$$Ln^{3+}(aq) + 3e^- \rightarrow Ln(s)$$

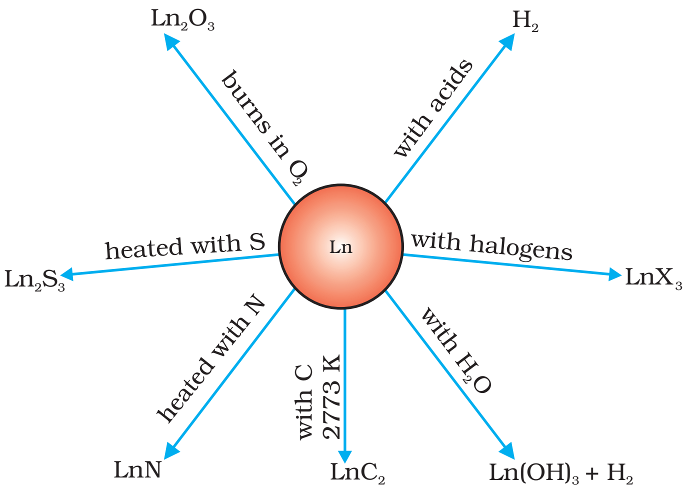


***Fig 4.7:*** *Chemical reactions of the lanthanoids.*

are in the range of –2.2 to –2.4 V except for Eu for which the value is – 2.0 V. This is, of course, a small variation. The metals combine with hydrogen when gently heated in the gas. The carbides, $Ln_3C$, $Ln_2C_3$ and $LnC_2$ are formed when the metals are heated with carbon. They liberate hydrogen from dilute acids and burn in halogens to form halides. They form oxides $M_2O_3$ and hydroxides $M(OH)_3$. The hydroxides are definite compounds, not just hydrated oxides. They are basic like alkaline earth metal oxides and hydroxides. Their general reactions are depicted in Fig. 4.7.

The best single use of the lanthanoids is for the production of alloy steels for plates and pipes. A well known alloy is *mischmetall* which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A good deal of **mischmetall** is used in Mg-based alloy to produce bullets, shell and lighter flint. Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

## 4.6 The Actinoids

The actinoids include the fourteen elements from Th to Lr. The names, symbols and some properties of these elements are given in Table 4.10.

**Table 4.10: Some Properties of Actinium and Actinoids**

| Atomic Number | Name | Symbol | Electronic configurations* | | | Radii/pm | |
|---|---|---|---|---|---|---|---|
| | | | M | $M^{3+}$ | $M^{4+}$ | $M^{3+}$ | $M^{4+}$ |
| 89 | Actinium | Ac | $6d^1 7s^2$ | $5f^0$ | | 111 | |
| 90 | Thorium | Th | $6d^2 7s^2$ | $5f^1$ | $5f^0$ | | 99 |
| 91 | Protactinium | Pa | $5f^2 6d^1 7s^2$ | $5f^2$ | $5f^1$ | | 96 |
| 92 | Uranium | U | $5f^3 6d^1 7s^2$ | $5f^3$ | $5f^2$ | 103 | 93 |
| 93 | Neptunium | Np | $5f^4 6d^1 7s^2$ | $5f^4$ | $5f^3$ | 101 | 92 |
| 94 | Plutonium | Pu | $5f^6 7s^2$ | $5f^5$ | $5f^4$ | 100 | 90 |
| 95 | Americium | Am | $5f^7 7s^2$ | $5f^6$ | $5f^5$ | 99 | 89 |
| 96 | Curium | Cm | $5f^7 6d^1 7s^2$ | $5f^7$ | $5f^6$ | 99 | 88 |
| 97 | Berkelium | Bk | $5f^9 7s^2$ | $5f^8$ | $5f^7$ | 98 | 87 |
| 98 | Californium | Cf | $5f^{10} 7s^2$ | $5f^9$ | $5f^8$ | 98 | 86 |
| 99 | Einstenium | Es | $5f^{11} 7s^2$ | $5f^{10}$ | $5f^9$ | – | – |
| 100 | Fermium | Fm | $5f^{12} 7s^2$ | $5f^{11}$ | $5f^{10}$ | – | – |
| 101 | Mendelevium | Md | $5f^{13} 7s^2$ | $5f^{12}$ | $5f^{11}$ | – | – |
| 102 | Nobelium | No | $5f^{14} 7s^2$ | $5f^{13}$ | $5f^{12}$ | – | – |
| 103 | Lawrencium | Lr | $5f^{14} 6d^1 7s^2$ | $5f^{14}$ | $5f^{13}$ | – | – |

The actinoids are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium ($Z$=103). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

### 4.6.1 Electronic Configurations

All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells. The fourteen electrons are formally added to 5*f*, though not in thorium (Z = 90) but from Pa onwards the 5*f* orbitals are complete at element 103. The irregularities in the electronic configurations of the actinoids, like those in the lanthanoids are related to the stabilities of the $f^0$, $f^7$ and $f^{14}$ occupancies of the 5f orbitals. Thus, the configurations of Am and Cm are [Rn] $5f^7 7s^2$ and [Rn] $5f^7 6d^1 7s^2$. Although the 5*f* orbitals resemble the 4*f* orbitals in their angular part of the wave-function, they are not as buried as 4*f* orbitals and hence 5*f* electrons can participate in bonding to a far greater extent.

### 4.6.2 Ionic Sizes

The general trend in lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or $M^{3+}$ ions across the series. This may be referred to as the **actinoid contraction** (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5*f* electrons.

### 4.6.3 Oxidation States

There is a greater range of oxidation states, which is in part attributed to the fact that the 5*f*, 6*d* and 7*s* levels are of comparable energies. The known oxidation states of actinoids are listed in Table 4.11.

The actinoids show in general +3 oxidation state. The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements (Table 4.11). The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse. Because the distribution of oxidation states among the actinoids is so uneven and so different for the former and later elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

**Table 4.11: Oxidation States of Actinium and Actinoids**

| Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 |  | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|  | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |  |  |  |  |  |  |
|  |  | 5 | 5 | 5 | 5 | 5 |  |  |  |  |  |  |  |  |
|  |  |  | 6 | 6 | 6 | 6 |  |  |  |  |  |  |  |  |
|  |  |  |  | 7 | 7 |  |  |  |  |  |  |  |  |  |

### 4.6.4 General Characteristics and Comparison with Lanthanoids

The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids.

The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.

The magnetic properties of the actinoids are more complex than those of the lanthanoids. Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired 5 *f* electrons is roughly parallel to the corresponding results for the lanthanoids, the latter have higher values.

It is evident from the behaviour of the actinoids that the ionisation enthalpies of the early actinoids, though not accurately known, but are lower than for the early lanthanoids. This is quite reasonable since it is to be expected that when 5*f* orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5*f* electrons, will therefore, be more effectively shielded from the nuclear charge than the 4*f* electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

A comparison of the actinoids with the lanthanoids, with respect to different characteristics as discussed above, reveals that behaviour similar to that of the lanthanoids is not evident until the second half of the actinoid series. However, even the early actinoids resemble the lanthanoids in showing close similarities with each other and in gradual variation in properties which do not entail change in oxidation state. The lanthanoid and actinoid contractions, have extended effects on the sizes, and therefore, the properties of the elements succeeding them in their respective periods. The lanthanoid contraction is more important because the chemistry of elements succeeding the actinoids are much less known at the present time.

**Example 4.10** Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

**Solution** Cerium ($Z = 58$)

**Intext Question**

**4.10** Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

## 4.7 Some Applications of d- and f-Block Elements

Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals such as Cr, Mn and Ni. Some compounds are manufactured for special purposes such as TiO for the pigment industry and $MnO_2$ for use in dry battery cells. The battery industry also requires Zn and Ni/Cd. The elements of Group 11 are still worthy of being called the coinage metals, although Ag and Au are restricted to collection items and the contemporary UK 'copper' coins are copper-coated steel. The 'silver' UK coins are a Cu/Ni alloy. Many of the metals and/or their compounds are essential catalysts in the chemical industry. $V_2O_5$ catalyses the oxidation of $SO_2$ in the manufacture of sulphuric acid. $TiCl_4$ with $A1(CH_3)_3$ forms the basis of the Ziegler catalysts used to manufacture polyethylene (polythene). Iron catalysts are used in the Haber process for the production of ammonia from $N_2/H_2$ mixtures. Nickel catalysts enable the hydrogenation of fats to proceed. In the Wacker process the oxidation of ethyne to ethanal is catalysed by $PdCl_2$. Nickel complexes are useful in the polymerisation of alkynes and other organic compounds such as benzene. The photographic industry relies on the special light-sensitive properties of AgBr.

## Summary

The ***d*-block** consisting of **Groups 3-12** occupies the large middle section of the **periodic table**. In these elements the inner *d* orbitals are progressively filled. The ***f*-block** is placed **outside** at the **bottom** of the **periodic table** and in the elements of this block, 4*f* and 5*f* orbitals are progressively filled.

Corresponding to the filling of 3*d*, 4*d* and 5*d* orbitals, three series of transition elements are well recognised. All the transition elements exhibit typical metallic properties such as –high tensile strength, ductility, malleability, thermal and electrical conductivity and metallic character. Their melting and boiling points are high which are attributed to the involvement of $(n-1)\,d$ electrons resulting into **strong interatomic bonding**. In many of these properties, the maxima occur at about the middle of each series which indicates that one unpaired electron per *d* orbital is particularly a favourable configuration for strong interatomic interaction.

**Successive ionisation enthalpies** do not increase as steeply as in the main group elements with increasing atomic number. Hence, the loss of variable number of electrons from $(n-1)\,d$ orbitals is not energetically unfavourable. The involvement of **$(n-1)\,d$ electrons** in the behaviour of transition elements impart certain distinct characteristics to these elements. Thus, in addition to variable oxidation states, they exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of coloured ions, interstitial compounds and complexes.

The **transition elements** vary widely in their chemical behaviour. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble'. Of the first series, with the exception of copper, all the metals are relatively reactive.

The transition metals react with a number of non-metals like oxygen, nitrogen, sulphur and halogens to form binary compounds. The first series transition metal oxides are generally formed from the reaction of metals with oxygen at high temperatures. These oxides dissolve in acids and bases to form oxometallic salts. Potassium dichromate and potassium permanganate are common examples. Potassium dichromate is prepared from the chromite ore by fusion with alkali in presence of air and acidifying the extract. Pyrolusite ore ($MnO_2$) is used for the preparation of potassium permanganate. Both the dichromate and the permanganate ions are strong oxidising agents.

The two series of **inner transition elements**, **lanthanoids** and **actinoids** constitute the ***f*-block** of the periodic table. With the successive filling of the inner orbitals, 4*f*, there is a gradual decrease in the atomic and ionic sizes of these metals along the series (**lanthanoid contraction**). This has far reaching consequences in the chemistry of the elements succeeding them. Lanthanum and all the lanthanoids are rather soft white metals. They react easily with water to give solutions giving +3 ions. The principal oxidation state is +3, although +4 and +2 oxidation states are also exhibited by some occasionally. The chemistry of the **actinoids** is more complex in view of their ability to exist in different oxidation states. Furthermore, many of the actinoid elements are radioactive which make the study of these elements rather difficult.

There are many useful applications of the *d*- and *f*-block elements and their compounds, notable among them being in varieties of steels, catalysts, complexes, organic syntheses, etc.

## Exercises

**4.1** Write down the electronic configuration of:

(i) $Cr^{3+}$ (iii) $Cu^{+}$ (v) $Co^{2}$+ (vii) $Mn^{2+}$
(ii) $Pm^{3+}$ (iv) $Ce^{4+}$ (vi) $Lu^{2+}$ (viii) $Th^{4+}$

**4.2** Why are $Mn^{2+}$ compounds more stable than $Fe^{2+}$ towards oxidation to their +3 state?

**4.3** Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?

**4.4** To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.

**4.5** What may be the stable oxidation state of the transition element with the following *d* electron configurations in the ground state of their atoms : $3d^3$, $3d^5$, $3d^8$ and $3d^4$?

**4.6** Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

**4.7** What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

**4.8** What are the characteristics of the transition elements and why are they called transition elements? Which of the *d*-block elements may not be regarded as the transition elements?

**4.9** In what way is the electronic configuration of the transition elements different from that of the non transition elements?

**4.10** What are the different oxidation states exhibited by the lanthanoids?

**4.11** Explain giving reasons:

(i) Transition metals and many of their compounds show paramagnetic behaviour.
(ii) The enthalpies of atomisation of the transition metals are high.
(iii) The transition metals generally form coloured compounds.
(iv) Transition metals and their many compounds act as good catalyst.

**4.12** What are interstitial compounds? Why are such compounds well known for transition metals?

**4.13** How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples.

**4.14** Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?

**4.15** Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:

(i) iodide (ii) iron(II) solution and (iii) $H_2S$

**4.16** Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions (ii) $SO_2$ and (iii) oxalic acid? Write the ionic equations for the reactions.

**4.17** For $M^{2+}/M$ and $M^{3+}/M^{2+}$ systems the $E^o$ values for some metals are as follows:

| | | | |
|---|---|---|---|
| $Cr^{2+}/Cr$ | -0.9V | $Cr^{3}/Cr^{2+}$ | -0.4 V |
| $Mn^{2+}/Mn$ | -1.2V | $Mn^{3+}/Mn^{2+}$ | +1.5 V |
| $Fe^{2+}/Fe$ | -0.4V | $Fe^{3+}/Fe^{2+}$ | +0.8 V |

Use this data to comment upon:

(i) the stability of $Fe^{3+}$ in acid solution as compared to that of $Cr^{3+}$ or $Mn^{3+}$ and

(ii) the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

**4.18** Predict which of the following will be coloured in aqueous solution? $Ti^{3+}$, $V^{3+}$, $Cu^{+}$, $Sc^{3+}$, $Mn^{2+}$, $Fe^{3+}$ and $Co^{2+}$. Give reasons for each.

**4.19** Compare the stability of +2 oxidation state for the elements of the first transition series.

**4.20** Compare the chemistry of actinoids with that of the lanthanoids with special reference to:

(i) electronic configuration

(ii) atomic and ionic sizes and

(iii) oxidation state

(iv) chemical reactivity.

**4.21** How would you account for the following:

(i) Of the $d^4$ species, $Cr^{2+}$ is strongly reducing while manganese(III) is strongly oxidising.

(ii) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.

(iii) The $d^1$ configuration is very unstable in ions.

**4.22** What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.

**4.23** Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

**4.24** Calculate the number of unpaired electrons in the following gaseous ions: $Mn^{3+}$, $Cr^{3+}$, $V^{3+}$ and $Ti^{3+}$. Which one of these is the most stable in aqueous solution?

**4.25** Give examples and suggest reasons for the following features of the transition metal chemistry:

(i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.

(ii) A transition metal exhibits highest oxidation state in oxides and fluorides.

(iii) The highest oxidation state is exhibited in oxoanions of a metal.

**4.26** Indicate the steps in the preparation of:

(i) $K_2Cr_2O_7$ from chromite ore.

(ii) $KMnO_4$ from pyrolusite ore.

**4.27** What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.

**4.28** What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements : 29, 59, 74, 95, 102, 104.

**4.29** The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

**4.30** Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.

**4.31** Use Hund's rule to derive the electronic configuration of $Ce^{3+}$ ion, and calculate its magnetic moment on the basis of 'spin-only' formula.

**4.32** Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configurations of these elements.

**4.33** Compare the chemistry of the actinoids with that of lanthanoids with reference to:

(i) electronic configuration (ii) oxidation states and (iii) chemical reactivity.

**4.34** Write the electronic configurations of the elements with the atomic numbers 61, 91, 101, and 109.

**4.35** Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points:

(i) electronic configurations (ii) oxidation states (iii) ionisation enthalpies and (iv) atomic sizes.

**4.36** Write down the number of 3d electrons in each of the following ions: $Ti^{2+}$, $V^{2+}$, $Cr^{3+}$, $Mn^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$. Indicate how would you expect the five 3d orbitals to be occupied for these hydrated ions (octahedral).

**4.37** Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.

**4.38** What can be inferred from the magnetic moment values of the following complex species ?

| Example | Magnetic Moment (BM) |
|---|---|
| $K_4[Mn(CN)_6)$ | 2.2 |
| $[Fe(H_2O)_6]^{2+}$ | 5.3 |
| $K_2[MnCl_4]$ | 5.9 |

## Answers to Some Intext Questions

**4.1** Silver (Z = 47) can exhibit +2 oxidation state wherein it will have incompletely filled *d*-orbitals (4*d*), hence a transition element.

**4.2** In the formation of metallic bonds, no eletrons from 3*d*-orbitals are involved in case of zinc, while in all other metals of the 3*d* series, electrons from the *d*-orbitals are always involved in the formation of metallic bonds.

**4.3** Manganese (Z = 25), as its atom has the maximum number of unpaired electrons.

**4.5** Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3*d*-configurations (e.g., $d^0$, $d^5$, $d^{10}$ are exceptionally stable).

**4.6** Because of small size and high electronegativity oxygen or fluorine can oxidise the metal to its highest oxidation state.

**4.7** $Cr^{2+}$ is stronger reducing agent than $Fe^{2+}$

Reason: $d^4 \rightarrow d^3$ occurs in case of $Cr^{2+}$ to $Cr^{3+}$

But $d^6 \rightarrow d^5$ occurs in case of $Fe^{2+}$ to $Fe^{3+}$

In a medium (like water) $d^3$ is more stable as compared to $d^5$ *(see CFSE)*

**4.9** $Cu^+$ in aqueous solution underoes disproportionation, i.e.,

$2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$

The $E^0$ value for this is favourable.

**4.10** The 5*f* electrons are more effectively shielded from nuclear charge. In other words the 5*f* electrons themselves provide poor shielding from element to element in the series.

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# Unit 5

# Coordination Compounds

## Objectives

After studying this Unit, you will be able to

- appreciate the postulates of Werner's theory of coordination compounds;
- know the meaning of the terms: coordination entity, central atom/ion, ligand, coordination number, coordination sphere, coordination polyhedron, oxidation number, homoleptic and heteroleptic;
- learn the rules of nomenclature of coordination compounds;
- write the formulas and names of mononuclear coordination compounds;
- define different types of isomerism in coordination compounds;
- understand the nature of bonding in coordination compounds in terms of the Valence Bond and Crystal Field theories;
- appreciate the importance and applications of coordination compounds in our day to day life.

*Coordination Compounds are the backbone of modern inorganic and bio–inorganic chemistry and chemical industry.*

In the previous Unit we learnt that the transition metals form a large number of **complex compounds** in which the metal atoms are bound to a number of anions or neutral molecules by sharing of electrons. In modern terminology such compounds are called **coordination compounds**. The chemistry of coordination compounds is an important and challenging area of modern inorganic chemistry. New concepts of chemical bonding and molecular structure have provided insights into the functioning of these compounds as vital components of biological systems. Chlorophyll, haemoglobin and vitamin $B_{12}$ are coordination compounds of magnesium, iron and cobalt respectively. Variety of metallurgical processes, industrial catalysts and analytical reagents involve the use of coordination compounds. Coordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

## 5.1 Werner's Theory of Coordination Compounds

**Alfred Werner** (1866-1919), a Swiss chemist was the first to formulate his ideas about the structures of coordination compounds. He prepared and characterised a large number of coordination compounds and studied their physical and chemical behaviour by simple experimental techniques. Werner proposed the concept of a **primary valence** and a **secondary valence** for a metal ion. Binary compounds such as $CrCl_3$, $CoCl_2$ or $PdCl_2$ have primary valence of 3, 2 and 2 respectively. In a series of compounds of cobalt(III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution.

| | | | |
|---|---|---|---|
| 1 mol | $CoCl_3.6NH_3$ (Yellow) | gave | 3 mol AgCl |
| 1 mol | $CoCl_3.5NH_3$ (Purple) | gave | 2 mol AgCl |
| 1 mol | $CoCl_3.4NH_3$ (Green) | gave | 1 mol AgCl |
| 1 mol | $CoCl_3.4NH_3$ (Violet) | gave | 1 mol AgCl |

These observations, together with the results of conductivity measurements in solution can be explained if (i) six groups in all, either chloride ions or ammonia molecules or both, remain bonded to the cobalt ion during the reaction and (ii) the compounds are formulated as shown in Table 5.1, where the atoms within the square brackets form a single entity which does not dissociate under the reaction conditions. Werner proposed the term **secondary valence** for the number of groups bound directly to the metal ion; in each of these examples the secondary valences are six.

**Table 5.1: Formulation of Cobalt(III) Chloride-Ammonia Complexes**

| Colour | Formula | Solution conductivity corresponds to |
|---|---|---|
| Yellow | $[Co(NH_3)_6]^{3+}3Cl^-$ | 1:3 electrolyte |
| Purple | $[CoCl(NH_3)_5]^{2+}2Cl^-$ | 1:2 electrolyte |
| Green | $[CoCl_2(NH_3)_4]^+Cl^-$ | 1:1 electrolyte |
| Violet | $[CoCl_2(NH_3)_4]^+Cl^-$ | 1:1 electrolyte |

Note that the last two compounds in Table 5.1 have identical empirical formula, $CoCl_3.4NH_3$, but distinct properties. Such compounds are termed as isomers. Werner in 1898, propounded his theory of coordination compounds. The main postulates are:

1. In coordination compounds metals show two types of linkages (valences)-primary and secondary.
2. The primary valences are normally ionisable and are satisfied by negative ions.
3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
4. The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

In modern formulations, such spatial arrangements are called coordination *polyhedra*. The species within the square bracket are coordination entities or complexes and the ions outside the square bracket are called counter ions.

He further postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals. Thus, $[Co(NH_3)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$ and $[CoCl_2(NH_3)_4]^+$ are octahedral entities, while $[Ni(CO)_4]$ and $[PtCl_4]^{2-}$ are tetrahedral and square planar, respectively.

**Example 5.1**

On the basis of the following observations made with aqueous solutions, assign secondary valences to metals in the following compounds:

| Formula | Moles of AgCl precipitated per mole of the compounds with excess $AgNO_3$ |
|---|---|
| (i) $PdCl_2.4NH_3$ | 2 |
| (ii) $NiCl_2.6H_2O$ | 2 |
| (iii) $PtCl_4.2HCl$ | 0 |
| (iv) $CoCl_3.4NH_3$ | 1 |
| (v) $PtCl_2.2NH_3$ | 0 |

**Solution**

(i) Secondary 4 (ii) Secondary 6
(iii) Secondary 6 (iv) Secondary 6 (v) Secondary 4

***Difference between a double salt and a complex***

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, they differ in the fact that double salts such as carnallite, $KCl.MgCl_2.6H_2O$, Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, potash alum, $KAl(SO_4)_2.12H_2O$, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as $[Fe(CN)_6]^{4-}$ of $K_4[Fe(CN)_6]$ do not dissociate into $Fe^{2+}$ and $CN^-$ ions.

(1866-1919)

**Werner** was born on December 12, 1866, in Mülhouse, a small community in the French province of Alsace. His study of chemistry began in Karlsruhe (Germany) and continued in Zurich (Switzerland), where in his doctoral thesis in 1890, he explained the difference in properties of certain nitrogen containing organic substances on the basis of isomerism. He extended vant Hoff's theory of tetrahedral carbon atom and modified it for nitrogen. Werner showed optical and electrical differences between complex compounds based on physical measurements. In fact, Werner was the first to discover optical activity in certain coordination compounds.

He, at the age of 29 years became a full professor at Technische Hochschule in Zurich in 1895. Alfred Werner was a chemist and educationist. His accomplishments included the development of the theory of coordination compounds. This theory, in which Werner proposed revolutionary ideas about how atoms and molecules are linked together, was formulated in a span of only three years, from 1890 to 1893. The remainder of his career was spent gathering the experimental support required to validate his new ideas. Werner became the first Swiss chemist to win the Nobel Prize in 1913 for his work on the linkage of atoms and the coordination theory.

## 5.2 Definitions of Some Important Terms Pertaining to Coordination Compounds

### (a) Coordination entity

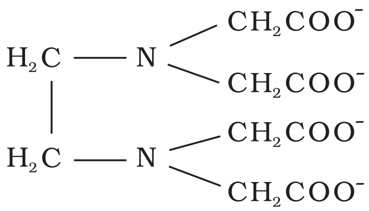
A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example, $[CoCl_3(NH_3)_3]$ is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are $[Ni(CO)_4]$, $[PtCl_2(NH_3)_2]$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$.

### (b) Central atom/ion

In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion. For example, the central atom/ion in the coordination entities: $[NiCl_2(H_2O)_4]$, $[CoCl(NH_3)_5]^{2+}$ and $[Fe(CN)_6]^{3-}$ are $Ni^{2+}$, $Co^{3+}$ and $Fe^{3+}$, respectively. These central atoms/ions are also referred to as **Lewis acids**.

### (c) Ligands

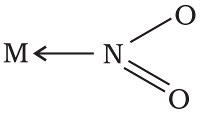
The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as $Cl^-$, small molecules such as $H_2O$ or $NH_3$, larger molecules such as $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or even macromolecules, such as proteins.



When a ligand is bound to a metal ion through a single donor atom, as with $Cl^-$, $H_2O$ or $NH_3$, the ligand is said to be **unidentate.** When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane-1,2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be **didentate** and when several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$, the ligand is said to be **polydentate**. Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

When a di- or polydentate ligand uses its two or more donor atoms simultaneously to bind a single metal ion, it is said to be a **chelate** ligand. The number of such ligating groups is called the **denticity** of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands. Ligand which has two different donor atoms and either of the two ligetes in the complex is called **ambidentate ligand**. Examples of such ligands are the $NO_2^-$ and $SCN^-$ ions. $NO_2^-$ ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion.

Similarly, $SCN^-$ ion can coordinate through the sulphur or nitrogen atom.



nitrito-N

$M \leftarrow O - N = O$

nitrito-O

$M \leftarrow SCN$ thiocyanato-S

$M \leftarrow NCS$ thiocyanato-N

### (d) Coordination number

The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. For example, in the complex ions, $[PtCl_6]^{2-}$ and $[Ni(NH_3)_4]^{2+}$, the coordination number of Pt and Ni are 6 and 4 respectively. Similarly, in the complex ions, $[Fe(C_2O_4)_3]^{3-}$ and $[Co(en)_3]^{3+}$, the coordination number of both, Fe and Co, is 6 because $C_2O_4^{2-}$ and en (ethane-1,2-diamine) are didentate ligands.

It is important to note here that coordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion. Pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.

### *(e) Coordination sphere*

The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the **coordination sphere**. The ionisable groups are written outside the bracket and are called counter ions. For example, in the complex $K_4[Fe(CN)_6]$, the coordination sphere is $[Fe(CN)_6]^{4-}$ and the counter ion is $K^+$.

### *(f) Coordination polyhedron*

The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. For example, $[Co(NH_3)_6]^{3+}$ is octahedral, $[Ni(CO)_4]$ is tetrahedral and $[PtCl_4]^{2-}$ is square planar. Fig. 5.1 shows the shapes of different coordination polyhedra.

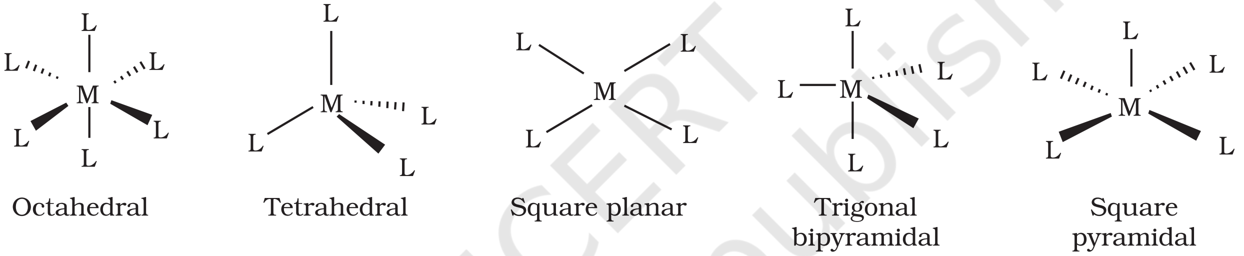


***Fig. 5.1:*** *Shapes of different coordination polyhedra. M represents the central atom/ion and L, a unidentate ligand.*

### *(g) Oxidation number of central atom*

The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity. For example, oxidation number of copper in $[Cu(CN)_4]^{3-}$ is +1 and it is written as Cu(I).

### *(h) Homoleptic and heteroleptic complexes*

Complexes in which a metal is bound to only one kind of donor groups, *e.g.*, $[Co(NH_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups, *e.g.*, $[Co(NH_3)_4Cl_2]^+$, are known as heteroleptic.

## 5.3 Nomenclature of Coordination Compounds

Nomenclature is important in Coordination Chemistry because of the need to have an unambiguous method of describing formulas and writing systematic names, particularly when dealing with isomers. The formulas and names adopted for coordination entities are based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC).

### 5.3.1 Formulas of Mononuclear Coordination Entities

The formula of a compound is a shorthand tool used to provide basic information about the constitution of the compound in a concise and convenient manner. Mononuclear coordination entities contain a single central metal atom. The following rules are applied while writing the formulas:

(i) The central atom is listed first.

(ii) The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.

(iii) Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.

(iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.

(v) There should be no space between the ligands and the metal within a coordination sphere.

(vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[Co(CN)_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, etc.

(vii) The charge of the cation(s) is balanced by the charge of the anion(s).

***Note:*** *The 2004 IUPAC draft recommends that ligands will be sorted alphabetically, irrespective of charge.*

### 5.3.2 Naming of Mononuclear Coordination Compounds

The names of coordination compounds are derived by following the principles of additive nomenclature. Thus, the groups that surround the central atom must be identified in the name. They are listed as prefixes to the name of the central atom along with any appropriate multipliers. The following rules are used when naming coordination compounds:

(i) The cation is named first in both positively and negatively charged coordination entities.

(ii) The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula).

(iii) Names of the anionic ligands end in –o, those of neutral and cationic ligands are the same except aqua for $H_2O$, ammine for $NH_3$, carbonyl for CO and nitrosyl for NO. While writing the formula of coordination entity, these are enclosed in brackets ( ).

(iv) Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, *bis*, *tris*, *tetrakis* are used, the ligand to which they refer being placed in parentheses. For example, $[NiCl_2(PPh_3)_2]$ is named as dichloridobis(triphenylphosphine)nickel(II).

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

(vi) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate. For example, Co in a complex anion, $\left[Co(SCN)_4\right]^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions, *e.g.*, ferrate for Fe.

**Note**: *The 2004 IUPAC draft recommends that anionic ligands will end with–ido so that chloro would become chlorido, etc.*

(vii) The neutral complex molecule is named similar to that of the complex cation.

The following examples illustrate the nomenclature for coordination compounds.

**1.** $[Cr(NH_3)_3(H_2O)_3]Cl_3$ is named as:
triamminetriaquachromium(III) chloride

*Explanation*: The complex ion is inside the square bracket, which is a cation. The amine ligands are named before the aqua ligands according to alphabetical order. Since there are three chloride ions in the compound, the charge on the complex ion must be +3 (since the compound is electrically neutral). From the charge on the complex ion and the charge on the ligands, we can calculate the oxidation number of the metal. In this example, all the ligands are neutral molecules. Therefore, the oxidation number of chromium must be the same as the charge of the complex ion, +3.

**2.** $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$ is named as:
tris(ethane-1,2–diamine)cobalt(III) sulphate

*Explanation*: The sulphate is the counter anion in this molecule. Since it takes 3 sulphates to bond with two complex cations, the charge on each complex cation must be +3. Further, ethane-1,2–diamine is a neutral molecule, so the oxidation number of cobalt in the complex ion must be +3. *Remember that you never have to indicate the number of cations and anions in the name of an ionic compound.*

*Notice how the name of the metal differs in cation and anion even though they contain the same metal ions.*

**3.** $[Ag(NH_3)_2][Ag(CN)_2]$ is named as:
diamminesilver(I) dicyanidoargentate(I)

**Example 5.2** Write the formulas for the following coordination compounds:

(a) Tetraammineaquachloridocobalt(III) chloride
(b) Potassium tetrahydroxidozincate(II)
(c) Potassium trioxalatoaluminate(III)
(d) Dichloridobis(ethane-1,2-diamine)cobalt(III)
(e) Tetracarbonylnickel(0)

**Solution** (a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ (b) $K_2[Zn(OH)_4]$ (c) $K_3[Al(C_2O_4)_3]$
(d) $[CoCl_2(en)_2]^+$ (e) $[Ni(CO)_4]$

**Example 5.3** Write the IUPAC names of the following coordination compounds:

(a) $[Pt(NH_3)_2Cl(NO_2)]$ (b) $K_3[Cr(C_2O_4)_3]$ (c) $[CoCl_2(en)_2]Cl$
(d) $[Co(NH_3)_5(CO_3)]Cl$ (e) $Hg[Co(SCN)_4]$

**Solution** (a) Diamminechloridonitrito-N-platinum(II)
(b) Potassium trioxalatochromate(III)
(c) Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
(d) Pentaamminecarbonatocobalt(III) chloride
(e) Mercury (I) tetrathiocyanato-S-cobaltate(III)

## Intext Questions

**5.1** Write the formulas for the following coordination compounds:

- (i) Tetraamminediaquacobalt(III) chloride
- (ii) Potassium tetracyanidonickelate(II)
- (iii) Tris(ethane–1,2–diamine) chromium(III) chloride
- (iv) Amminebromidochloridonitrito-N-platinate(II)
- (v) Dichloridobis(ethane–1,2–diamine)platinum(IV) nitrate
- (vi) Iron(III) hexacyanidoferrate(II)

**5.2** Write the IUPAC names of the following coordination compounds:

(i) $[Co(NH_3)_6]Cl_3$  (ii) $[Co(NH_3)_5Cl]Cl_2$  (iii) $K_3[Fe(CN)_6]$

(iv) $K_3[Fe(C_2O_4)_3]$  (v) $K_2[PdCl_4]$  (vi) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

## 5.4 Isomerism in Coordination Compounds

Isomers are two or more compounds that have the same chemical formula but a different arrangement of atoms. Because of the different arrangement of atoms, they differ in one or more physical or chemical properties. Two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided.

***(a) Stereoisomerism***

(i) Geometrical isomerism  (ii) Optical isomerism

***(b) Structural isomerism***

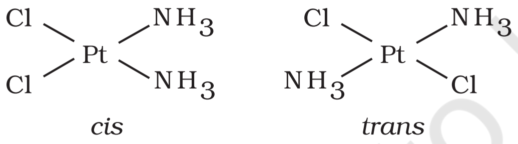
(i) Linkage isomerism  (ii) Coordination isomerism

(iii) Ionisation isomerism  (iv) Solvate isomerism

Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. Structural isomers have different bonds. A detailed account of these isomers are given below.

### 5.4.1 Geometric Isomerism

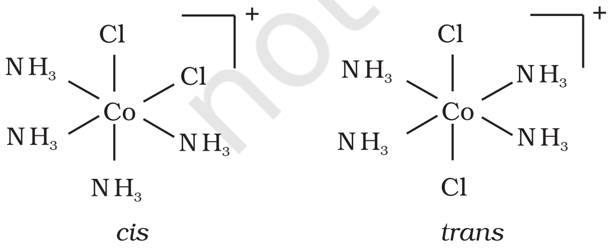
This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a ***cis*** isomer, or opposite to each other in a ***trans*** isomer as depicted in Fig. 5.2.



*cis*  *trans*

***Fig. 5.2:*** *Geometrical isomers (cis and trans) of Pt $[NH_3)_2Cl_2]$*

Other square planar complex of the type MABXL (where A, B, X, L are unidentates) shows three isomers-two *cis* and one *trans*. You may attempt to draw these structures. Such isomerism is not possible for a tetrahedral geometry but similar behaviour is possible in octahedral complexes of formula $[MX_2L_4]$ in which the two ligands X may be oriented ***cis*** or ***trans*** to each other (Fig. 5.3).



*cis*  *trans*

***Fig. 5.3:*** *Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]^+$*

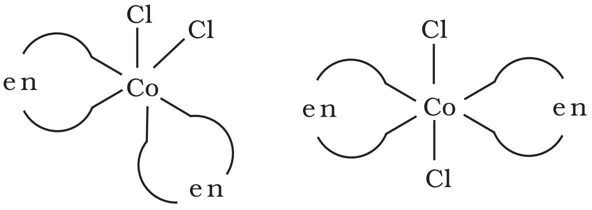
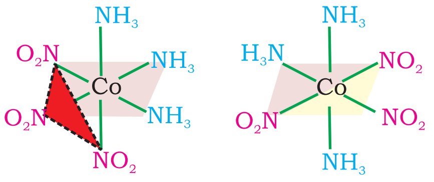


**Fig. 5.4:** *Geometrical isomers (cis and trans) of [CoCl$_2$(en)$_2$]*

This type of isomerism also arises when didentate ligands L – L [*e.g.*, $NH_2\ CH_2\ CH_2\ NH_2$ (en)] are present in complexes of formula $[MX_2(L–L)_2]$ (Fig. 5.4).

Another type of geometrical isomerism occurs in octahedral coordination entities of the type $[Ma_3b_3]$ like $[Co(NH_3)_3(NO_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the **facial (fac) isomer**. When the positions are around the meridian of the octahedron, we get the **meridional (mer) isomer** (Fig. 5.5).



*fac–* *mer–*

**Fig. 5.5** *The facial (fac) and meridional (mer) isomers of [Co(NH$_3$)$_3$(NO$_2$)$_3$]*

**Example 5.4**

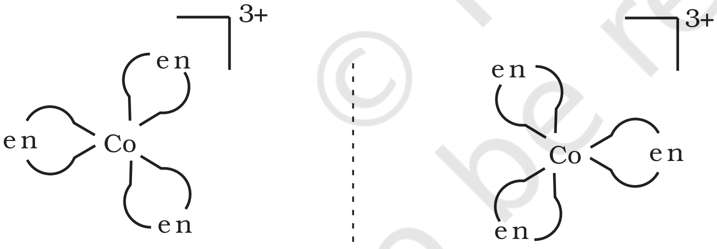
Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

**Solution**

Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other.

### 5.4.2 Optical Isomerism

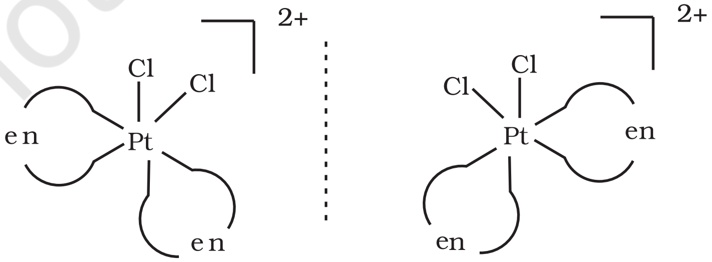
Optical isomers are mirror images that cannot be superimposed on one another. These are called as *enantiomers*. The molecules or ions that cannot be superimposed are called *chiral*. The two forms are called *dextro (d)* and *laevo (l)* depending upon the direction they rotate the plane of polarised light in a polarimeter (*d* rotates to the right, *l* to the left). Optical isomerism is common in octahedral complexes involving didentate ligands (Fig. 5.6).



*dextro* mirror *laevo*

**Fig.5.6:** Optical isomers (d and l) of $[Co(en)_3]^{3+}$

In a coordination entity of the type $[PtCl_2(en)_2]^{2+}$, only the *cis*-isomer shows optical activity (Fig. 5.7).

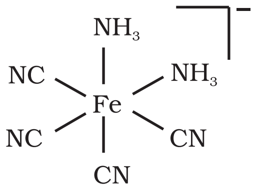


*dextro* mirror *laevo*

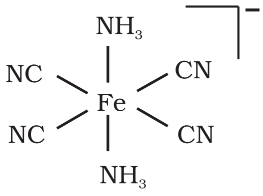
**Fig.5.7** *Optical isomers (d and l) of cis-[PtCl$_2$(en)$_2$]$^{2+}$*

**Example 5.5** Draw structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$

**Solution**



*cis*

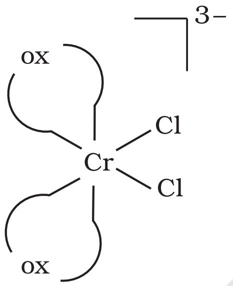


*trans*

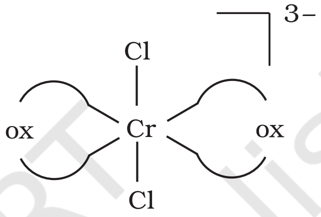
**Example 5.6** Out of the following two coordination entities which is chiral (optically active)?

(a) *cis*-$[CrCl_2(ox)_2]^{3-}$ (b) *trans*-$[CrCl_2(ox)_2]^{3-}$

**Solution** The two entities are represented as



(a) *cis* – $[CrCl_2(ox)_2]^{3-}$



(b) *trans* – $[CrCl_2(ox)_2]^{3-}$

Out of the two, (a) *cis* - $[CrCl_2(ox)_2]^{3-}$ is chiral (optically active).

### 5.4.3 Linkage Isomerism

Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, $NCS^-$, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN. Jørgensen discovered such behaviour in the complex $[Co(NH_3)_5(NO_2)]Cl_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen (–ONO), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($–NO_2$).

### 5.4.4 Coordination Isomerism

This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. An example is provided by $[Co(NH_3)_6][Cr(CN)_6]$, in which the $NH_3$ ligands are bound to $Co^{3+}$ and the $CN^-$ ligands to $Cr^{3+}$. In its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$, the $NH_3$ ligands are bound to $Cr^{3+}$ and the $CN^-$ ligands to $Co^{3+}$.

### 5.4.5 Ionisation Isomerism

This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionisation isomers $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$.

### 5.4.6 Solvate Isomerism

This form of isomerism is known as **'hydrate isomerism'** in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent moleculesin the crystal lattice. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

### Intext Questions

**5.3** Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

(i) $K[Cr(H_2O)_2(C_2O_4)_2]$
(ii) $[Co(en)_3]Cl_3$
(iii) $[Co(NH_3)_5(NO_2)](NO_3)_2$
(iv) $[Pt(NH_3)(H_2O)Cl_2]$

**5.4** Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$ are ionisation isomers.

## 5.5 Bonding in Coordination Compounds

Werner was the first to describe the bonding features in coordination compounds. But his theory could not answer basic questions like:

(i) Why only certain elements possess the remarkable property of forming coordination compounds?
(ii) Why the bonds in coordination compounds have directional properties?
(iii) Why coordination compounds have characteristic magnetic and optical properties?

Many approaches have been put forth to explain the nature of bonding in coordination compounds *viz.* Valence Bond Theory (VBT), Crystal Field Theory (CFT), **Ligand Field Theory** (LFT) and Molecular Orbital Theory (MOT). We shall focus our attention on elementary treatment of the application of VBT and CFT to coordination compounds.

### 5.5.1 Valence Bond Theory

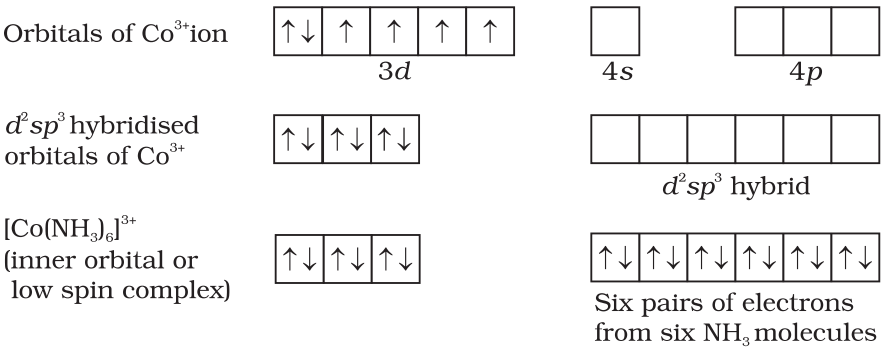
According to this theory, the metal atom or ion under the influence of ligands can use its (n-1)*d*, n*s*, n*p* or n*s*, n*p*, n*d* orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on (Table 5.2). These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding. This is illustrated by the following examples.

**Table 5.2: Number of Orbitals and Types of Hybridisations**

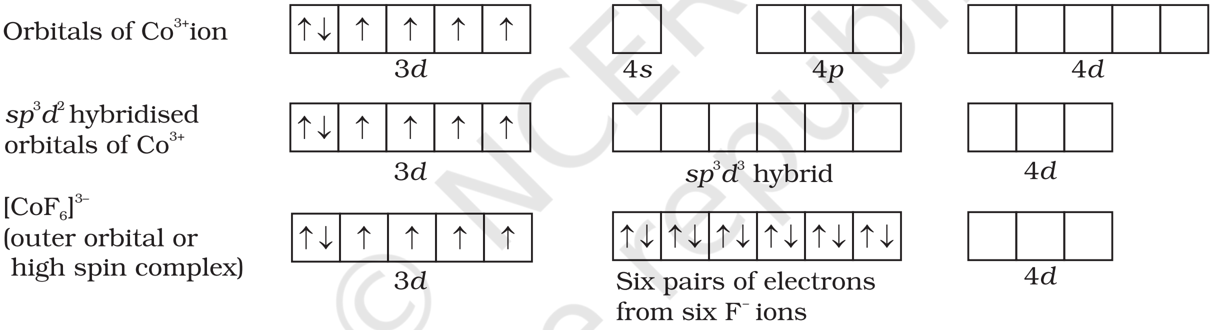
| Coordination number | Type of hybridisation | Distribution of hybrid orbitals in space |
|---|---|---|
| 4 | $sp^3$ | Tetrahedral |
| 4 | $dsp^2$ | Square planar |
| 5 | $sp^3d$ | Trigonal bipyramidal |
| 6 | $sp^3d^2$ | Octahedral |
| 6 | $d^2sp^3$ | Octahedral |

It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory.

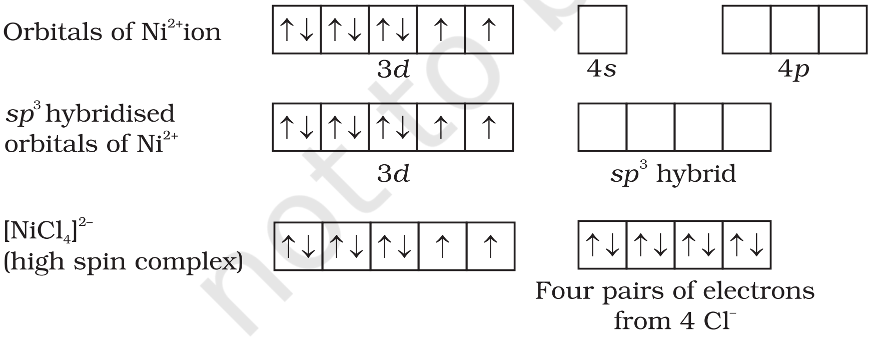
In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration $3d^6$. The hybridisation scheme is as shown in diagram.



Six pairs of electrons, one from each $NH_3$ molecule, occupy the six hybrid orbitals. Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. In the formation of this complex, since the inner *d* orbital (3*d*) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called an **inner orbital** or **low spin** or **spin paired complex**. The paramagnetic octahedral complex, $[CoF_6]^{3-}$ uses outer orbital (4*d* ) in hybridisation ($sp^3d^2$). It is thus called **outer orbital** or **high spin** or **spin free complex**. Thus:

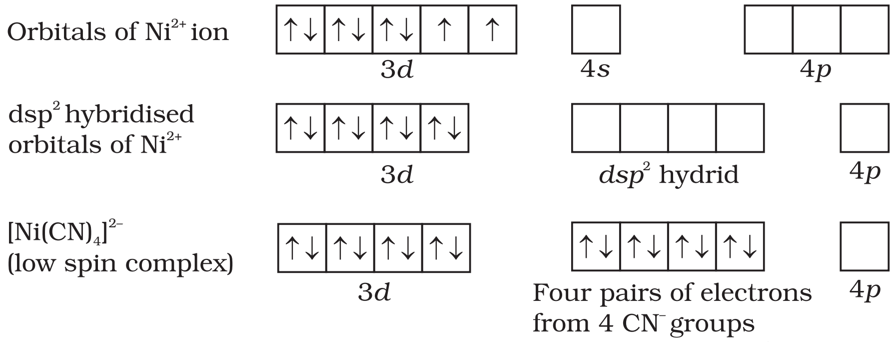


In tetrahedral complexes one *s* and three *p* orbitals are hybridised to form four equivalent orbitals oriented tetrahedrally. This is illustrated below for $[NiCl_4]^{2-}$. Here nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in diagram.



Each $Cl^-$ ion donates a pair of electrons. The compound is paramagnetic since it contains two unpaired electrons. Similarly, $[Ni(CO)_4]$ has tetrahedral geometry but is diamagnetic since nickel is in zero oxidation state and contains no unpaired electron.

In the square planar complexes, the hybridisation involved is $dsp^2$. An example is $[Ni(CN)_4]^{2-}$. Here nickel is in +2 oxidation state and has the electronic configuration $3d^8$. The hybridisation scheme is as shown in diagram:



Each of the hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electron.

It is important to note that the hybrid orbitals do not actually exist. In fact, hybridisation is a mathematical manipulation of wave equation for the atomic orbitals involved.

### 5.5.2 Magnetic Properties of Coordination Compounds

The magnetic moment of coordination compounds can be measured by the magnetic susceptibility experiments. The results can be used to obtain information about the number of unpaired electrons and hence structures adopted by metal complexes.

A critical study of the magnetic data of coordination compounds of metals of the first transition series reveals some complications. For metal ions with upto three electrons in the $d$ orbitals, like $Ti^{3+}$ ($d^1$); $V^{3+}$ ($d^2$); $Cr^{3+}$ ($d^3$); two vacant $d$ orbitals are available for octahedral hybridisation with $4s$ and $4p$ orbitals. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three $3d$ electrons are present, the required pair of $3d$ orbitals for octahedral hybridisation is not directly available (as a consequence of Hund's rule). Thus, for $d^4$ ($Cr^{2+}$, $Mn^{3+}$), $d^5$ ($Mn^{2+}$, $Fe^{3+}$), $d^6$ ($Fe^{2+}$, $Co^{3+}$) cases, a vacant pair of $d$ orbitals results only by pairing of $3d$ electrons which leaves two, one and zero unpaired electrons, respectively.

The magnetic data agree with maximum spin pairing in many cases, especially with coordination compounds containing $d^6$ ions. However, with species containing $d^4$ and $d^5$ ions there are complications. $[Mn(CN)_6]^{3-}$ has magnetic moment of two unpaired electrons while $[MnCl_6]^{3-}$ has a paramagnetic moment of four unpaired electrons. $[Fe(CN)_6]^{3-}$ has magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons. $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)_3]^{3-}$ is diamagnetic. This apparent anomaly is explained by valence bond theory in terms of formation of inner orbital and outer orbital coordination entities. $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are inner orbital complexes involving $d^2sp^3$ hybridisation, the former two complexes are paramagnetic and the latter diamagnetic. On the other hand, $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are outer orbital complexes involving $sp^3d^2$ hybridisation and are paramagnetic corresponding to four, five and four unpaired electrons.

**Example 5.7** The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion ?

**Solution** Since the coordination number of $Mn^{2+}$ ion in the complex ion is 4, it will be either tetrahedral ($sp^3$ hybridisation) or square planar ($dsp^2$ hybridisation). But the fact that the magnetic moment of the complex ion is 5.9 BM, it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the *d* orbitals.

### 5.5.3 Limitations of Valence Bond Theory

While the VB theory, to a larger extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following shortcomings:

(i) It involves a number of assumptions.
(ii) It does not give quantitative interpretation of magnetic data.
(iii) It does not explain the colour exhibited by coordination compounds.
(iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
(v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
(vi) It does not distinguish between weak and strong ligands.

### 5.5.4 Crystal Field Theory

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in case of anions or point dipoles in case of neutral molecules. The five *d* orbitals in an isolated gaseous metal atom/ion have same energy, *i.e.*, they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like $NH_3$ and $H_2O$) in a complex, it becomes asymmetrical and the degeneracy of the *d* orbitals is lifted. It results in splitting of the *d* orbitals. The pattern of splitting depends upon the nature of the crystal field. Let us explain this splitting in different crystal fields.

***(a) Crystal field splitting in octahedral coordination entities***

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal *d* orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal *d* orbital is directed towards the ligand than when it is away from the ligand. Thus, the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy; and the $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field. Thus, the degeneracy of the *d* orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, $t_{2g}$ set and two orbitals of higher energy, $e_g$ set. This splitting of the

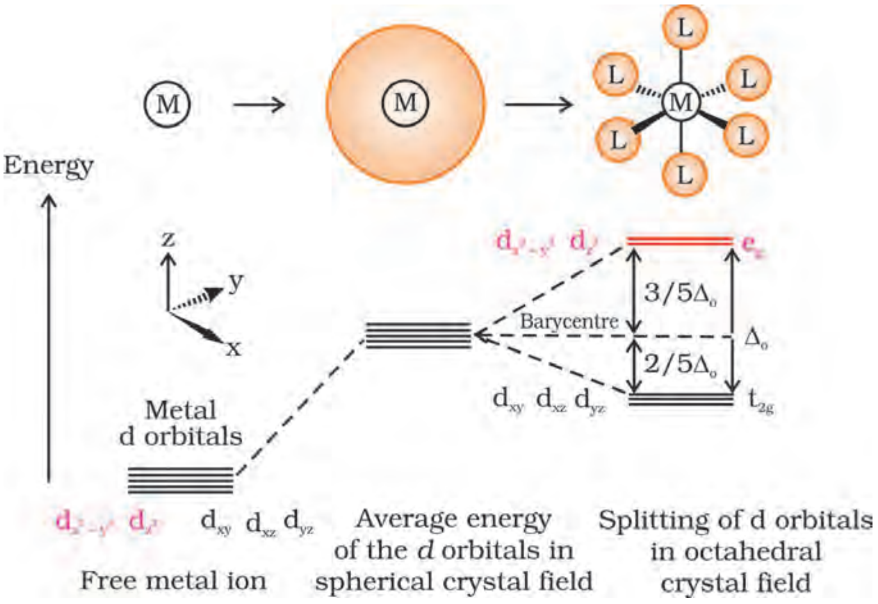


***Fig.5.8:*** *d orbital splitting in an octahedral crystal field*

degenerate levels due to the presence of ligands in a definite geometry is termed as **crystal field splitting** and the energy separation is denoted by $\Delta_o$ (the subscript o is for octahedral) (Fig.5.8). Thus, the energy of the two $e_g$ orbitals will increase by (3/5) $\Delta_o$ and that of the three $t_{2g}$ will decrease by $(2/5)\Delta_o$.

The crystal field splitting, $\Delta_o$, depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of *d* orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below:

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^-$$
$$< edta^{4-} < NH_3 < en < CN^- < CO$$

Such a series is termed as **spectrochemical series**. It is an experimentally determined series based on the absorption of light by complexes with different ligands. Let us assign electrons in the *d* orbitals of metal ion in octahedral coordination entities. Obviously, the single *d* electron occupies one of the lower energy $t_{2g}$ orbitals. In $d^2$ and $d^3$ coordination entities, the *d* electrons occupy the $t_{2g}$ orbitals singly in accordance with the Hund's rule. For $d^4$ ions, two possible patterns of electron distribution arise: (i) the fourth electron could either enter the $t_{2g}$ level and pair with an existing electron, or (ii) it could avoid paying the price of the pairing energy by occupying the $e_g$ level. Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, $\Delta_o$ and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two options are:

(i) If $\Delta_o$ < P, the fourth electron enters one of the $e_g$ orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o$ < P are known as *weak field ligands* and form high spin complexes.

(ii) If $\Delta_o$ > P, it becomes more energetically favourable for the fourth electron to occupy a $t_{2g}$ orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as *strong field ligands* and form low spin complexes.

Calculations show that $d^4$ to $d^7$ coordination entities are more stable for strong field as compared to weak field cases.

### *(b) Crystal field splitting in tetrahedral coordination entities*

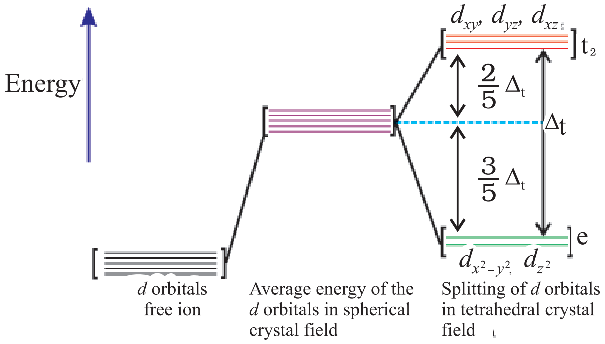


***Fig.5.9:** d orbital splitting in a tetrahedral crystal field.*

In tetrahedral coordination entity formation, the *d* orbital splitting (Fig. 5.9) is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\ \Delta_0$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed. The 'g' subscript is used for the octahedral and square planar complexes which have centre of symmetry. Since tetrahedral complexes lack symmetry, 'g' subscript is not used with energy levels.

## 5.5.5 Colour in Coordination Compounds

In the previous Unit, we learnt that one of the most distinctive properties of transition metal complexes is their wide range of colours. This means that some of the visible spectrum is being removed from white light as it passes through the sample, so the light that emerges is no longer white. The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over; if green light is absorbed by the complex, it appears red. Table 5.3 gives the relationship of the different wavelength absorbed and the colour observed.

**Table 5.3: Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities**

| Coordinaton entity | Wavelength of light absorbed (nm) | Colour of light absorbed | | Colour of coordination entity | |
|---|---|---|---|---|---|
| $[CoCl(NH_3)_5]^{2+}$ | 535 | Yellow | 🟨 | Violet | 🟪 |
| $[Co(NH_3)_5(H_2O)]^{3+}$ | 500 | Blue Green | 🟩 | Red | 🟥 |
| $[Co(NH_3)_6]^{3+}$ | 475 | Blue | 🟦 | Yellow Orange | 🟧 |
| $[Co(CN)_6]^{3-}$ | 310 | Ultraviolet | Not in visible region | Pale Yellow | 🟨 |
| $[Cu(H_2O)_4]^{2+}$ | 600 | Red | 🟥 | Blue | 🟦 |
| $[Ti(H_2O)_6]^{3+}$ | 498 | Blue Green | 🟩 | Violet | 🟪 |

The colour in the coordination compounds can be readily explained in terms of the crystal field theory. Consider, for example, the complex $[Ti(H_2O)_6]^{3+}$, which is violet in colour. This is an octahedral complex where the single electron ($Ti^{3+}$ is a $3d^1$ system) in the metal *d* orbital is in the $t_{2g}$ level in the ground state of the complex. The next higher state available for the electron is the empty $e_g$ level. If light corresponding to the energy of blue-green region is absorbed by the complex, it would excite the electron from $t_{2g}$ level to the $e_g$ level ($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$). Consequently, the complex appears violet in colour (Fig. 5.10). The crystal field theory attributes the colour of the coordination compounds to *d-d* transition of the electron.

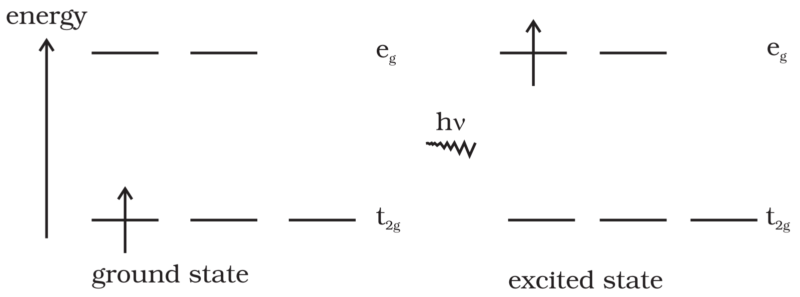


***Fig.5.10:** Transition of an electron in*

It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For example, removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4.5H_2O$ is blue in colour. The influence of the ligand on the colour of a complex may be illustrated by considering the $[Ni(H_2O)_6]^{2+}$ complex, which forms when nickel(II) chloride is dissolved in water. If the didentate ligand, ethane-1,2-diamine(en) is progressively added in the molar ratios en:Ni, 1:1, 2:1, 3:1, the following series of reactions and their associated colour changes occur:

$[Ni(H_2O)_6]^{2+}$ (aq) + en (aq) = $[Ni(H_2O)_4(en)]^{2+}$(aq) + $2H_2O$
green pale blue

$[Ni(H_2O)_4 (en)]^{2+}$(aq) + en (aq) = $[Ni(H_2O)_2(en)_2]^{2+}$(aq) + $2H_2O$
blue/purple

$[Ni(H_2O)_2(en)_2]^{2+}$(aq) + en (aq) = $[Ni(en)_3]^{2+}$(aq) + $2H_2O$
violet

This sequence is shown in Fig. 5.11.

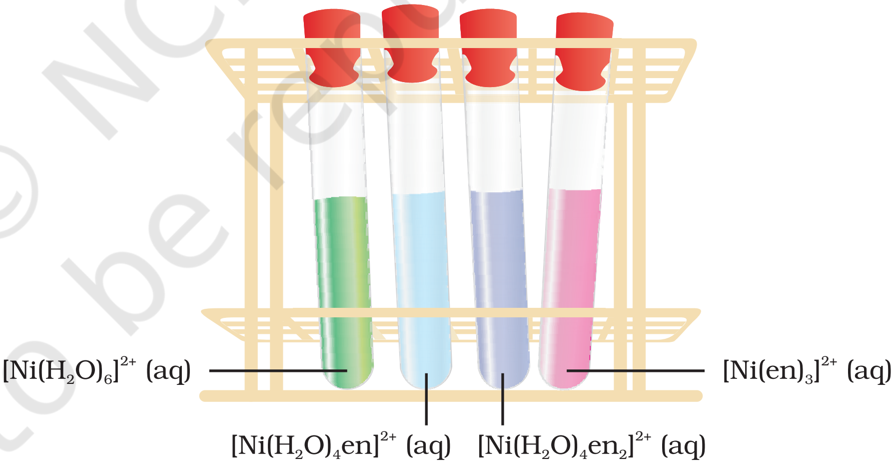


***Fig.5.11***
*Aqueous solutions of complexes of nickel(II) with an increasing number of ethane-1, 2-diamine ligands.*

### Colour of Some Gem Stones

The colours produced by electronic transitions within the *d* orbitals of a transition metal ion occur frequently in everyday life. Ruby [Fig.5.12(a)] is aluminium oxide ($Al_2O_3$) containing about 0.5-1% $Cr^{3+}$ ions ($d^3$), which are randomly distributed in positions normally occupied by $Al^{3+}$. We may view these chromium(III) species as octahedral chromium(III) complexes incorporated into the alumina lattice; *d–d* transitions at these centres give rise to the colour.

In emerald [Fig.5.12(b)], $Cr^{3+}$ ions occupy octahedral sites in the mineral beryl ($Be_3Al_2Si_6O_{18}$). The absorption bands seen in the ruby shift to longer wavelength, namely yellow-red and blue, causing emerald to transmit light in the green region.

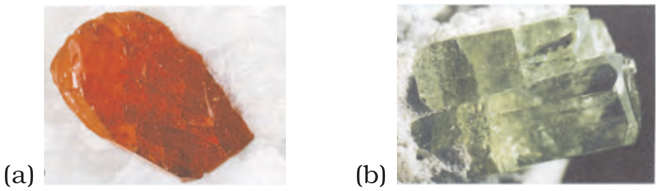


**Fig.5.12:** *(a) Ruby: this gemstone was found in marble from Mogok, Myanmar; (b) Emerald: this gemstone was found in Muzo, Columbia.*

### 5.5.6 Limitations of Crystal Field Theory

The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of coordination compounds to a large extent. However, from the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. The anionic ligands actually are found at the low end of the spectrochemical series. Further, it does not take into account the covalent character of bonding between the ligand and the central atom. These are some of the weaknesses of CFT, which are explained by ligand field theory (LFT) and molecular orbital theory which are beyond the scope of the present study.

### Intext Questions

**5.5** Explain on the basis of valence bond theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

**5.6** $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

**5.7** $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

**5.8** Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

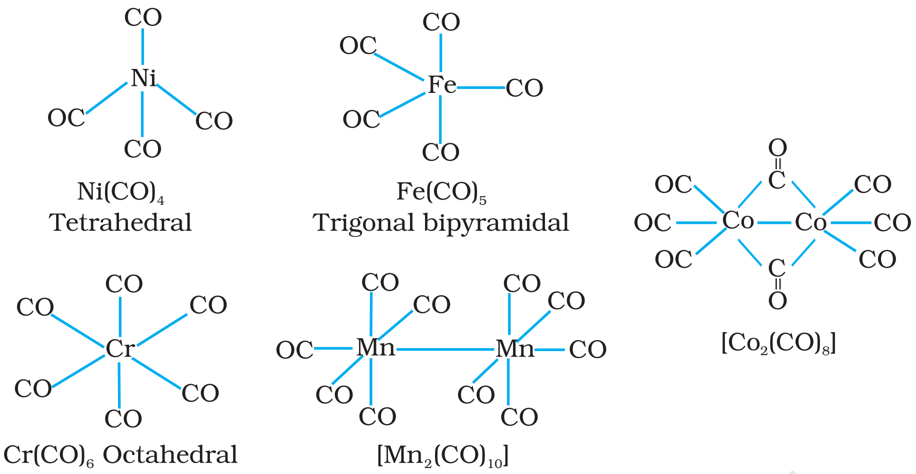
**5.9** Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.

**5.10** The hexaquo manganese(II) ion contains five unpaired electrons, while the hexacyanoion contains only one unpaired electron. Explain using Crystal Field Theory.

## 5.6 Bonding in Metal Carbonyls

The homoleptic carbonyls (compounds containing carbonyl ligands only) are formed by most of the transition metals. These carbonyls have simple, well defined structures. Tetracarbonylnickel(0) is tetrahedral, pentacarbonyliron(0) is trigonalbipyramidal while hexacarbonyl chromium(0) is octahedral.

Decacarbonyldimanganese(0) is made up of two square pyramidal $Mn(CO)_5$ units joined by a Mn – Mn bond. Octacarbonyldicobalt(0) has a Co – Co bond bridged by two CO groups (Fig.5.13).



$Ni(CO)_4$
Tetrahedral

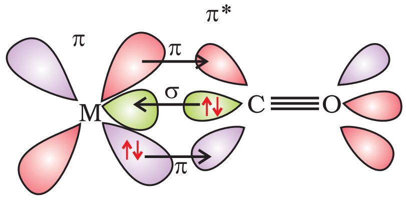
$Fe(CO)_5$
Trigonal bipyramidal

$[Co_2(CO)_8]$

$Cr(CO)_6$ Octahedral

$[Mn_2(CO)_{10}]$

***Fig. 5.13*** *Structures of some representative homoleptic metal carbonyls.*



Synergic bonding

***Fig. 5.14:*** *Example of synergic bonding interactions in a carbonyl complex.*

The metal-carbon bond in metal carbonyls possess both σ and π character. The M–C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–C π bond is formed by the donation of a pair of electrons from a filled *d* orbital of metal into the vacant antibonding π* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal (Fig.5.14).

## 5.7 Importance and Applications of Coordination Compounds

The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. These are described below:

- Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α–nitroso–β–naphthol, cupron, etc.
- Hardness of water is estimated by simple titration with $Na_2EDTA$. The $Ca^{2+}$ and $Mg^{2+}$ ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.
- Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc.
- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.

For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

- Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin $B_{12}$, cyanocobalamine, the anti–pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.
- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ than from a solution of simple metal ions.
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D–penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: *cis*–platin and related compounds.

## Summary

The **chemistry of coordination compounds** is an important and challenging area of modern inorganic chemistry. During the last fifty years, advances in this area, have provided development of new concepts and models of bonding and molecular structure, novel breakthroughs in **chemical industry** and vital insights into the functioning of critical components of **biological systems**.

The first systematic attempt at explaining the formation, reactions, structure and bonding of a coordination compound was made by **A. Werner**. His theory postulated the use of two types of **linkages** (**primary** and **secondary**) by a metal atom/ion in a coordination compound. In the modern language of chemistry these linkages are recognised as the ionisable (ionic) and non-ionisable (covalent) bonds, respectively. Using the property of isomerism, Werner predicted the geometrical shapes of a large number of coordination entities.

**The Valence Bond Theory (VBT)** explains with reasonable success, the formation, magnetic behaviour and geometrical shapes of coordination compounds. It, however, fails to provide a quantitative interpretation of magnetic behaviour and has nothing to say about the optical properties of these compounds.

**The Crystal Field Theory (CFT)** to coordination compounds is based on the effect of different crystal fields (provided by the ligands taken as point charges), on the degeneracy of *d* orbital energies of the central metal atom/ion. The splitting of the *d* orbitals provides different electronic arrangements in strong and weak crystal fields. The treatment provides for quantitative estimations of orbital separation energies, magnetic moments and spectral and stability parameters. However, the assumption that ligands consititute point charges creates many theoretical difficulties.

The metal–carbon bond in **metal carbonyls** possesses both σ and π character. The ligand to metal is σ bond and metal to ligand is π bond. This unique synergic bonding provides stability to metal carbonyls.

Coordination compounds are of great importance. These compounds provide critical insights into the functioning and structures of vital components of biological systems. Coordination compounds also find extensive applications in **metallurgical processes**, **analytical and medicinal chemistry**.

## Exercises

**5.1** Explain the bonding in coordination compounds in terms of Werner's postulates.

**5.2** $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of $Fe^{2+}$ ion but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of $Cu^{2+}$ ion. Explain why?

**5.3** Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

**5.4** What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

**5.5** Specify the oxidation numbers of the metals in the following coordination entities:

(i) $[Co(H_2O)(CN)(en)_2]^{2+}$
(ii) $[CoBr_2(en)_2]^{+}$
(iii) $[PtCl_4]^{2-}$
(iv) $K_3[Fe(CN)_6]$
(v) $[Cr(NH_3)_3Cl_3]$

**5.6** Using IUPAC norms write the formulas for the following:

(i) Tetrahydroxidozincate(II)
(ii) Potassium tetrachloridopalladate(II)
(iii) Diamminedichloridoplatinum(II)
(iv) Potassium tetracyanidonickelate(II)
(v) Pentaamminenitrito-O-cobalt(III)
(vi) Hexaamminecobalt(III) sulphate
(vii) Potassium tri(oxalato)chromate(III)
(viii) Hexaammineplatinum(IV)
(ix) Tetrabromidocuprate(II)
(x) Pentaamminenitrito-N-cobalt(III)

**5.7** Using IUPAC norms write the systematic names of the following:

(i) $[Co(NH_3)_6]Cl_3$
(ii) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$
(iii) $[Ti(H_2O)_6]^{3+}$
(iv) $[Co(NH_3)_4Cl(NO_2)]Cl$
(v) $[Mn(H_2O)_6]^{2+}$
(vi) $[NiCl_4]^{2-}$
(vii) $[Ni(NH_3)_6]Cl_2$
(viii) $[Co(en)_3]^{3+}$
(ix) $[Ni(CO)_4]$

**5.8** List various types of isomerism possible for coordination compounds, giving an example of each.

**5.9** How many geometrical isomers are possible in the following coordination entities?

(i) $[Cr(C_2O_4)_3]^{3-}$
(ii) $[Co(NH_3)_3Cl_3]$

**5.10** Draw the structures of optical isomers of:

(i) $[Cr(C_2O_4)_3]^{3-}$
(ii) $[PtCl_2(en)_2]^{2+}$
(iii) $[Cr(NH_3)_2Cl_2(en)]^{+}$

**5.11** Draw all the isomers (geometrical and optical) of:

(i) $[CoCl_2(en)_2]^+$ (ii) $[Co(NH_3)Cl(en)_2]^{2+}$ (iii) $[Co(NH_3)_2Cl_2(en)]^+$

**5.12** Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

**5.13** Aqueous copper sulphate solution (blue in colour) gives:

(i) a green precipitate with aqueous potassium fluoride and

(ii) a bright green solution with aqueous potassium chloride. Explain these experimental results.

**5.14** What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S(g)$ is passed through this solution?

**5.15** Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)_3]^{3-}$ (iv) $[CoF_6]^{3-}$

**5.16** Draw figure to show the splitting of *d* orbitals in an octahedral crystal field.

**5.17** What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

**5.18** What is crystal field splitting energy? How does the magnitude of $\Delta_o$ decide the actual configuration of *d* orbitals in a coordination entity?

**5.19** $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

**5.20** A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

**5.21** $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?

**5.22** Discuss the nature of bonding in metal carbonyls.

**5.23** Give the oxidation state, *d* orbital occupation and coordination number of the central metal ion in the following complexes:

(i) $K_3[Co(C_2O_4)_3]$ (iii) $(NH_4)_2[CoF_4]$

(ii) cis-$[CrCl_2(en)_2]Cl$ (iv) $[Mn(H_2O)_6]SO_4$

**5.24** Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:

(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ (iii) $[CrCl_3(py)_3]$ (v) $K_4[Mn(CN)_6]$

(ii) $[Co(NH_3)_5Cl.]Cl_2$ (iv) $Cs[FeCl_4]$

**5.25** Explain the violet colour of the complex $[Ti(H_2O)_6]^{3+}$ on the basis of crystal field theory.

**5.26** What is meant by the *chelate effect*? Give an example.

**5.27** Discuss briefly giving an example in each case the role of coordination compounds in:

(i) biological systems (iii) analytical chemistry

(ii) medicinal chemistry and (iv) extraction/metallurgy of metals.

**5.28** How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution?

(i) 6 (ii) 4 (iii) 3 (iv) 2

**5.29** Amongst the following ions which one has the highest magnetic moment value?
(i) $[Cr(H_2O)_6]^{3+}$ (ii) $[Fe(H_2O)_6]^{2+}$ (iii) $[Zn(H_2O)_6]^{2+}$

**5.30** Amongst the following, the most stable complex is
(i) $[Fe(H_2O)_6]^{3+}$ (ii) $[Fe(NH_3)_6]^{3+}$ (iii) $[Fe(C_2O_4)_3]^{3-}$ (iv) $[FeCl_6]^{3-}$

**5.31** What will be the correct order for the wavelengths of absorption in the visible region for the following:
$[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$ ?

## Answers to Some Intext Questions

**5.1** (i) $[Co(NH_3)_4(H_2O)_2]Cl_3$
(ii) $K_2[Ni(CN)_4]$
(iii) $[Cr(en)_3]Cl_3$
(iv) $[Pt(NH_3)BrCl(NO_2)]^-$
(v) $[PtCl_2(en)_2](NO_3)_2$
(vi) $Fe_4[Fe(CN)_6]_3$

**5.2** (i) Hexaamminecobalt(III) chloride
(ii) Pentaamminechloridocobalt(III) chloride
(iii) Potassium hexacyanidoferrate(III)
(iv) Potassium trioxalatoferrate(III)
(v) Potassium tetrachloridopalladate(II)
(vi) Diamminechlorido(methanamine)platinum(II) chloride

**5.3** (i) Both geometrical (*cis*-, *trans*-) and optical isomers for *cis* can exist.
(ii) Two optical isomers can exist.
(iii) There are 10 possible isomers. (Hint: There are geometrical, ionisation and linkage isomers possible).
(iv) Geometrical (*cis*-, *trans*-) isomers can exist.

**5.4** The ionisation isomers dissolve in water to yield different ions and thus react differently to various reagents:
$[Co(NH_3)_5Br]SO_4 + Ba^{2+} \rightarrow BaSO_4\ (s)$
$[Co(NH_3)_5SO_4]Br + Ba^{2+} \rightarrow$ No reaction
$[Co(NH_3)_5Br]SO_4 + Ag^+ \rightarrow$ No reaction
$[Co(NH_3)_5SO_4]Br + Ag^+ \rightarrow AgBr\ (s)$

**5.6** In $Ni(CO)_4$, Ni is in zero oxidation state whereas in $NiCl_4^{2-}$, it is in +2 oxidation state. In the presence of CO ligand, the unpaired *d* electrons of Ni pair up but $Cl^-$ being a weak ligand is unable to pair up the unpaired electrons.

**5.7** In presence of $CN^-$, (a strong ligand) the 3*d* electrons pair up leaving only one unpaired electron. The hybridisation is $d^2sp^3$ forming inner orbital complex. In the presence of $H_2O$, (a weak ligand), 3*d* electrons do not pair up. The hybridisation is $sp^3d^2$ forming an outer orbital complex containing five unpaired electrons, it is strongly paramagnetic.

**5.8** In the presence of $NH_3$, the 3*d* electrons pair up leaving two *d* orbitals empty to be involved in $d^2sp^3$ hybridisation forming inner orbital complex in case of $[Co(NH_3)_6]^{3+}$.
In $Ni(NH_3)_6^{2+}$, Ni is in +2 oxidation state and has $d^8$ configuration, the hybridisation involved is $sp^3d^2$ forming outer orbital complex.

**5.9** For square planar shape, the hybridisation is $dsp^2$. Hence the unpaired electrons in 5*d* orbital pair up to make one *d* orbital empty for $dsp^2$ hybridisation. Thus there is no unpaired electron.