Chemistry

Part II

Textbook for Class XI

राष्ट्रीय शैक्षिक अनुसंधान और प्रशिक्षण परिषद्
NATIONAL COUNCIL OF EDUCATIONAL RESEARCH AND TRAINING

First Edition
March 2006 Phalguna 1927
Reprinted
October 2006 Kartika 1928
November 2007 Kartika 1929
January 2009 Magha 1930
December 2009 Pausa 1931
November 2010 Kartika 1932
January 2012 Pausa 1933
November 2012 Kartika 1934
November 2013 Kartika 1935
December 2014 Pausa 1936
December 2015 Agrahayna 1937
Febuary 2017 Phalguna 1938
Febuary 2018 Phalguna 1939

PD 500T BS

₹ 105.00

Printed on 80 GSM paper with NCERT watermark

Published at the Publication Division by the Secretary, National Council of Educational Research and Training, Sri Aurobindo Marg, New Delhi 110 016 and printed at Aravali Printers & Publishers (P) Ltd., 50/7, Site-IV Industrial Area, Sahibabad

ISBN 81-7450-494-X (Part I)
ISBN 81-7450-535-0 (Part II)

OFFICES OF THE PUBLICATION DIVISION, NCERT

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Maligaon
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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. We are especially grateful to the members of the National Monitoring Committee, appointed by the Department of Secondary and Higher Education, Ministry of Human Resource Development under the Chairpersonship of Professor Mrinal Miri and Professor G.P. Deshpande, for their valuable time and contribution. 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
20 December 2005

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ACKNOWLEDGEMENTS

The National Council of Educational Research and Training acknowledges the valuable contributions of the individuals and organisations involved in the development of Chemistry textbook for Class XI. It also acknowledges that some useful material from the reprint editions (2005) of Chemistry textbooks has been utilised in the development of the present textbook. The following academics contributed effectively for editing, reviewing, refining and finalisation of the manuscript of this book: G.T. Bhandage, *Professor*, RIE, Mysuru; N. Ram, *Professor*, IIT, New Delhi; R. Sindhu, *Reader*, RIE (NCERT), Bhopal; Sanjeev Kumar, *Reader,* Desh Bandhu College, Kalkaji, New Delhi; Shampa Bhattacharya, *Reader*, Hans Raj College, Delhi; Vijay Sarda, *Reader*, Zakir Husain College, New Delhi. K.K. Arora, *Reader,* Zakir Husain College, New Delhi; Shashi Saxena, *Reader*, Hans Raj College, Delhi; Anuradha Sen, Apeejay School, Sheikh Sarai, New Delhi; C. Shrinivas, *PGT,* Kendriya Vidyalaya, Pushp Vihar, New Delhi; D.L. Bharti, *PGT*, Ramjas School, Sector IV, R.K. Puram, New Delhi; Ila Sharma, *PGT*, Delhi Public School, Dwarka, Sector-B, New Delhi; Raj Lakshmi Karthikeyan, *Head* (Science), Mother's International School, Sri Aurobindo Marg, New Delhi; Sushma Kiran Setia, *Principal*, Sarvodaya Kanya Vidyalaya, Hari Nagar (CT), New Delhi; Nidhi Chaudray, *PGT*, CRPF Public School, Rohini, Delhi; and Veena Suri, *PGT*, Bluebells School, Kailash, New Delhi. We are thankful to them.

We express gratitude to R.S. Sindhu, *Professor* (Retd.), DESM, NCERT, New Delhi, for editing, reviewing and refining the textbook right from the initial stage.

We are also grateful to Ruchi Verma, *Associate Professor*, DESM, NCERT, New Delhi; Pramila Tanwar, *Assistant Professor*, DESM, NCERT, New Delhi; R.B. Pareek, *Associate Professor*, RIE, Ajmer and A.K. Arya, *Associate professor*, RIE, Ajmer, for reviewing and refining the content of the textbook.

Special thanks are due to M. Chandra, *Professor and Head*, DESM, NCERT for her support.

The Council also gratefully acknowledges the contribution of Surendra Kumar and Hari Darshan Lodhi *DTP Operator*; Subhash Saluja, Ramendra Kumar Sharma and Abhimanyu Mohanty, *Proof Readers;* Bhavna Saxena, *Copy Editor* and Deepak Kapoor, *Incharge,* Computer Station, in shaping this book. The contributions of the Publication Department in bringing out this book are also duly acknowledged.

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UNIT 8

REDOX REACTIONS

Objectives

After studying this unit you will be able to

- identify redox reactions as a class of reactions in which oxidation and reduction reactions occur simultaneously;
- define the terms oxidation, reduction, oxidant (oxidising agent) and reductant (reducing agent);
- explain mechanism of redox reactions by electron transfer process;
- use the concept of oxidation number to identify oxidant and reductant in a reaction;
- classify redox reaction into combination (synthesis), decomposition, displacement and disproportionation reactions;
- suggest a comparative order among various reductants and oxidants;
- balance chemical equations using (i) oxidation number (ii) half reaction method;
- learn the concept of redox reactions in terms of electrode processes.

> *“Where there is oxidation, there is always reduction – Chemistry is essentially a study of redox systems.”*

Chemistry deals with varieties of matter and change of one kind of matter into the other. Transformation of matter from one kind into another occurs through the various types of reactions. One important category of such reactions is **Redox Reactions**. A number of phenomena, both physical as well as biological, are concerned with redox reactions. These reactions find extensive use in pharmaceutical, biological, industrial, metallurgical and agricultural areas. The importance of these reactions is apparent from the fact that burning of different types of fuels for obtaining energy for domestic, transport and other commercial purposes, electrochemical processes for extraction of highly reactive metals and non-metals, manufacturing of chemical compounds like caustic soda, operation of dry and wet batteries and corrosion of metals fall within the purview of redox processes. Of late, environmental issues like **Hydrogen Economy** (use of liquid hydrogen as fuel) and development of **‘Ozone Hole’** have started figuring under redox phenomenon.

8.1 CLASSICAL IDEA OF REDOX REACTIONS – OXIDATION AND REDUCTION REACTIONS

Originally, the term **oxidation** was used to describe the addition of oxygen to an element or a compound. Because of the presence of dioxygen in the atmosphere (~20%), many elements combine with it and this is the principal reason why they commonly occur on the earth in the form of their oxides. The following reactions represent oxidation processes according to the limited definition of oxidation:

$$2\,Mg\,(s) + O_2\,(g) \rightarrow 2\,MgO\,(s) \qquad (8.1)$$

$$S\,(s) + O_2\,(g) \rightarrow SO_2\,(g) \qquad (8.2)$$

In reactions (8.1) and (8.2), the elements magnesium and sulphur are oxidised on account of addition of oxygen to them. Similarly, methane is oxidised owing to the addition of oxygen to it.

CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (l) (8.3)

A careful examination of reaction (8.3) in which hydrogen has been replaced by oxygen prompted chemists to reinterpret oxidation in terms of removal of hydrogen from it and, therefore, the scope of term oxidation was broadened to include the removal of hydrogen from a substance. The following illustration is another reaction where removal of hydrogen can also be cited as an oxidation reaction.

2 H_2S(g) + O_2 (g) → 2 S (s) + 2 H_2O (l) (8.4)

As knowledge of chemists grew, it was natural to extend the term oxidation for reactions similar to (8.1 to 8.4), which do not involve oxygen but other electronegative elements. The oxidation of magnesium with fluorine, chlorine and sulphur etc. occurs according to the following reactions :

Mg (s) + F_2 (g) → MgF_2 (s) (8.5)

Mg (s) + Cl_2 (g) → $MgCl_2$ (s) (8.6)

Mg (s) + S (s) → MgS (s) (8.7)

Incorporating the reactions (8.5 to 8.7) within the fold of oxidation reactions encouraged chemists to consider not only the removal of hydrogen as oxidation, but also the removal of electropositive elements as oxidation. Thus the reaction :

$$2K_4[Fe(CN)_6](aq) + H_2O_2(aq) \rightarrow 2K_3[Fe(CN)_6](aq) + 2\,KOH(aq)$$

is interpreted as oxidation due to the removal of electropositive element potassium from potassium ferrocyanide before it changes to potassium ferricyanide. To summarise, the term **"oxidation"** is defined as the **addition of oxygen/electronegative element to a substance or removal of hydrogen/ electropositive element from a substance.**

In the beginning, reduction was considered as removal of oxygen from a compound. However, the term **reduction** has been broadened these days to include **removal of oxygen/electronegative element from a substance or addition of hydrogen/ electropositive element to a substance.**

According to the definition given above, the following are the examples of reduction processes:

2 HgO (s) $\xrightarrow{\Delta}$ 2 Hg (l) + O_2 (g) (8.8)

(removal of oxygen from mercuric oxide)

2 $FeCl_3$ (aq) + H_2 (g) →2 $FeCl_2$ (aq) + 2 HCl(aq) (8.9)

(removal of electronegative element, chlorine from ferric chloride)

$CH_2 = CH_2$ (g) + H_2 (g) → $H_3C - CH_3$ (g) (8.10)

(addition of hydrogen)

$2HgCl_2$ (aq) + $SnCl_2$ (aq) → Hg_2Cl_2 (s)+$SnCl_4$ (aq) (8.11)

(addition of mercury to mercuric chloride)

In reaction (8.11) simultaneous oxidation of stannous chloride to stannic chloride is also occurring because of the addition of electronegative element chlorine to it. It was soon realised that oxidation and reduction always occur simultaneously (as will be apparent by re-examining all the equations given above), hence, the word **"redox"** was coined for this class of chemical reactions.

Problem 8.1

In the reactions given below, identify the species undergoing oxidation and reduction:

(i) H_2S (g) + Cl_2 (g) → 2 HCl (g) + S (s)

(ii) $3Fe_3O_4$ (s) + 8 Al (s) → 9 Fe (s) + $4Al_2O_3$ (s)

(iii) 2 Na (s) + H_2 (g) → 2 NaH (s)

Solution

(i) H_2S is oxidised because a more electronegative element, chlorine is added to hydrogen (or a more electropositive element, hydrogen has been removed from S). Chlorine is reduced due to addition of hydrogen to it.

(ii) Aluminium is oxidised because oxygen is added to it. Ferrous ferric oxide

(Fe_3O_4) is reduced because oxygen has been removed from it.

(iii) With the careful application of the concept of electronegativity only we may infer that sodium is oxidised and hydrogen is reduced.

Reaction (iii) chosen here prompts us to think in terms of another way to define redox reactions.

8.2 REDOX REACTIONS IN TERMS OF ELECTRON TRANSFER REACTIONS

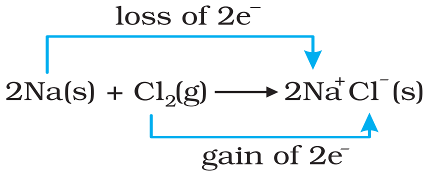
We have already learnt that the reactions

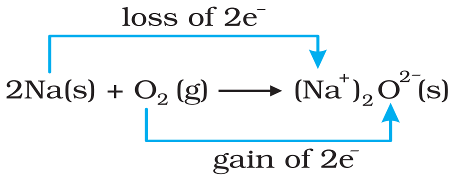
$2Na(s) + Cl_2(g) \rightarrow 2NaCl\,(s)$ (8.12)

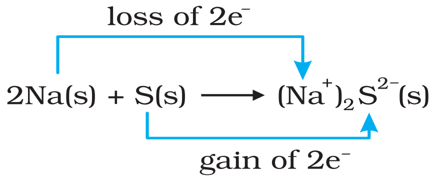
$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$ (8.13)

$2Na(s) + S(s) \rightarrow Na_2S(s)$ (8.14)

are redox reactions because in each of these reactions sodium is oxidised due to the addition of either oxygen or more electronegative element to sodium. Simultaneously, chlorine, oxygen and sulphur are reduced because to each of these, the electropositive element sodium has been added. From our knowledge of chemical bonding we also know that sodium chloride, sodium oxide and sodium sulphide are ionic compounds and perhaps better written as Na^+Cl^- (s), $(Na^+)_2O^{2-}$(s), and $(Na^+)_2\ S^{2-}$(s). Development of charges on the species produced suggests us to rewrite the reactions (8.12 to 8.14) in the following manner :







For convenience, each of the above processes can be considered as two separate steps, one involving the loss of electrons and the other the gain of electrons. As an illustration, we may further elaborate one of these, say, the formation of sodium chloride.

$2\ Na(s) \rightarrow 2\ Na^+(g)\ +\ 2e^-$

$Cl_2(g) + 2e^- \rightarrow 2\ Cl^-(g)$

Each of the above steps is called a half reaction, which explicitly shows involvement of electrons. Sum of the half reactions gives the overall reaction :

$2\ Na(s) + Cl_2\,(g) \rightarrow 2\ Na^+\ Cl^-$ (s) or $2\ NaCl$ (s)

Reactions 8.12 to 8.14 **suggest that half reactions that involve loss of electrons are called oxidation reactions. Similarly, the half reactions that involve gain of electrons are called reduction reactions.** It may not be out of context to mention here that the new way of defining oxidation and reduction has been achieved only by establishing a correlation between the behaviour of species as per the classical idea and their interplay in electron-transfer change. In reactions (8.12 to 8.14) sodium, which is oxidised, acts as **a reducing agent** because it donates electron to each of the elements interacting with it and thus helps in reducing them. Chlorine, oxygen and sulphur are reduced and act as oxidising agents because these accept electrons from sodium. To summarise, we may mention that

***Oxidation*:** Loss of electron(s) by any species.

***Reduction*:** Gain of electron(s) by any species.

***Oxidising agent* :** Acceptor of electron(s).

***Reducing agent* :** Donor of electron(s).

Problem 8.2 Justify that the reaction :

$2\ Na(s) + H_2(g) \rightarrow 2\ NaH$ (s) is a redox change.

Solution

Since in the above reaction the compound formed is an ionic compound, which may also be represented as Na^+H^- (s), this suggests that one half reaction in this process is :

$2\ Na\ (s) \rightarrow 2\ Na^+(g)\ +\ 2e^-$

and the other half reaction is:

$H_2\,(g) + 2e^- \rightarrow 2\,H^-(g)$

This splitting of the reaction under examination into two half reactions automatically reveals that here sodium is oxidised and hydrogen is reduced, therefore, the complete reaction is a redox change.

8.2.1 Competitive Electron Transfer Reactions

Place a strip of metallic zinc in an aqueous solution of copper nitrate as shown in Fig. 8.1, for about one hour. You may notice that the strip becomes coated with reddish metallic copper and the blue colour of the solution disappears. Formation of Zn^{2+} ions among the products can easily be judged when the blue colour of the solution due to Cu^{2+} has disappeared. If hydrogen sulphide gas is passed through the colourless solution containing Zn^{2+} ions, appearance of white zinc sulphide, ZnS can be seen on making the solution alkaline with ammonia.

The reaction between metallic zinc and the aqueous solution of copper nitrate is :

$$Zn(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu(s) \qquad (8.15)$$

In reaction (8.15), zinc has lost electrons to form Zn^{2+} and, therefore, zinc is oxidised. Evidently, now if zinc is oxidised, releasing electrons, something must be reduced, accepting the electrons lost by zinc. Copper ion is reduced by gaining electrons from the zinc.

Reaction (8.15) may be rewritten as :

$$\begin{array}{c}\text{release of } 2e^- \\ Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \\ \text{gain of } 2e^- \end{array}$$

At this stage we may investigate the state of equilibrium for the reaction represented by equation (8.15). For this purpose, let us place a strip of metallic copper in a zinc sulphate solution. No visible reaction is noticed and attempt to detect the presence of Cu^{2+} ions by passing H_2S gas through the solution to produce the black colour of cupric sulphide, CuS, does not succeed. Cupric sulphide has such a low solubility that this is an extremely sensitive test; yet the amount of Cu^{2+} formed cannot be detected. We thus conclude that the state of equilibrium for the reaction (8.15) greatly favours the products over the reactants.

Let us extend electron transfer reaction now to copper metal and silver nitrate solution in water and arrange a set-up as shown in Fig. 8.2. The solution develops blue colour due to the formation of Cu^{2+} ions on account of the reaction:

$$\begin{array}{c}\text{release of } 2e^- \\ Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s) \\ \text{gain of } 2e^- \end{array} \qquad (8.16)$$

Here, Cu(s) is oxidised to $Cu^{2+}(aq)$ and $Ag^+(aq)$ is reduced to Ag(s). Equilibrium greatly favours the products Cu^{2+} (aq) and Ag(s).

By way of contrast, let us also compare the reaction of metallic cobalt placed in nickel sulphate solution. The reaction that occurs here is :

$$\begin{array}{c}\text{release of } 2e^- \\ Co(s) + Ni^{2+}(aq) \longrightarrow Co^{2+}(aq) + Ni(s) \\ \text{gain of } 2e^- \end{array} \qquad (8.17)$$

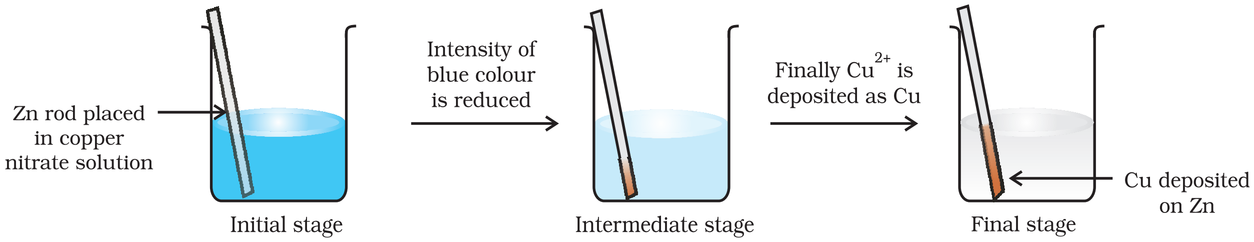


Fig. 8.1 *Redox reaction between zinc and aqueous solution of copper nitrate occurring in a beaker.*

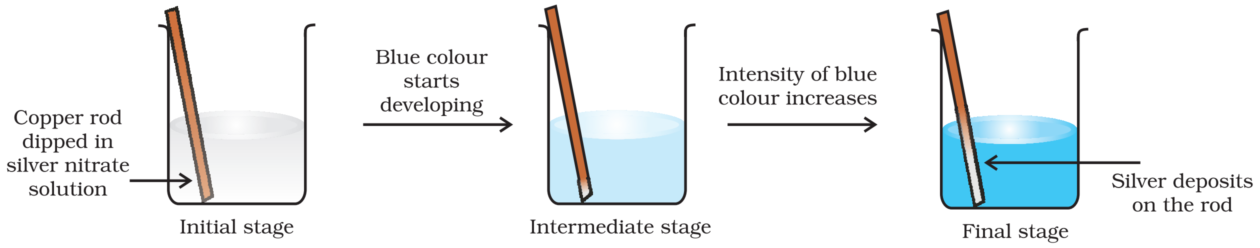


Fig. 8.2 *Redox reaction between copper and aqueous solution of silver nitrate occurring in a beaker.*

At equilibrium, chemical tests reveal that both $Ni^{2+}(aq)$ and $Co^{2+}(aq)$ are present at moderate concentrations. In this case, neither the reactants [Co(s) and $Ni^{2+}(aq)$] nor the products [$Co^{2+}(aq)$ and Ni (s)] are greatly favoured.

This competition for release of electrons incidently reminds us of the competition for release of protons among acids. The similarity suggests that we might develop a table in which metals and their ions are listed on the basis of their tendency to release electrons just as we do in the case of acids to indicate the strength of the acids. As a matter of fact we have already made certain comparisons. By comparison we have come to know that zinc releases electrons to copper and copper releases electrons to silver and, therefore, the electron releasing tendency of the metals is in the order: Zn>Cu>Ag. We would love to make our list more vast and design a **metal activity series or electrochemical series**. The competition for electrons between various metals helps us to design a class of cells, named as Galvanic cells in which the chemical reactions become the source of electrical energy. We would study more about these cells in Class XII.

8.3 OXIDATION NUMBER

A less obvious example of electron transfer is realised when hydrogen combines with oxygen to form water by the reaction:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad (8.18)$$

Though not simple in its approach, yet we can visualise the H atom as going from a neutral (zero) state in H_2 to a positive state in H_2O, the O atom goes from a zero state in O_2 to a dinegative state in H_2O. It is assumed that there is an electron transfer from H to O and consequently H_2 is oxidised and O_2 is reduced. However, as we shall see later, the charge transfer is only partial and is perhaps better described as an electron shift rather than a complete loss of electron by H and gain by O. What has been said here with respect to equation (8.18) may be true for a good number of other reactions involving covalent compounds. Two such examples of this class of the reactions are:

$$H_2(s) + Cl_2(g) \rightarrow 2HCl(g) \qquad (8.19)$$

and,

$$CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(l) + 4HCl(g) \qquad (8.20)$$

In order to keep track of electron shifts in chemical reactions involving formation of covalent compounds, a more practical method of using **oxidation number** has been developed. In this method, it is always assumed that there is a complete transfer of electron from a less electronegative atom to a more electonegative atom. For example, we rewrite equations (8.18 to 8.20) to show charge on each of the atoms forming part of the reaction :

$$2\overset{0}{H_2}(g) + \overset{0}{O_2}(g) \rightarrow 2\overset{+1}{H_2}\overset{-2}{O}(l) \qquad (8.21)$$

$$\overset{0}{H_2}(s) + \overset{0}{Cl_2}(g) \rightarrow 2\overset{+1}{H}\overset{-1}{Cl}(g) \qquad (8.22)$$

$$\overset{-4}{C}\overset{+1}{H_4}(g) + 4\overset{0}{Cl_2}(g) \rightarrow \overset{+4}{C}\overset{-1}{Cl_4}(l) + 4\overset{+1}{H}\overset{-1}{Cl}(g) \qquad (8.23)$$

It may be emphasised that the assumption of electron transfer is made for book-keeping purpose only and it will become obvious at a later stage in this unit that it leads to the simple description of redox reactions.

Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that

electron pair in a covalent bond belongs entirely to more electronegative element.

It is not always possible to remember or make out easily in a compound/ion, which element is more electronegative than the other. Therefore, a set of rules has been formulated to determine the oxidation number of an element in a compound/ion. If two or more than two atoms of an element are present in the molecule/ion such as $Na_2S_2O_3/Cr_2O_7^{2-}$, the oxidation number of the atom of that element will then be the average of the oxidation number of all the atoms of that element. We may at this stage, state the rules for the calculation of oxidation number. These rules are:

1. In elements, in the free or the uncombined state, each atom bears an oxidation number of zero. Evidently each atom in H_2, O_2, Cl_2, O_3, P_4, S_8, Na, Mg, Al has the oxidation number zero.
2. For ions composed of only one atom, the oxidation number is equal to the charge on the ion. Thus Na^+ ion has an oxidation number of +1, Mg^{2+} ion, +2, Fe^{3+} ion, +3, Cl^- ion, –1, O^{2-} ion, –2; and so on. In their compounds all alkali metals have oxidation number of +1, and all alkaline earth metals have an oxidation number of +2. Aluminium is regarded to have an oxidation number of +3 in all its compounds.
3. The oxidation number of oxygen in most compounds is –2. However, we come across two kinds of exceptions here. One arises in the case of peroxides and superoxides, the compounds of oxygen in which oxygen atoms are directly linked to each other. While in peroxides (e.g., H_2O_2, Na_2O_2), each oxygen atom is assigned an oxidation number of –1, in superoxides (e.g., KO_2, RbO_2) each oxygen atom is assigned an oxidation number of –(½). The second exception appears rarely, i.e. when oxygen is bonded to fluorine. In such compounds e.g., oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_2), the oxygen is assigned an oxidation number of +2 and +1, respectively. The number assigned to oxygen will depend upon the bonding state of oxygen but this number would now be a positive figure only.
4. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds (that is compounds containing two elements). For example, in LiH, NaH, and CaH_2, its oxidation number is –1.
5. In all its compounds, fluorine has an oxidation number of –1. Other halogens (Cl, Br, and I) also have an oxidation number of –1, when they occur as halide ions in their compounds. Chlorine, bromine and iodine when combined with oxygen, for example in oxoacids and oxoanions, have positive oxidation numbers.
6. The algebraic sum of the oxidation number of all the atoms in a compound must be zero. In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion. Thus, the sum of oxidation number of three oxygen atoms and one carbon atom in the carbonate ion, $(CO_3)^{2-}$ must equal –2.

By the application of above rules, we can find out the oxidation number of the desired element in a molecule or in an ion. It is clear that the metallic elements have positive oxidation number and nonmetallic elements have positive or negative oxidation number. The atoms of transition elements usually display several positive oxidation states. The highest oxidation number of a representative element is the group number for the first two groups and the group number minus 10 (following the long form of periodic table) for the other groups. Thus, it implies that the highest value of oxidation number exhibited by an atom of an element generally increases across the period in the periodic table. In the third period, the highest value of oxidation number changes from 1 to 7 as indicated below in the compounds of the elements.

A term that is often used interchangeably with the oxidation number is the **oxidation state.** Thus in CO_2, the oxidation state of carbon is +4, that is also its oxidation number and similarly the oxidation state as well as oxidation number of oxygen is – 2. This implies that the oxidation number denotes the oxidation state of an element in a compound.

Group	**1**	**2**	**13**	**14**	**15**	**16**	**17**
Element	Na	Mg	Al	Si	P	S	Cl
Compound	NaCl	$MgSO_4$	AlF_3	$SiCl_4$	P_4O_{10}	SF_6	$HClO_4$
Highest oxidation number state of the group element	+1	+2	+3	+4	+5	+6	+7

The oxidation number/state of a metal in a compound is sometimes presented according to the notation given by German chemist, Alfred Stock. It is popularly known as **Stock notation.** According to this, the oxidation number is expressed by putting a Roman numeral representing the oxidation number in parenthesis after the symbol of the metal in the molecular formula. Thus aurous chloride and auric chloride are written as Au(I)Cl and $Au(III)Cl_3$. Similarly, stannous chloride and stannic chloride are written as $Sn(II)Cl_2$ and $Sn(IV)Cl_4$. This change in oxidation number implies change in oxidation state, which in turn helps to identify whether the species is present in oxidised form or reduced form. Thus, $Hg_2(I)Cl_2$ is the reduced form of $Hg(II)\ Cl_2$.

Problem 8.3

Using Stock notation, represent the following compounds :$HAuCl_4$, Tl_2O, FeO, Fe_2O_3, CuI, CuO, MnO and MnO_2.

Solution

By applying various rules of calculating the oxidation number of the desired element in a compound, the oxidation number of each metallic element in its compound is as follows:

$HAuCl_4$ → Au has 3
Tl_2O → Tl has 1
FeO → Fe has 2
Fe_2O_3 → Fe has 3
CuI → Cu has 1
CuO → Cu has 2
MnO → Mn has 2
MnO_2 → Mn has 4

Therefore, these compounds may be represented as:

$HAu(III)Cl_4$, $Tl_2(I)O$, Fe(II)O, $Fe_2(III)O_3$, Cu(I)I, Cu(II)O, Mn(II)O, $Mn(IV)O_2$.

The idea of oxidation number has been invariably applied to define oxidation, reduction, oxidising agent (oxidant), reducing agent (reductant) and the redox reaction. To summarise, we may say that:

Oxidation: An increase in the oxidation number of the element in the given substance.

Reduction: A decrease in the oxidation number of the element in the given substance.

Oxidising agent: A reagent which can increase the oxidation number of an element in a given substance. These reagents are called as **oxidants** also.

Reducing agent: A reagent which lowers the oxidation number of an element in a given substance. These reagents are also called as **reductants**.

Redox reactions: Reactions which involve change in oxidation number of the interacting species.

Problem 8.4

Justify that the reaction:

$$2Cu_2O(s) + Cu_2S(s) \rightarrow 6Cu(s) + SO_2(g)$$

is a redox reaction. Identify the species oxidised/reduced, which acts as an oxidant and which acts as a reductant.

Solution

Let us assign oxidation number to each of the species in the reaction under examination. This results into:

$$2\overset{+1}{Cu_2}\overset{-2}{O}(s) + \overset{+1}{Cu_2}\overset{-2}{S}(s) \rightarrow 6\overset{0}{Cu}(s) + \overset{+4}{S}\overset{-2}{O_2}$$

We therefore, conclude that in this reaction *copper is reduced* from +1 state to zero oxidation state and *sulphur is oxidised* from –2 state to +4 state. The above reaction is thus a *redox reaction.*

Further, Cu_2O helps sulphur in Cu_2S to increase its oxidation number, therefore, Cu(I) is an oxidant; and sulphur of Cu_2S helps copper both in Cu_2S itself and Cu_2O to decrease its oxidation number; therefore, sulphur of Cu_2S is reductant.

8.3.1 Types of Redox Reactions

1. Combination reactions

A combination reaction may be denoted in the manner:

$$A + B \rightarrow C$$

Either A and B or both A and B must be in the elemental form for such a reaction to be a redox reaction. All combustion reactions, which make use of elemental dioxygen, as well as other reactions involving elements other than dioxygen, are redox reactions. Some important examples of this category are:

$$\overset{0}{C}(s) + \overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4}{C}\overset{-2}{O_2}(g) \qquad (8.24)$$

$$3\overset{0}{Mg}(s) + \overset{0}{N_2}(g) \xrightarrow{\Delta} \overset{+2}{Mg_3}\overset{-3}{N_2}(s) \qquad (8.25)$$

$$\overset{-4}{C}\overset{+1}{H_4}(g) + 2\overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4}{C}\overset{-2}{O_2}(g) + 2\overset{+1}{H_2}\overset{-2}{O}(l)$$

2. Decomposition reactions

Decomposition reactions are the opposite of combination reactions. Precisely, a decomposition reaction leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state. Examples of this class of reactions are:

$$2\overset{+1}{H_2}\overset{-2}{O}(l) \xrightarrow{\Delta} 2\overset{0}{H_2}(g) + \overset{0}{O_2}(g) \qquad (8.26)$$

$$2\overset{+1}{Na}\overset{-1}{H}(s) \xrightarrow{\Delta} 2\overset{0}{Na}(s) + \overset{0}{H_2}(g) \qquad (8.27)$$

$$2\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O_3}(s) \xrightarrow{\Delta} 2\overset{+1}{K}\overset{-1}{Cl}(s) + 3\overset{0}{O_2}(g) \qquad (8.28)$$

It may carefully be noted that there is no change in the oxidation number of hydrogen in methane under combination reactions and that of potassium in potassium chlorate in reaction (8.28). This may also be noted here that all decomposition reactions are not redox reactions. For example, decomposition of calcium carbonate is not a redox reaction.

$$\overset{+2}{Ca}\overset{+4}{C}\overset{-2}{O_3}(s) \xrightarrow{\Delta} \overset{+2}{Ca}\overset{-2}{O}(s) + \overset{+4}{C}\overset{-2}{O_2}(g)$$

3. Displacement reactions

In a displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be denoted as:

$$X + YZ \rightarrow XZ + Y$$

Displacement reactions fit into two categories: metal displacement and non-metal displacement.

(a) Metal displacement: A metal in a compound can be displaced by another metal in the uncombined state. We have already discussed about this class of the reactions under section 8.2.1. Metal displacement reactions find many applications in metallurgical processes in which pure metals are obtained from their compounds in ores. A few such examples are:

$$\overset{+2}{Cu}\overset{+6}{S}\overset{-2}{O_4}(aq) + \overset{0}{Zn}(s) \rightarrow \overset{0}{Cu}(s) + \overset{+2}{Zn}\overset{+6}{S}\overset{-2}{O_4}(aq) \qquad (8.29)$$

$$\overset{+5}{V_2}\overset{-2}{O_5}(s) + 5\overset{0}{Ca}(s) \xrightarrow{\Delta} 2\overset{0}{V}(s) + 5\overset{+2}{Ca}\overset{-2}{O}(s) \qquad (8.30)$$

$$\overset{+4}{Ti}\overset{-1}{Cl_4}(l) + 2\overset{0}{Mg}(s) \xrightarrow{\Delta} \overset{0}{Ti}(s) + 2\overset{+2}{Mg}\overset{-1}{Cl_2}(s) \qquad (8.31)$$

$$\overset{+3}{Cr_2}\overset{-2}{O_3}(s) + 2\overset{0}{Al}(s) \xrightarrow{\Delta} \overset{+3}{Al_2}\overset{-2}{O_3}(s) + 2\overset{0}{Cr}(s) \qquad (8.32)$$

In each case, the reducing metal is a better reducing agent than the one that is being reduced which evidently shows more capability to lose electrons as compared to the one that is reduced.

(b) Non-metal displacement: The non-metal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement.

All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) which are very good reductants, will displace hydrogen from cold water.

$$2\overset{0}{Na}(s) + 2\overset{+1}{H_2}\overset{-2}{O}(l) \rightarrow 2\overset{+1}{Na}\overset{-2}{O}\overset{+1}{H}(aq) + \overset{0}{H_2}(g) \tag{8.33}$$

$$\overset{0}{Ca}(s) + 2\overset{+1}{H_2}\overset{-2}{O}(l) \rightarrow \overset{+2}{Ca}(\overset{-2}{O}\overset{+1}{H})_2(aq) + \overset{0}{H_2}(g) \tag{8.34}$$

Less active metals such as magnesium and iron react with steam to produce dihydrogen gas:

$$\overset{0}{Mg}(s) + 2\overset{+1}{H_2}\overset{-2}{O}(l) \xrightarrow{\Delta} \overset{+2}{Mg}(\overset{-2}{O}\overset{+1}{H})_2(s) + \overset{0}{H_2}(g) \tag{8.35}$$

$$2\overset{0}{Fe}(s) + 3\overset{+1}{H_2}\overset{-2}{O}(l) \xrightarrow{\Delta} \overset{+3}{Fe_2}\overset{-2}{O_3}(s) + 3\overset{0}{H_2}(g) \tag{8.36}$$

Many metals, including those which do not react with cold water, are capable of displacing hydrogen from acids. Dihydrogen from acids may even be produced by such metals which do not react with steam. Cadmium and tin are the examples of such metals. A few examples for the displacement of hydrogen from acids are:

$$\overset{0}{Zn}(s) + 2\overset{+1}{H}\overset{-1}{Cl}(aq) \rightarrow \overset{+2}{Zn}\overset{-1}{Cl_2}(aq) + \overset{0}{H_2}(g) \tag{8.37}$$

$$\overset{0}{Mg}(s) + 2\overset{+1}{H}\overset{-1}{Cl}(aq) \rightarrow \overset{+2}{Mg}\overset{-1}{Cl_2}(aq) + \overset{0}{H_2}(g) \tag{8.38}$$

$$\overset{0}{Fe}(s) + 2\overset{+1}{H}\overset{-1}{Cl}(aq) \rightarrow \overset{+2}{Fe}\overset{-1}{Cl_2}(aq) + \overset{0}{H_2}(g) \tag{8.39}$$

Reactions (8.37 to 8.39) are used to prepare dihydrogen gas in the laboratory. Here, the reactivity of metals is reflected in the rate of hydrogen gas evolution, which is the slowest for the least active metal Fe, and the fastest for the most reactive metal, Mg. Very less active metals, which may occur in the native state such as silver (Ag), and gold (Au) do not react even with hydrochloric acid.

In section (8.2.1) we have already discussed that the metals – zinc (Zn), copper (Cu) and silver (Ag) through tendency to lose electrons show their reducing activity in the order Zn> Cu>Ag. Like metals, activity series also exists for the halogens. The power of these elements as oxidising agents decreases as we move down from fluorine to iodine in group 17 of the periodic table. This implies that fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. In fact, fluorine is so reactive that it attacks water and displaces the oxygen of water :

$$2\overset{+1}{H_2}\overset{-2}{O}(l) + 2\overset{0}{F_2}(g) \rightarrow 4\overset{+1}{H}\overset{-1}{F}(aq) + \overset{0}{O_2}(g) \tag{8.40}$$

It is for this reason that the displacement reactions of chlorine, bromine and iodine using fluorine are not generally carried out in aqueous solution. On the other hand, chlorine can displace bromide and iodide ions in an aqueous solution as shown below:

$$\overset{0}{Cl_2}(g) + 2\overset{+1}{K}\overset{-1}{Br}(aq) \rightarrow 2\overset{+1}{K}\overset{-1}{Cl}(aq) + \overset{0}{Br_2}(l) \tag{8.41}$$

$$\overset{0}{Cl_2}(g) + 2\overset{+1}{K}\overset{-1}{I}(aq) \rightarrow 2\overset{+1}{K}\overset{-1}{Cl}(aq) + \overset{0}{I_2}(s) \tag{8.42}$$

As Br_2 and I_2 are coloured and dissolve in CCl_4, can easily be identified from the colour of the solution. The above reactions can be written in ionic form as:

$$\overset{0}{Cl_2}(g) + 2\overset{-1}{Br^-}(aq) \rightarrow 2\overset{-1}{Cl^-}(aq) + \overset{0}{Br_2}(l) \tag{8.41a}$$

$$\overset{0}{Cl_2}(g) + 2\overset{-1}{I^-}(aq) \rightarrow 2\overset{-1}{Cl^-}(aq) + \overset{0}{I_2}(s) \tag{8.42b}$$

Reactions (8.41) and (8.42) form the basis of identifying Br^- and I^- in the laboratory through the test popularly known as 'Layer Test'. It may not be out of place to mention here that bromine likewise can displace iodide ion in solution:

$$\overset{0}{Br_2}(l) + 2\overset{-1}{I^-}(aq) \rightarrow 2\overset{-1}{Br^-}(aq) + \overset{0}{I_2}(s) \tag{8.43}$$

The halogen displacement reactions have a direct industrial application. The recovery of halogens from their halides requires an oxidation process, which is represented by:

$$2X^- \rightarrow X_2 + 2e^- \tag{8.44}$$

here X denotes a halogen element. Whereas chemical means are available to oxidise Cl^-, Br^- and I^-, as fluorine is the strongest oxidising agent; there is no way to convert F^- ions to F_2 by chemical means. The only way to achieve F_2 from F^- is to oxidise electrolytically, the details of which you will study at a later stage.

4. Disproportionation reactions

Disproportionation reactions are a special type of redox reactions. In a disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states. The element in the form of reacting substance is in the intermediate oxidation state; and both higher and lower oxidation states of that element are formed in the reaction. The decomposition of hydrogen peroxide is a familiar example of the reaction, where oxygen experiences disproportionation.

$$\overset{+1\ -1}{2H_2O_2}\ (aq) \rightarrow \overset{+1\ -2}{2H_2O}(l) + \overset{0}{O_2}(g) \qquad (8.45)$$

Here the oxygen of peroxide, which is present in –1 state, is converted to zero oxidation state in O_2 and decreases to –2 oxidation state in H_2O.

Phosphorous, sulphur and chlorine undergo disproportionation in the alkaline medium as shown below :

$$\overset{0}{P_4}(s) + 3OH^-(aq) + 3H_2O(l) \rightarrow \overset{-3}{PH_3}(g) + \overset{+1}{3H_2PO_2^-}(aq) \qquad (8.46)$$

$$\overset{0}{S_8}(s) + 12\ OH^-\ (aq) \rightarrow \overset{-2}{4S^{2-}}\ (aq) + \overset{+2}{2S_2O_3^{2-}}(aq) + 6H_2O(l) \qquad (8.47)$$

$$\overset{0}{Cl_2}\ (g) + 2\ OH^-\ (aq) \rightarrow \overset{+1}{ClO^-}\ (aq) + \overset{-1}{Cl^-}\ (aq) + H_2O\ (l) \qquad (8.48)$$

The reaction (8.48) describes the formation of household bleaching agents. The hypochlorite ion (ClO^-) formed in the reaction oxidises the colour-bearing stains of the substances to colourless compounds.

It is of interest to mention here that whereas bromine and iodine follow the same trend as exhibited by chlorine in reaction (8.48), fluorine shows deviation from this behaviour when it reacts with alkali. The reaction that takes place in the case of fluorine is as follows:

$$2\ F_2(g) + 2OH^-(aq) \rightarrow 2\ F^-(aq) + OF_2(g) + H_2O(l) \qquad (8.49)$$

(It is to be noted with care that fluorine in reaction (8.49) will undoubtedly attack water to produce some oxygen also). This departure shown by fluorine is not surprising for us as we know the limitation of fluorine that, being the most electronegative element, it cannot exhibit any positive oxidation state. This means that among halogens, fluorine does not show a disproportionation tendency.

Problem 8.5

Which of the following species, do not show disproportionation reaction and why ?

ClO^-, ClO_2^-, ClO_3^- and ClO_4^-

Also write reaction for each of the species that disproportionates.

Solution

Among the oxoanions of chlorine listed above, ClO_4^- does not disproportionate because in this oxoanion chlorine is present in its highest oxidation state that is, +7. The disproportionation reactions for the other three oxoanions of chlorine are as follows:

$$\overset{+1}{3ClO^-} \rightarrow \overset{-1}{2Cl^-} + \overset{+5}{ClO_3^-}$$

$$\overset{+3}{6\ ClO_2^-} \xrightarrow{hv} \overset{+5}{4ClO_3^-} + \overset{-1}{2Cl^-}$$

$$\overset{+5}{4ClO_3^-} \rightarrow \overset{-1}{Cl^-} + \overset{+7}{3\ ClO_4^-}$$

Problem 8.6

Suggest a scheme of classification of the following redox reactions

(a) $N_2\ (g) + O_2\ (g) \rightarrow 2\ NO\ (g)$

(b) $2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4\ NO_2\ (g) + O_2\ (g)$

(c) $NaH(s) + H_2O(l) \rightarrow NaOH(aq) + H_2\ (g)$

(d) $2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-\ (aq) + H_2O(l)$

Solution

In reaction (a), the compound nitric oxide is formed by the combination of the elemental substances, nitrogen and oxygen; therefore, this is an example of combination redox reactions. The reaction (b) involves the breaking down of lead nitrate into three components; therefore, this is categorised under decomposition redox reaction. In reaction (c), hydrogen of water has been displaced by hydride ion into dihydrogen gas. Therefore, this may be called as displacement redox reaction. The reaction (d) involves disproportionation of NO_2 (+4 state) into NO_2^- (+3 state) and NO_3^- (+5 state). Therefore reaction (d) is an example of disproportionation redox reaction.

The Paradox of Fractional Oxidation Number

Sometimes, we come across with certain compounds in which the oxidation number of a particular element in the compound is in fraction. Examples are:

C_3O_2 [where oxidation number of carbon is (4/3)],

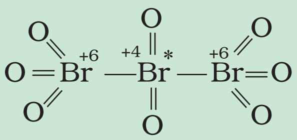
Br_3O_8 [where oxidation number of bromine is (16/3)]

and $Na_2S_4O_6$ (where oxidation number of sulphur is 2.5).

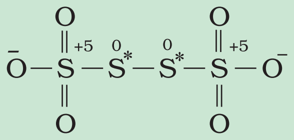
We know that the idea of fractional oxidation number is unconvincing to us, because electrons are never shared/transferred in fraction. Actually this fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is present in different oxidation states. Structure of the species C_3O_2, Br_3O_8 and $S_4O_6^{2-}$ reveal the following bonding situations:

$$O = \overset{+2}{C} = \overset{0}{C^*} = \overset{+2}{C} = O$$

Structure of C_3O_2
(carbon suboxide)



Structure of Br_3O_8 (tribromooctaoxide)



Structure of $S_4O_6^{2-}$ (tetrathionate ion)

The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in C_3O_2, two carbon atoms are present in +2 oxidation state each, whereas the third one is present in zero oxidation state and the average is 4/3. However, the realistic picture is +2 for two terminal carbons and zero for the middle carbon. Likewise in Br_3O_8, each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality, is 16/3. In the same fashion, in the species $S_4O_6^{2-}$, each of the two extreme sulphurs exhibits oxidation state of +5 and the two middle sulphurs as zero. The average of four oxidation numbers of sulphurs of the $S_4O_6^{2-}$ is 2.5, whereas the reality being + 5,0,0 and +5 oxidation number respectively for each sulphur.

We may thus, in general, conclude that the idea of fractional oxidation state should be taken with care and the reality is revealed by the structures only. Further, whenever we come across with fractional oxidation state of any particular element in any species, we must understand that this is the average oxidation number only. In reality (revealed by structures only), the element in that particular species is present in more than one whole number oxidation states. Fe_3O_4, Mn_3O_4, Pb_3O_4 are some of the other examples of the compounds, which are mixed oxides, where we come across with fractional oxidation states of the metal atom. However, the oxidation states may be in fraction as in O_2^+ and O_2^- where it is +½ and –½ respectively.

Problem 8.7

Why do the following reactions proceed differently ?

$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + Cl_2 + 4H_2O$

and

$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

Solution

Pb_3O_4 is actually a stoichiometric mixture of 2 mol of PbO and 1 mol of PbO_2. In PbO_2, lead is present in +4 oxidation state, whereas the stable oxidation state of lead in PbO is +2. PbO_2 thus can act as an oxidant (oxidising agent) and, therefore, can oxidise Cl^- ion of HCl into chlorine. We may also keep in mind that PbO is a basic oxide. Therefore, the reaction

$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + Cl_2 + 4H_2O$

can be splitted into two reactions namely:

$2PbO + 4HCl \rightarrow 2PbCl_2 + 2H_2O$

(acid-base reaction)

$$\overset{+4}{Pb}O_2 + 4H\overset{-1}{Cl} \rightarrow \overset{+2}{Pb}Cl_2 + \overset{0}{Cl_2} + 2H_2O$$

(redox reaction)

Since HNO_3 itself is an oxidising agent therefore, it is unlikely that the reaction may occur between PbO_2 and HNO_3. However, the acid-base reaction occurs between PbO and HNO_3 as:

$2PbO + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O$

It is the passive nature of PbO_2 against HNO_3 that makes the reaction different from the one that follows with HCl.

8.3.2 Balancing of Redox Reactions

Two methods are used to balance chemical equations for redox processes. One of these methods is based on the change in the oxidation number of reducing agent and the oxidising agent and the other method is based on splitting the redox reaction into two half reactions — one involving oxidation and the other involving reduction. Both these methods are in use and the choice of their use rests with the individual using them.

(a) Oxidation Number Method: In writing equations for oxidation-reduction reactions, just as for other reactions, the compositions and formulas must be known for the substances that react and for the products that are formed. The oxidation number method is now best illustrated in the following steps:

Step 1: Write the correct formula for each reactant and product.

Step 2: Identify atoms which undergo change in oxidation number in the reaction by assigning the oxidation number to all elements in the reaction.

Step 3: Calculate the increase or decrease in the oxidation number per atom and for the entire molecule/ion in which it occurs. If these are not equal then multiply by suitable number so that these become equal. (If you realise that two substances are reduced and nothing is oxidised or vice-versa, something is wrong. Either the formulas of reactants or products are wrong or the oxidation numbers have not been assigned properly).

Step 4: Ascertain the involvement of ions if the reaction is taking place in water, add H^+ or OH^- ions to the expression on the appropriate side so that the total ionic charges of reactants and products are equal. If the reaction is carried out in acidic solution, use H^+ ions in the equation; if in basic solution, use OH^- ions.

Step 5 : Make the numbers of hydrogen atoms in the expression on the two sides equal by adding water (H_2O) molecules to the reactants or products. Now, also check the number of oxygen atoms. If there are the same number of oxygen atoms in the reactants and products, the equation then represents the balanced redox reaction.

Let us now explain the steps involved in the method with the help of a few problems given below:

Problem 8.8

Write the net ionic equation for the reaction of potassium dichromate(VI), $K_2Cr_2O_7$ with sodium sulphite, Na_2SO_3, in an acid solution to give chromium(III) ion and the sulphate ion.

Solution

Step 1: The skeletal ionic equation is:

$$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$

Step 2: Assign oxidation numbers for Cr and S

$$\overset{+6}{Cr}_2\overset{-2}{O}_7^{2-}(aq) + \overset{+4}{S}\overset{-2}{O}_3^{2-}(aq) \rightarrow \overset{+3}{Cr}(aq) + \overset{+6}{S}\overset{-2}{O}_4^{2-}(aq)$$

This indicates that the dichromate ion is the oxidant and the sulphite ion is the reductant.

Step 3: Calculate the increase and decrease of oxidation number, and make them equal: from step-2 we can notice that there is change in oxidation state of chromium and sulphur. Oxidation state of chromium changes form +6 to +3. There is decrease of +3 in oxidation state of chromium on right hand side of the equation. Oxidation state of sulphur changes from +4 to +6. There is an increase of +2 in the oxidation state of sulphur on right hand side. To make the increase and decrease of oxidation state equal, place numeral 2 before cromium ion on right hand side and numeral 3 before sulphate ion on right hand side and balance the chromium and sulphur atoms on both the sides of the equation. Thus we get

$$\overset{+6}{Cr}_2\overset{-2}{O}_7^{2-}(aq) + 3\overset{+4}{S}\overset{-2}{O}_3^{2-}(aq) \rightarrow 2\overset{+3}{Cr}{}^{3+}(aq) + 3\overset{+6}{S}\overset{-2}{O}_4^{2-}(aq)$$

Step 4: As the reaction occurs in the acidic medium, and further the ionic charges are not equal on both the sides, add $8H^+$ on the left to make ionic charges equal

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+ \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$$

Step 5: Finally, count the hydrogen atoms, and add appropriate number of water molecules (i.e., $4H_2O$) on the right to achieve balanced redox change.

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$$

Problem 8.9

Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced ionic equation for the reaction.

Solution

Step 1: The skeletal ionic equation is :

$$MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$$

Step 2: Assign oxidation numbers for Mn and Br

$$\overset{+7}{Mn}O_4^-(aq) + \overset{-1}{Br}{}^-(aq) \rightarrow \overset{+4}{Mn}O_2(s) + \overset{+5}{Br}O_3^-(aq)$$

this indicates that permanganate ion is the oxidant and bromide ion is the reductant.

Step 3: Calculate the increase and decrease of oxidation number, and make the increase equal to the decrease.

$$2\overset{+7}{Mn}O_4^-(aq) + \overset{-1}{Br}{}^-(aq) \rightarrow 2\overset{+4}{Mn}O_2(s) + \overset{+5}{Br}O_3^-(aq)$$

Step 4: As the reaction occurs in the basic medium, and the ionic charges are not equal on both sides, add 2 OH^- ions on the right to make ionic charges equal.

$$2MnO_4^-(aq) + Br^-(aq) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$

Step 5: Finally, count the hydrogen atoms and add appropriate number of water molecules (i.e. one H_2O molecule) on the left side to achieve balanced redox change.

$$2MnO_4^-(aq) + Br^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$

(b) Half Reaction Method: In this method, the two half equations are balanced separately and then added together to give balanced equation.

Suppose we are to balance the equation showing the oxidation of Fe^{2+} ions to Fe^{3+} ions by dichromate ions $(Cr_2O_7)^{2-}$ in acidic medium, wherein, $Cr_2O_7^{2-}$ ions are reduced to Cr^{3+} ions. The following steps are involved in this task.

Step 1: Produce unbalanced equation for the reaction in ionic form :

$$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq) \tag{8.50}$$

Step 2: Separate the equation into half-reactions:

Oxidation half : $\overset{+2}{\mathrm{Fe}}{}^{2+}\,(aq) \rightarrow \overset{+3}{\mathrm{Fe}}{}^{3+}(aq)$ (8.51)

Reduction half : $\overset{+6}{\mathrm{Cr}}{}_2\overset{-2}{\mathrm{O}}{}_7^{2-}(aq) \rightarrow \overset{+3}{\mathrm{Cr}}{}^{3+}(aq)$ (8.52)

Step 3: Balance the atoms other than O and H in each half reaction individually. Here the oxidation half reaction is already balanced with respect to Fe atoms. For the reduction half reaction, we multiply the Cr^{3+} by 2 to balance Cr atoms.

$Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq)$ (8.53)

Step 4: For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms.

Thus, we get :

$Cr_2O_7^{2-}\ (aq) + 14H^+\ (aq) \rightarrow 2\ Cr^{3+}(aq) + 7H_2O\ (l)$ (8.54)

Step 5: Add electrons to one side of the half reaction to balance the charges. If need be, make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate number.

The oxidation half reaction is thus rewritten to balance the charge:

$Fe^{2+}\ (aq) \rightarrow Fe^{3+}\ (aq) + e^-$ (8.55)

Now in the reduction half reaction there are net twelve positive charges on the left hand side and only six positive charges on the right hand side. Therefore, we add six electrons on the left side.

$Cr_2O_7^{2-}\ (aq) + 14H^+\ (aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O\ (l)$ (8.56)

To equalise the number of electrons in both the half reactions, we multiply the oxidation half reaction by 6 and write as :

$6Fe^{2+}\ (aq) \rightarrow 6Fe^{3+}(aq) + 6e^-$ (8.57)

Step 6: We add the two half reactions to achieve the overall reaction and cancel the electrons on each side. This gives the net ionic equation as :

$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6\ Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$ (8.58)

Step 7: Verify that the equation contains the same type and number of atoms and the same charges on both sides of the equation. This last check reveals that the equation is fully balanced with respect to number of atoms and the charges.

For the reaction in a basic medium, first balance the atoms as is done in acidic medium. Then for each H^+ ion, add an equal number of OH^- ions to both sides of the equation. Where H^+ and OH^- appear on the same side of the equation, combine these to give H_2O.

Problem 8.10

Permanganate(VII) ion, MnO_4^- in basic solution oxidises iodide ion, I^- to produce molecular iodine (I_2) and manganese (IV) oxide (MnO_2). Write a balanced ionic equation to represent this redox reaction.

Solution

Step 1: First we write the skeletal ionic equation, which is

$MnO_4^-\ (aq) + I^-\ (aq) \rightarrow MnO_2(s) + I_2(s)$

Step 2: The two half-reactions are:

Oxidation half : $\overset{-1}{\mathrm{I}}{}^-(aq) \rightarrow \overset{0}{\mathrm{I}}{}_2\ (s)$

Reduction half: $\overset{+7}{\mathrm{Mn}}\mathrm{O}_4^-(aq) \rightarrow \overset{+4}{\mathrm{Mn}}\mathrm{O}_2(s)$

Step 3: To balance the I atoms in the oxidation half reaction, we rewrite it as:

$2I^-\ (aq) \rightarrow I_2\ (s)$

Step 4: To balance the O atoms in the reduction half reaction, we add two water molecules on the right:

$MnO_4^-\ (aq) \rightarrow MnO_2\ (s) + 2\ H_2O\ (l)$

To balance the H atoms, we add four H^+ ions on the left:

$MnO_4^-(aq) + 4\ H^+\ (aq) \rightarrow MnO_2(s) + 2H_2O\ (l)$

As the reaction takes place in a basic solution, therefore, for four H^+ ions, we add four OH^- ions to both sides of the equation:

$MnO_4^-\ (aq) + 4H^+\ (aq) + 4OH^-(aq) \rightarrow MnO_2\ (s) + 2\ H_2O(l) + 4OH^-\ (aq)$

Replacing the H^+ and OH^- ions with water, the resultant equation is:

$MnO_4^-(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 4OH^-(aq)$

Step 5 : In this step we balance the charges of the two half-reactions in the manner depicted as:

$$2I^-(aq) \rightarrow I_2(s) + 2e^-$$

$$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$$

Now to equalise the number of electrons, we multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2.

$$6I^-(aq) \rightarrow 3I_2(s) + 6e^-$$

$$2MnO_4^-(aq) + 4H_2O(l) + 6e^- \rightarrow 2MnO_2(s) + 8OH^-(aq)$$

Step 6: Add two half-reactions to obtain the net reactions after cancelling electrons on both sides.

$$6I^-(aq) + 2MnO_4^-(aq) + 4H_2O(l) \rightarrow 3I_2(s) + 2MnO_2(s) + 8OH^-(aq)$$

Step 7: A final verification shows that the equation is balanced in respect of the number of atoms and charges on both sides.

8.3.3 Redox Reactions as the Basis for Titrations

In acid-base systems we come across with a titration method for finding out the strength of one solution against the other using a pH sensitive indicator. Similarly, in redox systems, the titration method can be adopted to determine the strength of a reductant/oxidant using a redox sensitive indicator. The usage of indicators in redox titration is illustrated below:

(i) In one situation, the reagent itself is intensely coloured, e.g., permanganate ion, MnO_4^-. Here MnO_4^- acts as the self indicator. The visible end point in this case is achieved after the last of the reductant (Fe^{2+} or $C_2O_4^{2-}$) is oxidised and the first lasting tinge of pink colour appears at MnO_4^- concentration as low as 10^{-6} mol dm^{-3} (10^{-6} mol L^{-1}). This ensures a minimal 'overshoot' in colour beyond the equivalence point, the point where the reductant and the oxidant are equal in terms of their mole stoichiometry.

(ii) If there is no dramatic auto-colour change (as with MnO_4^- titration), there are indicators which are oxidised immediately after the last bit of the reactant is consumed, producing a dramatic colour change. The best example is afforded by $Cr_2O_7^{2-}$, which is not a self-indicator, but oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour, thus signalling the end point.

(iii) There is yet another method which is interesting and quite common. Its use is restricted to those reagents which are able to oxidise I^- ions, say, for example, Cu(II):

$$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow Cu_2I_2(s) + I_2(aq) \quad (8.59)$$

This method relies on the facts that iodine itself gives an intense blue colour with starch and has a very specific reaction with thiosulphate ions ($S_2O_3^{2-}$), which too is a redox reaction:

$$I_2(aq) + 2\,S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq) \quad (8.60)$$

I_2, though insoluble in water, remains in solution containing KI as KI_3.

On addition of starch after the liberation of iodine from the reaction of Cu^{2+} ions on iodide ions, an intense blue colour appears. This colour disappears as soon as the iodine is consumed by the thiosulphate ions. Thus, the end-point can easily be tracked and the rest is the stoichiometric calculation only.

8.3.4 Limitations of Concept of Oxidation Number

As you have observed in the above discussion, the concept of redox processes has been evolving with time. This process of evolution is continuing. In fact, in recent past the oxidation process is visualised as a decrease in electron density and reduction process as an increase in electron density around the atom(s) involved in the reaction.

8.4 REDOX REACTIONS AND ELECTRODE PROCESSES

The experiment corresponding to reaction (8.15), can also be observed if zinc rod is dipped in copper sulphate solution. The redox reaction takes place and during the reaction, zinc is oxidised to zinc ions and copper ions are reduced to metallic copper due to direct transfer of electrons from zinc to copper ion. During this reaction heat is also evolved. Now we modify the experiment in such a manner that for the same redox reaction transfer of electrons takes place indirectly. This necessitates the separation of zinc metal from copper sulphate solution. We take copper sulphate solution in a beaker and put a copper strip or rod in it. We also take zinc sulphate solution in another beaker and put a zinc rod or strip in it. Now reaction takes place in either of the beakers and at the interface of the metal and its salt solution in each beaker both the reduced and oxidized forms of the same species are present. These represent the species in the reduction and oxidation half reactions. A **redox couple** is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction.

This is represented by separating the oxidised form from the reduced form by a vertical line or a slash representing an interface (e.g. solid/solution). For example in this experiment the two redox couples are represented as Zn^{2+}/Zn and Cu^{2+}/Cu. In both cases, oxidised form is put before the reduced form. Now we put the beaker containing copper sulphate solution and the beaker containing zinc sulphate solution side by side (Fig. 8.3). We connect solutions in two beakers by a salt bridge (a U-tube containing a solution of potassium chloride or ammonium nitrate usually solidified by boiling with agar agar and later cooling to a jelly like substance). This provides an electric contact between the two solutions without allowing them to mix with each other. The zinc and copper rods are connected by a metallic wire with a provision for an ammeter and a switch. The set-up as shown in Fig.8.3 is known as Daniell cell. When the switch is in the off position, no reaction takes place in either of the beakers and no current flows through the metallic wire. As soon as the switch is in the on position, we make the following observations:

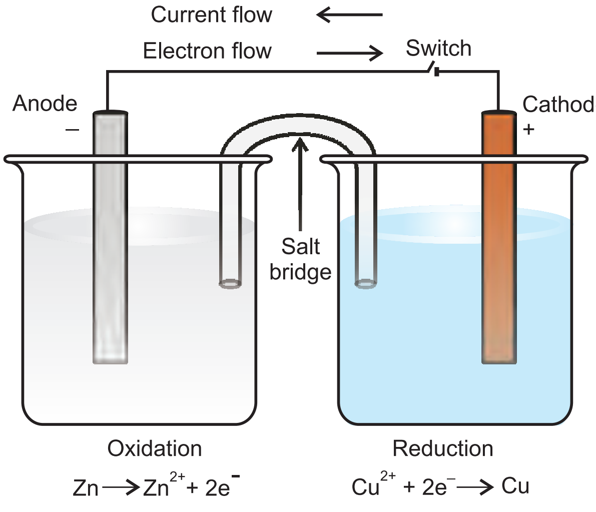


Fig.8.3 *The set-up for Daniell cell. Electrons produced at the anode due to oxidation of Zn travel through the external circuit to the cathode where these reduce the copper ions. The circuit is completed inside the cell by the migration of ions through the salt bridge. It may be noted that the direction of current is opposite to the direction of electron flow.*

1. The transfer of electrons now does not take place directly from Zn to Cu^{2+} but through the metallic wire connecting the two rods as is apparent from the arrow which indicates the flow of current.
2. The electricity from solution in one beaker to solution in the other beaker flows by the migration of ions through the salt bridge. We know that the flow of current is possible only if there is a potential difference between the copper and zinc rods known as **electrodes** here.

The potential associated with each electrode is known as **electrode potential**. If the concentration of each species taking part in the electrode reaction is unity (if any gas appears in the electrode reaction, it is confined to 1 atmospheric pressure) and further the reaction is carried out at 298K, then the potential of each electrode is said to be the **Standard Electrode Potential**. By convention, the standard electrode potential ($E^{\ominus}$) of hydrogen electrode is 0.00 volts. The electrode potential value for each electrode process is a measure of the relative tendency of the active species in the process to remain in the oxidised/reduced form. A negative $E^{\ominus}$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple. A positive $E^\ominus$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple. The standard electrode potentials are very important and we can get a lot of other useful information from them. The values of standard electrode potentials for some selected electrode processes (reduction reactions) are given in Table 8.1. You will learn more about electrode reactions and cells in Class XII.

Table 8.1 The 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 respectively.

Reaction (Oxidised form + ne^-	**$\rightarrow$ Reduced form)**	**$E^\ominus$ / 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
$I_2(s) + 2e^-$	$\rightarrow 2I^-$	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
$2H^+ + 2e^-$	**$\rightarrow H_2(g)$**	**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
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-$	–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

Increasing strength of oxidising agent ↑

Increasing strength of reducing agent ↓

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

SUMMARY

Redox reactions form an important class of reactions in which **oxidation** and **reduction** occur simultaneously. Three tier conceptualisation viz, classical, electronic and oxidation number, which is usually available in the texts, has been presented in detail. Oxidation, reduction, oxidising agent (**oxidant**) and reducing agent (**reductant**) have been viewed according to each conceptualisation. **Oxidation numbers** are assigned in accordance with a consistent set of rules. Oxidation number and ion-electron method both are useful means in writing equations for the redox reactions. Redox reactions are classified into four categories: combination, decomposition displacement and disproportionation reactions. The concept of **redox couple** and **electrode processes** is introduced here. The redox reactions find wide applications in the study of electrode processes and cells.

EXERCISES

8.1 Assign oxidation number to the underlined elements in each of the following species:

(a) $NaH_2\underline{P}O_4$ (b) $NaH\underline{S}O_4$ (c) $H_4\underline{P}_2O_7$ (d) $K_2\underline{Mn}O_4$

(e) $Ca\underline{O}_2$ (f) $Na\underline{B}H_4$ (g) $H_2\underline{S}_2O_7$ (h) $KAl(\underline{S}O_4)_2.12\ H_2O$

8.2 What are the oxidation number of the underlined elements in each of the following and how do you rationalise your results ?

(a) $K\underline{I}_3$ (b) $H_2\underline{S}_4O_6$ (c) $\underline{Fe}_3O_4$ (d) $\underline{C}H_3\underline{C}H_2OH$ (e) $\underline{C}H_3\underline{C}OOH$

8.3 Justify that the following reactions are redox reactions:

(a) $CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$

(b) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

(c) $4BCl_3(g) + 3LiAlH_4(s) \rightarrow 2B_2H_6(g) + 3LiCl(s) + 3\ AlCl_3\ (s)$

(d) $2K(s) + F_2(g) \rightarrow 2K^+F^-\ (s)$

(e) $4\ NH_3(g) + 5\ O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

8.4 Fluorine reacts with ice and results in the change:

$H_2O(s) + F_2(g) \rightarrow HF(g) + HOF(g)$

Justify that this reaction is a redox reaction.

8.5 Calculate the oxidation number of sulphur, chromium and nitrogen in H_2SO_5, $Cr_2O_7^{2-}$ and NO_3^-. Suggest structure of these compounds. Count for the fallacy.

8.6 Write formulas for the following compounds:

(a) Mercury(II) chloride (b) Nickel(II) sulphate

(c) Tin(IV) oxide (d) Thallium(I) sulphate

(e) Iron(III) sulphate (f) Chromium(III) oxide

8.7 Suggest a list of the substances where carbon can exhibit oxidation states from –4 to +4 and nitrogen from –3 to +5.

8.8 While sulphur dioxide and hydrogen peroxide can act as oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. Why ?

8.9 Consider the reactions:

(a) $6\ CO_2(g) + 6H_2O(l) \rightarrow C_6\ H_{12}\ O_6(aq) + 6O_2(g)$

(b) $O_3(g) + H_2O_2(l) \rightarrow H_2O(l) + 2O_2(g)$

Why it is more appropriate to write these reactions as :

(a) $6CO_2(g) + 12H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$

(b) $O_3(g) + H_2O_2(l) \rightarrow H_2O(l) + O_2(g) + O_2(g)$

Also suggest a technique to investigate the path of the above (a) and (b) redox reactions.

8.10 The compound AgF_2 is unstable compound. However, if formed, the compound acts as a very strong oxidising agent. Why ?

8.11 Whenever a reaction between an oxidising agent and a reducing agent is carried out, a compound of lower oxidation state is formed if the reducing agent is in excess and a compound of higher oxidation state is formed if the oxidising agent is in excess. Justify this statement giving three illustrations.

8.12 How do you count for the following observations ?

(a) Though alkaline potassium permanganate and acidic potassium permanganate both are used as oxidants, yet in the manufacture of benzoic acid from toluene we use alcoholic potassium permanganate as an oxidant. Why ? Write a balanced redox equation for the reaction.

(b) When concentrated sulphuric acid is added to an inorganic mixture containing chloride, we get colourless pungent smelling gas HCl, but if the mixture contains bromide then we get red vapour of bromine. Why ?

8.13 Identify the substance oxidised reduced, oxidising agent and reducing agent for each of the following reactions:

(a) $2AgBr(s) + C_6H_6O_2(aq) \rightarrow 2Ag(s) + 2HBr(aq) + C_6H_4O_2(aq)$

(b) $HCHO(l) + 2[Ag(NH_3)_2]^+(aq) + 3OH^-(aq) \rightarrow 2Ag(s) + HCOO^-(aq) + 4NH_3(aq) + 2H_2O(l)$

(c) $HCHO(l) + 2Cu^{2+}(aq) + 5OH^-(aq) \rightarrow Cu_2O(s) + HCOO^-(aq) + 3H_2O(l)$

(d) $N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l)$

(e) $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

8.14 Consider the reactions :

$2S_2O_3^{2-}(aq) + I_2(s) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

$S_2O_3^{2-}(aq) + 2Br_2(l) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 4Br^-(aq) + 10H^+(aq)$

Why does the same reductant, thiosulphate react differently with iodine and bromine ?

8.15 Justify giving reactions that among halogens, fluorine is the best oxidant and among hydrohalic compounds, hydroiodic acid is the best reductant.

8.16 Why does the following reaction occur ?

$XeO_6^{4-}(aq) + 2F^-(aq) + 6H^+(aq) \rightarrow XeO_3(g) + F_2(g) + 3H_2O(l)$

What conclusion about the compound Na_4XeO_6 (of which XeO_6^{4-} is a part) can be drawn from the reaction.

8.17 Consider the reactions:

(a) $H_3PO_2(aq) + 4AgNO_3(aq) + 2H_2O(l) \rightarrow H_3PO_4(aq) + 4Ag(s) + 4HNO_3(aq)$

(b) $H_3PO_2(aq) + 2CuSO_4(aq) + 2H_2O(l) \rightarrow H_3PO_4(aq) + 2Cu(s) + H_2SO_4(aq)$

(c) $C_6H_5CHO(l) + 2[Ag(NH_3)_2]^+(aq) + 3OH^-(aq) \rightarrow C_6H_5COO^-(aq) + 2Ag(s) + 4NH_3(aq) + 2H_2O(l)$

(d) $C_6H_5CHO(l) + 2Cu^{2+}(aq) + 5OH^-(aq) \rightarrow$ No change observed.

What inference do you draw about the behaviour of Ag^+ and Cu^{2+} from these reactions ?

8.18 Balance the following redox reactions by ion – electron method :

(a) MnO_4^- (aq) + I^- (aq) $\rightarrow$ MnO_2 (s) + I_2(s) (in basic medium)

(b) MnO_4^- (aq) + SO_2 (g) $\rightarrow$ Mn^{2+} (aq) + HSO_4^- (aq) (in acidic solution)

(c) H_2O_2 (aq) + Fe^{2+} (aq) $\rightarrow$ Fe^{3+} (aq) + H_2O (l) (in acidic solution)

(d) $Cr_2O_7^{2-}$ + SO_2(g) $\rightarrow$ Cr^{3+} (aq) + SO_4^{2-} (aq) (in acidic solution)

8.19 Balance the following equations in basic medium by ion-electron method and oxidation number methods and identify the oxidising agent and the reducing agent.

(a) P_4(s) + OH^-(aq) $\rightarrow$ PH_3(g) + HPO_2^- (aq)

(b) N_2H_4(l) + ClO_3^-(aq) $\rightarrow$ NO(g) + Cl^-(g)

(c) Cl_2O_7 (g) + H_2O_2(aq) $\rightarrow$ ClO_2^-(aq) + O_2(g) + H^+

8.20 What sorts of informations can you draw from the following reaction ?

$(CN)_2$(g) + $2OH^-$(aq) $\rightarrow$ CN^-(aq) + CNO^-(aq) + H_2O(l)

8.21 The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2, and H^+ ion. Write a balanced ionic equation for the reaction.

8.22 Consider the elements :

Cs, Ne, I and F

(a) Identify the element that exhibits only negative oxidation state.

(b) Identify the element that exhibits only postive oxidation state.

(c) Identify the element that exhibits both positive and negative oxidation states.

(d) Identify the element which exhibits neither the negative nor does the positive oxidation state.

8.23 Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess of chlorine is removed by treating with sulphur dioxide. Present a balanced equation for this redox change taking place in water.

8.24 Refer to the periodic table given in your book and now answer the following questions:

(a) Select the possible non metals that can show disproportionation reaction.

(b) Select three metals that can show disproportionation reaction.

8.25 In Ostwald's process for the manufacture of nitric acid, the first step involves the oxidation of ammonia gas by oxygen gas to give nitric oxide gas and steam. What is the maximum weight of nitric oxide that can be obtained starting only with 10.00 g. of ammonia and 20.00 g of oxygen ?

8.26 Using the standard electrode potentials given in the Table 8.1, predict if the reaction between the following is feasible:

(a) Fe^{3+}(aq) and I^-(aq)

(b) Ag^+(aq) and Cu(s)

(c) Fe^{3+} (aq) and Cu(s)

(d) Ag(s) and Fe^{3+}(aq)

(e) Br_2(aq) and Fe^{2+}(aq).

8.27 Predict the products of electrolysis in each of the following:

(i) An aqueous solution of $AgNO_3$ with silver electrodes

(ii) An aqueous solution $AgNO_3$ with platinum electrodes

(iii) A dilute solution of H_2SO_4 with platinum electrodes

(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

8.28 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.

8.29 Given the standard electrode potentials,

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

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

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

arrange these metals in their increasing order of reducing power.

8.30 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, and

(iii) individual reaction at each electrode.

UNIT 9

HYDROGEN

Objectives

After studying this unit, you will be able to

- present informed opinions on the position of hydrogen in the periodic table;
- identify the modes of occurrence and preparation of dihydrogen on a small and commercial scale; describe isotopes of hydrogen;
- explain how different elements combine with hydrogen to form ionic, molecular and non-stoichiometric compounds;
- describe how an understanding of its properties can lead to the production of useful substances, and new technologies;
- understand the structure of water and use the knowledge for explaining physical and chemical properties;
- explain how environmental water quality depends on a variety of dissolved substances; difference between 'hard' and 'soft' water and learn about water softening;
- acquire the knowledge about heavy water and its importance;
- understand the structure of hydrogen peroxide, learn its preparatory methods and properties leading to the manufacture of useful chemicals and cleaning of environment;
- understand and use certain terms e.g., electron-deficient, electron-precise, electron-rich, hydrogen economy, hydrogenation etc.

> ***"Hydrogen, the most abundant element in the universe and the third most abundant on the surface of the globe, is being visualised as the major future source of energy."***

Hydrogen has the simplest atomic structure among all the elements around us in Nature. In atomic form it consists of only one proton and one electron. However, in elemental form it exists as a diatomic (H_2) molecule and is called dihydrogen. It forms more compounds than any other element. Do you know that the global concern related to energy can be overcome to a great extent by the use of hydrogen as a source of energy? In fact, hydrogen is of great industrial importance as you will learn in this unit.

9.1 POSITION OF HYDROGEN IN THE PERIODIC TABLE

Hydrogen is the first element in the periodic table. However, its placement in the periodic table has been a subject of discussion in the past. As you know by now that the elements in the periodic table are arranged according to their electronic configurations.

Hydrogen has electronic configuration $1s^1$. On one hand, its electronic configuration is similar to the outer electronic configuration (ns^1) of alkali metals , which belong to the first group of the periodic table. On the other hand, like halogens (with ns^2np^5 configuration belonging to the seventeenth group of the periodic table), it is short by one electron to the corresponding noble gas configuration, helium ($1s^2$). Hydrogen, therefore, has resemblance to alkali metals, which lose one electron to form unipositive ions, as well as with halogens, which gain one electron to form uninegative ion. Like alkali metals, hydrogen forms oxides, halides and sulphides. However, unlike alkali metals, it has a very high ionization enthalpy and does not possess metallic characteristics under normal conditions. In fact, in terms of ionization enthalpy, hydrogen resembles more with halogens, $\Delta_i H$ of Li is 520 kJ mol^{-1}, F is 1680 kJ mol^{-1} and that of H is 1312 kJ mol^{-1}. Like halogens, it forms a diatomic molecule, combines with elements to form hydrides and a large number of covalent compounds. However, in terms of reactivity, it is very low as compared to halogens.

Inspite of the fact that hydrogen, to a certain extent resembles both with alkali metals and halogens, it differs from them as well. Now the pertinent question arises as where should it be placed in the periodic table? Loss of the electron from hydrogen atom results in nucleus (H^+) of ~1.5×10^{-3} pm size. This is extremely small as compared to normal atomic and ionic sizes of 50 to 200pm. As a consequence, H^+ does not exist freely and is always associated with other atoms or molecules. Thus, it is unique in behaviour and is, therefore, best placed separately in the periodic table (Unit 3).

9.2 DIHYDROGEN, H_2

9.2.1 Occurrence

Dihydrogen is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist mostly of hydrogen. However, due to its light nature, it is much less abundant (0.15% by mass) in the earth's atmosphere. Of course, in the combined form it constitutes 15.4% of the earth's crust and the oceans. In the combined form besides in water, it occurs in plant and animal tissues, carbohydrates, proteins, hydrides including hydrocarbons and many other compounds.

9.2.2 Isotopes of Hydrogen

Hydrogen has three isotopes: **protium**, ${}^1_1H$, **deuterium**, ${}^2_1H$ or D and **tritium**, ${}^3_1H$ or T. Can you guess how these isotopes differ from each other ? These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen, protium, has no neutrons, deuterium (also known as heavy hydrogen) has one and tritium has two neutrons in the nucleus. In the year 1934, an American scientist, Harold C. Urey, got Nobel Prize for separating hydrogen isotope of mass number 2 by physical methods.

The predominant form is protium. Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD. The tritium concentration is about one atom per 10^{18} atoms of protium. Of these isotopes, only tritium is radioactive and emits low energy β^- particles ($t_{½}$, 12.33 years).

Table 9.1 Atomic and Physical Properties of Hydrogen

Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	10^{-15}
Relative atomic mass (g mol^{-1})	1.008	2.014	3.016
Melting point / K	13.96	18.73	20.62
Boiling point/ K	20.39	23.67	25.0
Density / gL^{-1}	0.09	0.18	0.27
Enthalpy of fusion/kJ mol^{-1}	0.117	0.197	-
Enthalpy of vaporization/kJ mol^{-1}	0.904	1.226	-
Enthalpy of bond dissociation/kJ mol^{-1} at 298.2K	435.88	443.35	-
Internuclear distance/pm	74.14	74.14	-
Ionization enthalpy/kJ mol^{-1}	1312	-	-
Electron gain enthalpy/kJ mol^{-1}	–73	-	-
Covalent radius/pm	37	-	-
Ionic radius(H^-)/pm	208		

Since the isotopes have the same electronic configuration, they have almost the same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthalpy of bond dissociation (Table 9.1). However, in physical properties these isotopes differ considerably due to their large mass differences.

9.3 PREPARATION OF DIHYDROGEN, H_2

There are a number of methods for preparing dihydrogen from metals and metal hydrides.

9.3.1 Laboratory Preparation of Dihydrogen

(i) It is usually prepared by the reaction of granulated zinc with dilute hydrochloric acid.

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

(ii) It can also be prepared by the reaction of zinc with aqueous alkali.

$$Zn + 2NaOH \rightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2$$

9.3.2 Commercial Production of Dihydrogen

The commonly used processes are outlined below:

(i) Electrolysis of acidified water using platinum electrodes gives hydrogen.

$$2H_2O(l) \xrightarrow[\text{Traces of acid / base}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

(ii) High purity (>99.95%) dihydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.

(iii) It is obtained as a byproduct in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution. During electrolysis, the reactions that take place are:

at anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

at cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

The overall reaction is

$$2Na^+(aq) + 2Cl^-(aq) + 2H_2O(l)$$
$$\downarrow$$
$$Cl_2(g) + H_2(g) + 2Na^+(aq) + 2OH^-(aq)$$

(iv) Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields hydrogen.

$$C_nH_{2n+2} + nH_2O \xrightarrow[\text{Ni}]{1270K} nCO + (2n+1)H_2$$

e.g.,

$$CH_4(g) + H_2O(g) \xrightarrow[\text{Ni}]{1270K} CO(g) + 3H_2(g)$$

The mixture of CO and H_2 is called *water gas*. As this mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called *synthesis gas* or **'syngas'**. Nowadays 'syngas' is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called *'coal gasification'*.

$$C(s) + H_2O(g) \xrightarrow{1270K} CO(g) + H_2(g)$$

The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst.

$$CO(g) + H_2O(g) \xrightarrow[\text{catalyst}]{673K} CO_2(g) + H_2(g)$$

This is called *water-gas shift reaction*. Carbon dioxide is removed by scrubbing with sodium arsenite solution.

Presently ~77% of the industrial dihydrogen is produced from petro-chemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

9.4 PROPERTIES OF DIHYDROGEN

9.4.1 Physical Properties

Dihydrogen is a colourless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water. Its other physical properties alongwith those of deuterium are given in Table 9.1.

9.4.2 Chemical Properties

The chemical behaviour of dihydrogen (and for that matter any molecule) is determined, to a large extent, by bond dissociation enthalpy. The H–H bond dissociation enthalpy is the highest for a single bond between two atoms of any element. What inferences would you draw from this fact ? It is because of this factor that the dissociation of dihydrogen into its atoms is only ~0.081% around 2000K which increases to 95.5% at 5000K. Also, it is relatively inert at room temperature due to the high H–H bond enthalpy. Thus, the atomic hydrogen is produced at a high temperature in an electric arc or under ultraviolet radiations. Since its orbital is incomplete with $1s^1$ electronic configuration, it does combine with almost all the elements. It accomplishes reactions by (i) loss of the only electron to give H^+, (ii) gain of an electron to form H^-, and (iii) sharing electrons to form a single covalent bond.

The chemistry of dihydrogen can be illustrated by the following reactions:

Reaction with halogens: It reacts with halogens, X_2 to give hydrogen halides, HX,

$$H_2(g) + X_2(g) \rightarrow 2HX(g) \quad (X = F, Cl, Br, I)$$

While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

Reaction with dioxygen: It reacts with dioxygen to form water. The reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow{\text{catalyst or heating}} 2H_2O(l);$$

$$\Delta H^\ominus = -285.9 \text{ kJ mol}^{-1}$$

Reaction with dinitrogen: With dinitrogen it forms ammonia.

$$3H_2(g) + N_2(g) \xrightarrow[\text{Fe}]{\text{673K, 200atm}} 2NH_3(g);$$

$$\Delta H^\ominus = -92.6 \text{ kJ mol}^{-1}$$

This is the method for the manufacture of ammonia by the Haber process.

Reactions with metals: With many metals it combines at a high temperature to yield the corresponding hydrides (section 9.5)

$H_2(g) + 2M(g) \rightarrow 2MH(s);$

where M is an alkali metal

Reactions with metal ions and metal oxides: It reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.

$$H_2(g) + Pd^{2+}(aq) \rightarrow Pd(s) + 2H^+(aq)$$

$$yH_2(g) + M_xO_y(s) \rightarrow xM(s) + yH_2O(l)$$

Reactions with organic compounds: It reacts with many organic compounds in the presence of catalysts to give useful hydrogenated products of commercial importance. For example :

(i) Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine and vanaspati ghee)

(ii) Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.

$$H_2 + CO + RCH = CH_2 \rightarrow RCH_2CH_2CHO$$

$$H_2 + RCH_2CH_2CHO \rightarrow RCH_2CH_2CH_2OH$$

Problem 9.1

Comment on the reactions of dihydrogen with (i) chlorine, (ii) sodium, and (iii) copper(II) oxide

Solution

(i) Dihydrogen reduces chlorine into chloride (Cl^-) ion and itself gets oxidised to H^+ ion by chlorine to form hydrogen chloride. An electron pair is shared between H and Cl leading to the formation of a covalent molecule.

(ii) Dihydrogen is reduced by sodium to form NaH. An electron is transferred from Na to H leading to the formation of an ionic compound, Na^+H^-.

(iii) Dihydrogen reduces copper(II) oxide to copper in zero oxidation state and itself gets oxidised to H_2O, which is a covalent molecule.

9.4.3 Uses of Dihydrogen

- The largest single use of dihydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.
- Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soyabean, cotton seeds etc.
- It is used in the manufacture of bulk organic chemicals, particularly methanol.

$$CO(g) + 2H_2(g) \xrightarrow[\text{catalyst}]{\text{cobalt}} CH_3OH(l)$$

- It is widely used for the manufacture of metal hydrides (Section 9.5)
- It is used for the preparation of hydrogen chloride, a highly useful chemical.

- In metallurgical processes, it is used to reduce heavy metal oxides to metals.
- Atomic hydrogen and oxy-hydrogen torches find use for cutting and welding purposes. Atomic hydrogen atoms (produced by dissociation of dihydrogen with the help of an electric arc) are allowed to recombine on the surface to be welded to generate the temperature of 4000 K.
- It is used as a rocket fuel in space research.
- Dihydrogen is used in fuel cells for generating electrical energy. It has many advantages over the conventional fossil fuels and electric power. It does not produce any pollution and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

9.5 HYDRIDES

Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called **hydrides**. If 'E' is the symbol of an element then hydride can be expressed as EH_x (e.g., MgH_2) or E_mH_n (e.g., B_2H_6).

The hydrides are classified into three categories :

(i) Ionic or saline or saltlike hydrides
(ii) Covalent or molecular hydrides
(iii) Metallic or non-stoichiometric hydrides

9.5.1 Ionic or Saline Hydrides

These are stoichiometric compounds of dihydrogen formed with most of the *s*-block elements which are highly electropositive in character. However, significant covalent character is found in the lighter metal hydrides such as LiH, BeH_2 and MgH_2. In fact BeH_2 and MgH_2 are polymeric in structure. The ionic hydrides are crystalline, non-volatile and non-conducting in solid state. However, their melts conduct electricity and on electrolysis liberate dihydrogen gas at anode, which confirms the existence of H^- ion.

$$2H^-(\text{melt}) \xrightarrow{\text{anode}} H_2(g) + 2e^-$$

Saline hydrides react violently with water producing dihydrogen gas.

$$NaH(s) + H_2O(aq) \rightarrow NaOH(aq) + H_2(g)$$

Lithium hydride is rather unreactive at moderate temperatures with O_2 or Cl_2. It is, therefore, used in the synthesis of other useful hydrides, e.g.,

$$8LiH + Al_2Cl_6 \rightarrow 2LiAlH_4 + 6LiCl$$

$$2LiH + B_2H_6 \rightarrow 2LiBH_4$$

9.5.2 Covalent or Molecular Hydride

Dihydrogen forms molecular compounds with most of the *p*-block elements. Most familiar examples are CH_4, NH_3, H_2O and HF. For convenience hydrogen compounds of non-metals have also been considered as hydrides. Being covalent, they are volatile compounds.

Molecular hydrides are further classified according to the relative numbers of electrons and bonds in their Lewis structure into : **(i) electron-deficient, (ii) electron-precise, and (iii) electron-rich hydrides.**

An electron-deficient hydride, as the name suggests, has too few electrons for writing its conventional Lewis structure. Diborane (B_2H_6) is an example. In fact all elements of group 13 will form electron-deficient compounds. What do you expect from their behaviour? They act as Lewis acids i.e., electron acceptors.

Electron-precise compounds have the required number of electrons to write their conventional Lewis structures. All elements of group 14 form such compounds (e.g., CH_4) which are tetrahedral in geometry.

Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. (NH_3 has 1- lone pair, H_2O – 2 and HF –3 lone pairs). What do you expect from the behaviour of such compounds ? They will behave as Lewis bases i.e., electron donors. The presence of lone pairs on highly electronegative atoms like N, O and F in hydrides results in hydrogen bond formation between the molecules. This leads to the association of molecules.

Problem 9.2

Would you expect the hydrides of N, O and F to have lower boiling points than the hydrides of their subsequent group members ? Give reasons.

Solution

On the basis of molecular masses of NH_3, H_2O and HF, their boiling points are expected to be lower than those of the subsequent group member hydrides. However, due to higher electronegativity of N, O and F, the magnitude of hydrogen bonding in their hydrides will be quite appreciable. Hence, the boiling points NH_3, H_2O and HF will be higher than the hydrides of their subsequent group members.

9.5.3 Metallic or Non-stoichiometric (or Interstitial) Hydrides

These are formed by many *d*-block and *f*-block elements. However, the metals of group 7, 8 and 9 do not form hydride. Even from group 6, only chromium forms CrH. These hydrides conduct heat and electricity though not as efficiently as their parent metals do. Unlike saline hydrides, they are almost always non-stoichiometric, being deficient in hydrogen. For example, $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5–1.8}$, $ZrH_{1.3–1.75}$, $VH_{0.56}$, $NiH_{0.6–0.7}$, $PdH_{0.6–0.8}$ etc. In such hydrides, the law of constant composition does not hold good.

Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. Consequently, they were termed as interstitial hydrides. However, recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have lattice different from that of the parent metal. The property of absorption of hydrogen on transition metals is widely used in catalytic reduction / hydrogenation reactions for the preparation of large number of compounds. Some of the metals (e.g., Pd, Pt) can accommodate a very large volume of hydrogen and, therefore, can be used as its storage media. This property has high potential for **hydrogen storage** and as a **source of energy**.

Problem 9.3

Can phosphorus with outer electronic configuration $3s^2 3p^3$ form PH_5 ?

Solution

Although phosphorus exhibits +3 and +5 oxidation states, it cannot form PH_5. Besides some other considerations, high $\Delta_a H$ value of dihydrogen and $\Delta_{eg} H$ value of hydrogen do not favour to exhibit the highest oxidation state of P, and consequently the formation of PH_5.

9.6 WATER

A major part of all living organisms is made up of water. Human body has about 65% and some plants have as much as 95% water. It is a crucial compound for the survival of all life forms. It is a solvent of great importance. The distribution of water over the earth's surface is not uniform. The estimated world water supply is given in Table 9.2

Table 9.2 Estimated World Water Supply

Source	% of Total
Oceans	97.33
Saline lakes and inland seas	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Lakes	0.009
Soil moisture	0.005
Atmospheric water vapour	0.001
Rivers	0.0001

9.6.1 Physical Properties of Water

It is a colourless and tasteless liquid. Its physical properties are given in Table 9.3 along with the physical properties of heavy water.

The unusual properties of water in the condensed phase (liquid and solid states) are due to the presence of extensive hydrogen bonding between water molecules. This leads to high freezing point, high boiling point, high heat of vaporisation and high heat of fusion in comparison to H_2S and H_2Se. In comparison to other liquids, water has a higher specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant, etc. These properties allow water to play a key role in the biosphere.

Table 9.3 Physical Properties of H_2O and D_2O

Property	H_2O	D_2O
Molecular mass (g mol^{-1})	18.0151	20.0276
Melting point/K	273.0	276.8
Boiling point/K	373.0	374.4
Enthalpy of formation/kJ mol^{-1}	–285.9	–294.6
Enthalpy of vaporisation (373K)/kJ mol^{-1}	40.66	41.61
Enthalpy of fusion/kJ mol^{-1}	6.01	-
Temp of max. density/K	276.98	284.2
Density (298K)/g cm^{-3}	1.0000	1.1059
Viscosity/centipoise	0.8903	1.107
Dielectric constant/$C^2/N.m^2$	78.39	78.06
Electrical conductivity (293K/ohm^{-1} cm^{-1})	5.7×10^{-8}	-

The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of ions and molecules required for plant and animal metabolism. Due to hydrogen bonding with polar molecules, even covalent compounds like alcohol and carbohydrates dissolve in water.

9.6.2 Structure of Water

In the gas phase water is a bent molecule with a bond angle of 104.5°, and O–H bond length of 95.7 pm as shown in Fig 9.1(a). It is a highly polar molecule, (Fig 9.1(b)). Its orbital overlap picture is shown in Fig. 9.1(c). In the liquid phase water molecules are associated together by hydrogen bonds.

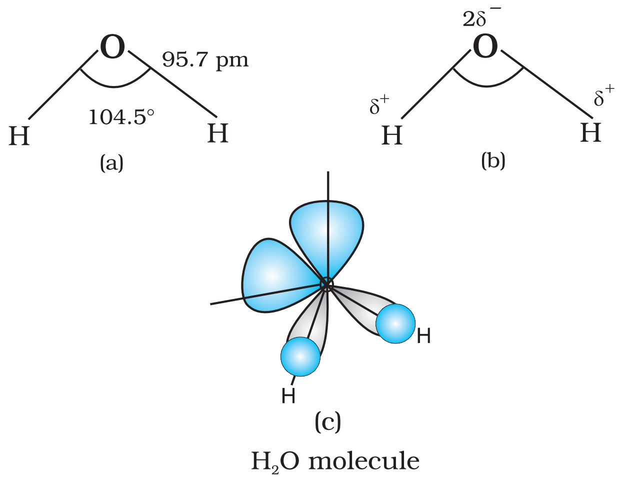


Fig. 9.1 *(a) The bent structure of water; (b) the water molecule as a dipole and (c) the orbital overlap picture in water molecule.*

The crystalline form of water is ice. At atmospheric pressure ice crystallises in the hexagonal form, but at very low temperatures it condenses to cubic form. Density of ice is less than that of water. Therefore, an ice cube floats on water. In winter season ice formed on the surface of a lake provides thermal insulation which ensures the survival of the aquatic life. This fact is of great ecological significance.

9.6.3 Structure of Ice

Ice has a highly ordered three dimensional hydrogen bonded structure as shown in Fig. 9.2. Examination of ice crystals with

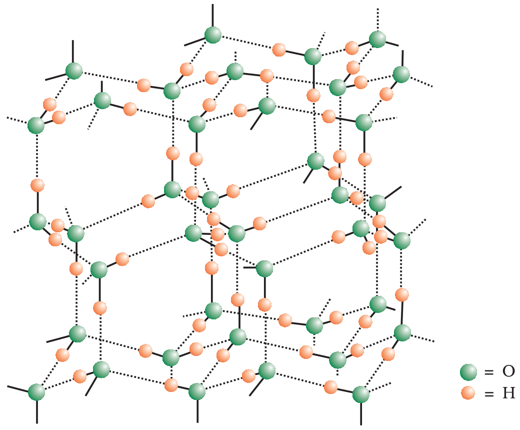


Fig. 9.2 *The structure of ice*

X-rays shows that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm.

Hydrogen bonding gives ice a rather open type structure with wide holes. These holes can hold some other molecules of appropriate size interstitially.

9.6.4 Chemical Properties of Water

Water reacts with a large number of substances. Some of the important reactions are given below.

(1) Amphoteric Nature: It has the ability to act as an acid as well as a base i.e., it behaves as an amphoteric substance. In the Brönsted sense it acts as an acid with NH_3 and a base with H_2S.

$$H_2O(l) + NH_3(aq) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$$

$$H_2O(l) + H_2S(aq) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$$

The auto-protolysis (self-ionization) of water takes place as follows :

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

acid-1 (acid)	base-2 (base)	acid-2 (conjugate acid)	base-1 (conjugate base)

(2) Redox Reactions Involving Water: Water can be easily reduced to dihydrogen by highly electropositive metals.

$$2H_2O(l) + 2Na(s) \rightarrow 2NaOH(aq) + H_2(g)$$

Thus, it is a great source of dihydrogen.

Water is oxidised to O_2 during photosynthesis.

$$6CO_2(g) + 12H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$$

With fluorine also it is oxidised to O_2.

$$2F_2(g) + 2H_2O(l) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

(3) Hydrolysis Reaction: Due to high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic compounds. However, certain covalent and some ionic compounds are hydrolysed in water.

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

$$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$$

$$N^{3-}(s) + 3H_2O(l) \rightarrow NH_3(g) + 3OH^-(aq)$$

(4) Hydrates Formation: From aqueous solutions many salts can be crystallised as hydrated salts. Such an association of water is of different types viz.,

(i) coordinated water e.g.,

$\left[Cr(H_2O)_6\right]^{3+} 3Cl^-$

(ii) interstitial water e.g., $BaCl_2.2H_2O$

(iii) hydrogen-bonded water e.g.,

$\left[Cu(H_2O)_4\right]^{2+} SO_4^{2-}.H_2O$ in $CuSO_4.5H_2O$,

Problem 9.4

How many hydrogen-bonded water molecule(s) are associated in $CuSO_4.5H_2O$?

Solution

Only one water molecule, which is outside the brackets (coordination sphere), is hydrogen-bonded. The other four molecules of water are coordinated.

9.6.5 Hard and Soft Water

Rain water is almost pure (may contain some dissolved gases from the atmosphere). Being a good solvent, when it flows on the surface of the earth, it dissolves many salts. Presence of calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate in water makes water **'hard'**. **Hard water** does not give lather with soap. Water free from soluble salts of calcium and magnesium is called **Soft water**. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca/Mg stearate.

$$2C_{17}H_{35}COONa(aq) + M^{2+}(aq) \rightarrow$$

$$(C_{17}H_{35}COO)_2 M \downarrow + 2Na^+(aq); \text{M is Ca / Mg}$$

It is, therefore, unsuitable for laundry. It is harmful for boilers as well, because of deposition of salts in the form of scale. This reduces the efficiency of the boiler. The hardness of water is of two types: (i) temporary hardness, and (ii) permanent hardness.

9.6.6 Temporary Hardness

Temporary hardness is due to the presence of magnesium and calcium hydrogen-carbonates. It can be removed by :

(i) Boiling: During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed to insoluble $CaCO_3$. It is because of high solubility product of $Mg(OH)_2$ as compared to that of $MgCO_3$, that $Mg(OH)_2$ is precipitated. These precipitates can be removed by filtration. Filtrate thus obtained will be soft water.

$$Mg(HCO_3)_2 \xrightarrow{\text{Heating}} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

$$Ca(HCO_3)_2 \xrightarrow{\text{Heating}} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

(ii) Clark's method: In this method calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$$

9.6.7 Permanent Hardness

It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water. Permanent hardness is not removed by boiling. It can be removed by the following methods:

(i) Treatment with washing soda (sodium carbonate): Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

$$MCl_2 + Na_2CO_3 \rightarrow MCO_3 \downarrow + 2NaCl \qquad (M = Mg, Ca)$$

$$MSO_4 + Na_2CO_3 \rightarrow MCO_3 \downarrow + Na_2SO_4$$

(ii) Calgon's method: Sodium hexametaphosphate ($Na_6P_6O_{18}$), commercially called 'calgon', when added to hard water, the following reactions take place.

$$Na_6P_6O_{18} \rightarrow 2Na^+ + Na_4P_6O_{18}^{2-} \qquad (M = Mg, Ca)$$

$$M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$$

The complex anion keeps the Mg^{2+} and Ca^{2+} ions in solution.

(iii) Ion-exchange method: This method is also called zeolite/permutit process. Hydrated sodium aluminium silicate is zeolite/permutit. For the sake of simplicity, sodium aluminium silicate ($NaAlSiO_4$) can be written as NaZ. When this is added in hard water, exchange reactions take place.

$$2NaZ(s) + M^{2+}(aq) \rightarrow MZ_2(s) + 2Na^+(aq) \qquad (M = Mg, Ca)$$

Permutit/zeolite is said to be exhausted when all the sodium in it is used up. It is regenerated for further use by treating with an aqueous sodium chloride solution.

$$MZ_2(s) + 2NaCl(aq) \rightarrow 2NaZ(s) + MCl_2(aq)$$

(iv) Synthetic resins method: Nowadays hard water is softened by using synthetic cation exchangers. This method is more efficient than zeolite process. Cation exchange resins contain large organic molecule with - SO_3H group and are water insoluble. Ion exchange resin (RSO_3H) is changed to RNa by treating it with NaCl. The resin exchanges Na^+ ions with Ca^{2+} and Mg^{2+} ions present in hard water to make the water soft. Here R is resin anion.

$$2RNa(s) + M^{2+}(aq) \rightarrow R_2M(s) + 2Na^+(aq)$$

The resin can be regenerated by adding aqueous NaCl solution.

Pure de-mineralised (de-ionized) water free from all soluble mineral salts is obtained by passing water successively through a cation exchange (in the H^+ form) and an anion-exchange (in the OH^- form) resins:

$$2RH(s) + M^{2+}(aq) \rightleftharpoons MR_2(s) + 2H^+(aq)$$

In this cation exchange process, H^+ exchanges for Na^+, Ca^{2+}, Mg^{2+} and other cations present in water. This process results in proton release and thus makes the water acidic. In the anion exchange process:

$$RNH_2(s) + H_2O(l) \rightleftharpoons RNH_3^+.OH^-(s)$$

$$RNH_3^+.OH^-(s) + X^-(aq) \rightleftharpoons RNH_3^+.X^-(s) + OH^-(aq)$$

OH^- exchanges for anions like Cl^-, HCO_3^-, SO_4^{2-} etc. present in water. OH^- ions, thus, liberated neutralise the H^+ ions set free in the cation exchange.

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

The exhausted cation and anion exchange resin beds are regenerated by treatment with dilute acid and alkali solutions respectively.

9.7 HYDROGEN PEROXIDE (H_2O_2)

Hydrogen peroxide is an important chemical used in pollution control treatment of domestic and industrial effluents.

9.7.1 Preparation

It can be prepared by the following methods.

(i) Acidifying barium peroxide and removing excess water by evaporation under reduced pressure gives hydrogen peroxide.

$$BaO_2.8H_2O(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(l)$$

(ii) Peroxodisulphate, obtained by electrolytic oxidation of acidified sulphate solutions at high current density, on hydrolysis yields hydrogen peroxide.

$$2HSO_4^-(aq) \xrightarrow{\text{Electrolysis}} HO_3SOOSO_3H(aq) \xrightarrow{\text{Hydrolysis}} 2HSO_4^-(aq) + 2H^+(aq) + H_2O_2(aq)$$

This method is now used for the laboratory preparation of D_2O_2.

$$K_2S_2O_8(s) + 2D_2O(l) \rightarrow 2KDSO_4(aq) + D_2O_2(l)$$

(iii) Industrially it is prepared by the auto-oxidation of 2-alklylanthraquinols.

$$2-\text{ethylanthraquinol} \underset{H_2/Pd}{\overset{O_2(\text{air})}{\rightleftharpoons}} H_2O_2 + (\text{oxidised product})$$

In this case 1% H_2O_2 is formed. It is extracted with water and concentrated to ~30% (by mass) by distillation under reduced pressure. It can be further concentrated to ~85% by careful distillation under low pressure. The remaining water can be frozen out to obtain pure H_2O_2.

9.7.2 Physical Properties

In the pure state H_2O_2 is an almost colourless (very pale blue) liquid. Its important physical properties are given in Table 9.4.

H_2O_2 is miscible with water in all proportions and forms a hydrate $H_2O_2.H_2O$ (mp 221K). A 30% solution of H_2O_2 is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30% H_2O_2 solution will give 100 mL of oxygen at STP. Commercially marketed sample is 10 V, which means that the sample contains 3% H_2O_2.

Problem 9.5

Calculate the strength of 10 volume solution of hydrogen peroxide.

Solution

10 volume solution of H_2O_2 means that 1L of this H_2O_2 solution will give 10 L of oxygen at STP

$$2H_2O_2(l) \rightarrow O_2(g) + H_2O(l)$$

2×34 g 22.7 L at STP

68 g

On the basis of above equation 22.7 L of O_2 is produced from 68 g H_2O_2 at STP

10 L of O_2 at STP is produced from

$$\frac{68 \times 10}{22.7} g = 29.9 \text{ g} \approx 30 \text{ g } H_2O_2$$

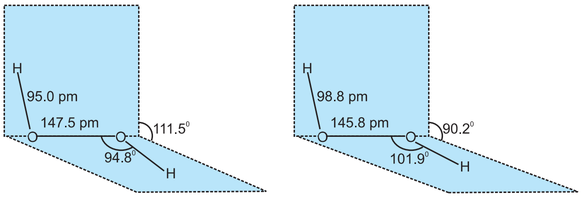
Therefore, strength of H_2O_2 in 10 volume H_2O_2 solution = 30 g/L = 3% H_2O_2 solution

Table 9.4 Physical Properties of Hydrogen Peroxide

Melting point/K	272.4	Density (liquid at 298 K)/g cm^{-3}	1.44
Boiling point(exrapolated)/K	423	Viscosity (290K)/centipoise	1.25
Vapour pressure(298K)/mmHg	1.9	Dielectric constant (298K)/C^2/N m^2	70.7
Density (solid at 268.5K)/g cm^{-3}	1.64	Electrical conductivity (298K)/Ω^{-1} cm^{-1}	5.1×10^{-8}

9.7.3 Structure

Hydrogen peroxide has a non-planar structure. The molecular dimensions in the gas phase and solid phase are shown in Fig 9.3



(a) Gas phase (b) Solid phase

Fig. 9.3 *(a) H_2O_2 structure in gas phase, dihedral angle is 111.5°. (b) H_2O_2 structure in solid phase at 110K, dihedral angle is 90.2°.*

9.7.4 Chemical Properties

It acts as an oxidising as well as reducing agent in both acidic and alkaline media. Simple reactions are described below.

(i) Oxidising action in acidic medium

$$2Fe^{2+}(aq) + 2H^{+}(aq) + H_2O_2(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$$

$$PbS(s) + 4H_2O_2(aq) \rightarrow PbSO_4(s) + 4H_2O(l)$$

(ii) Reducing action in acidic medium

$$2MnO_4^{-} + 6H^{+} + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

$$HOCl + H_2O_2 \rightarrow H_3O^{+} + Cl^{-} + O_2$$

(iii) Oxidising action in basic medium

$$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^{-}$$

$$Mn^{2+} + H_2O_2 \rightarrow Mn^{4+} + 2OH^{-}$$

(iv) Reducing action in basic medium

$$I_2 + H_2O_2 + 2OH^{-} \rightarrow 2I^{-} + 2H_2O + O_2$$

$$2MnO_4^{-} + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^{-}$$

9.7.5 Storage

H_2O_2 decomposes slowly on exposure to light.

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. It is, therefore, stored in wax-lined glass or plastic vessels in dark. Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.

9.7.6 Uses

Its wide scale use has led to tremendous increase in the industrial production of H_2O_2. Some of the uses are listed below:

(i) In daily life it is used as a hair bleach and as a mild disinfectant. As an antiseptic it is sold in the market as perhydrol.

(ii) It is used to manufacture chemicals like sodium perborate and per-carbonate, which are used in high quality detergents.

(iii) It is used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.

(iv) It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.

(v) Nowadays it is also used in Environmental (Green) Chemistry. For example, in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.

9.8 HEAVY WATER, D_2O

It is extensively used as a moderator in nuclear reactors and in exchange reactions for the study of reaction mechanisms. It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries. Its physical properties are given in Table 9.3. It is used for the preparation of other deuterium compounds, for example:

$$CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca(OD)_2$$

$$SO_3 + D_2O \rightarrow D_2SO_4$$

$$Al_4C_3 + 12D_2O \rightarrow 3CD_4 + 4Al(OD)_3$$

9.9 DIHYDROGEN AS A FUEL

Dihydrogen releases large quantities of heat on combustion. The data on energy released by combustion of fuels like dihydrogen, methane, LPG etc. are compared in terms of the same amounts in mole, mass and volume, are shown in Table 9.5.

From this table it is clear that on a mass for mass basis dihydrogen can release more energy than petrol (about three times). Moreover, pollutants in combustion of dihydrogen will be less than petrol. The only pollutants will be the oxides of dinitrogen (due to the presence of dinitrogen as impurity with dihydrogen). This, of course, can be minimised by injecting a small amount of water into the cylinder to lower the temperature so that the reaction between dinitrogen and dioxygen may not take place. However, the mass of the containers in which dihydrogen will be kept must be taken into consideration. A cylinder of compressed dihydrogen weighs about 30 times as much as a tank of petrol containing the same amount of energy. Also, dihydrogen gas is converted into liquid state by cooling to 20K. This would require expensive insulated tanks. Tanks of metal alloy like $NaNi_5$, $Ti–TiH_2$, $Mg–MgH_2$ etc. are in use for storage of dihydrogen in small quantities. These limitations have prompted researchers to search for alternative techniques to use dihydrogen in an efficient way.

In this view **Hydrogen Economy** is an alternative. The basic principle of hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous dihydrogen. Advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power. It is for the first time in the history of India that a pilot project using dihydrogen as fuel was launched in October 2005 for running automobiles. Initially 5% dihydrogen has been mixed in CNG for use in four-wheeler vehicles. The percentage of dihydrogen would be gradually increased to reach the optimum level.

Nowadays, it is also used in fuel cells for generation of electric power. It is expected that economically viable and safe sources of dihydrogen will be identified in the years to come, for its usage as a common source of energy.

Table 9.5 The Energy Released by Combustion of Various Fuels in Moles, Mass and Volume

Energy released on combustion in kJ state)	Dihydrogen (in gaseous state)	Dihydrogen (in liquid)	LPG	CH_4 gas	Octane (in liquid state)
per mole	286	285	2220	880	5511
per gram	143	142	50	53	47
per litre	12	9968	25590	35	34005

SUMMARY

Hydrogen is the lightest atom with only one electron. Loss of this electron results in an elementary particle, the proton. Thus, it is unique in character. It has three isotopes, namely : **protium** (^1_1H), **deuterium** (D or ^2_1H) and **tritium** (T or ^3_1H). Amongst these three, only tritium is radioactive. Inspite of its resemblance both with alkali metals and halogens, it occupies a separate position in the periodic table because of its unique properties.

Hydrogen is the most abundant element in the universe. In the free state it is almost not found in the earth's atmosphere. However, in the combined state, it is the third most abundant element on the earth's surface.

Dihydrogen on the industrial scale is prepared by the **water-gas shift** reaction from petrochemicals. It is obtained as a byproduct by the electrolysis of brine.

The H–H **bond dissociation enthalpy** of dihydrogen (435.88 kJ mol^{-1}) is the highest for a single bond between two atoms of any elements. This property is made use of in the atomic hydrogen torch which generates a temperature of ~4000K and is ideal for welding of high melting metals.

Though dihydrogen is rather inactive at room temperature because of very high negative dissociation enthalpy, it combines with almost all the elements under appropriate conditions to form **hydrides.** All the type of hydrides can be classified into three categories: ionic or saline hydrides, covalent or molecular hydrides and metallic or non-stoichiometric hydrides. Alkali metal hydrides are good reagents for preparing other hydride compounds. Molecular hydrides (e.g., B_2H_6, CH_4, NH_3, H_2O) are of great importance in day-to-day life. Metallic hydrides are useful for ultrapurification of dihydrogen and as dihydrogen storage media.

Among the other chemical reactions of dihydrogen, **reducing reactions** leading to the formation hydrogen halides, water, ammonia, methanol, vanaspati ghee, etc. are of great importance. In metallurgical process, it is used to reduce metal oxides. In space programmes, it is used as a rocket fuel. In fact, it has promising potential for use as a non-polluting fuel of the near future **(Hydrogen Economy)**.

Water is the most common and abundantly available substance. It is of a great chemical and biological significance. The ease with which water is transformed from liquid to solid and to gaseous state allows it to play a vital role in the **biosphere.** The water molecule is highly polar in nature due to its bent structure. This property leads to hydrogen bonding which is the maximum in ice and least in water vapour. The polar nature of water makes it: (a) a very good solvent for ionic and partially ionic compounds; (b) to act as an amphoteric (acid as well as base) substance; and (c) to form hydrates of different types. Its property to dissolve many salts, particularly in large quantity, makes it hard and hazardous for industrial use. Both temporary and permanent **hardness** can be removed by the use of zeolites, and synthetic ion-exchangers.

Heavy water, D_2O is another important compound which is manufactured by the electrolytic enrichment of normal water. It is essentially used as a moderator in nuclear reactors.

Hydrogen peroxide, H_2O_2 has an interesting non-polar structure and is widely used as an industrial bleach and in pharmaceutical and pollution control treatment of industrial and domestic effluents.

EXERCISES

9.1 Justify the position of hydrogen in the periodic table on the basis of its electronic configuration.

9.2 Write the names of isotopes of hydrogen. What is the mass ratio of these isotopes?

9.3 Why does hydrogen occur in a diatomic form rather than in a monoatomic form under normal conditions?

9.4 How can the production of dihydrogen, obtained from ‘coal gasification’, be increased?

9.5 Describe the bulk preparation of dihydrogen by electrolytic method. What is the role of an electrolyte in this process ?

9.6 Complete the following reactions:

(i) $H_2(g) + M_mO_o(s) \xrightarrow{\Delta}$

(ii) $CO(g) + H_2(g) \xrightarrow[\text{catalyst}]{\Delta}$

(iii) $C_3H_8(g) + 3H_2O(g) \xrightarrow[\text{catalyst}]{\Delta}$

(iv) $Zn(s) + NaOH(aq) \xrightarrow{\text{heat}}$

9.7 Discuss the consequences of high enthalpy of H–H bond in terms of chemical reactivity of dihydrogen.

9.8 What do you understand by (i) electron-deficient, (ii) electron-precise, and (iii) electron-rich compounds of hydrogen? Provide justification with suitable examples.

9.9 What characteristics do you expect from an electron-deficient hydride with respect to its structure and chemical reactions?

9.10 Do you expect the carbon hydrides of the type (C_nH_{2n+2}) to act as 'Lewis' acid or base? Justify your answer.

9.11 What do you understand by the term "non-stoichiometric hydrides"? Do you expect this type of the hydrides to be formed by alkali metals? Justify your answer.

9.12 How do you expect the metallic hydrides to be useful for hydrogen storage? Explain.

9.13 How does the atomic hydrogen or oxy-hydrogen torch function for cutting and welding purposes ? Explain.

9.14 Among NH_3, H_2O and HF, which would you expect to have highest magnitude of hydrogen bonding and why?

9.15 Saline hydrides are known to react with water violently producing fire. Can CO_2, a well known fire extinguisher, be used in this case? Explain.

9.16 Arrange the following

(i) CaH_2, BeH_2 and TiH_2 in order of increasing electrical conductance.

(ii) LiH, NaH and CsH in order of increasing ionic character.

(iii) H–H, D–D and F–F in order of increasing bond dissociation enthalpy.

(iv) NaH, MgH_2 and H_2O in order of increasing reducing property.

9.17 Compare the structures of H_2O and H_2O_2.

9.18 What do you understand by the term ’auto-protolysis’ of water? What is its significance?

9.19 Consider the reaction of water with F_2 and suggest, in terms of oxidation and reduction, which species are oxidised/reduced.

9.20 Complete the following chemical reactions.

(i) $PbS(s) + H_2O_2(aq) \rightarrow$

(ii) $MnO_4^-(aq) + H_2O_2(aq) \rightarrow$

(iii) $CaO(s) + H_2O(g) \rightarrow$

(v) $AlCl_3(g) + H_2O(l) \rightarrow$

(vi) $Ca_3N_2(s) + H_2O(l) \rightarrow$

Classify the above into (a) hydrolysis, (b) redox and (c) hydration reactions.

9.21 Describe the structure of the common form of ice.

9.22 What causes the temporary and permanent hardness of water ?

9.23 Discuss the principle and method of softening of hard water by synthetic ion-exchange resins.

9.24 Write chemical reactions to show the amphoteric nature of water.

9.25 Write chemical reactions to justify that hydrogen peroxide can function as an oxidising as well as reducing agent.

9.26 What is meant by ‘demineralised’ water and how can it be obtained ?

9.27 Is demineralised or distilled water useful for drinking purposes? If not, how can it be made useful?

9.28 Describe the usefulness of water in biosphere and biological systems.

9.29 What properties of water make it useful as a solvent? What types of compound can it (i) dissolve, and (ii) hydrolyse ?

9.30 Knowing the properties of H_2O and D_2O, do you think that D_2O can be used for drinking purposes?

9.31 What is the difference between the terms ‘hydrolysis’ and ‘hydration’ ?

9.32 How can saline hydrides remove traces of water from organic compounds?

9.33 What do you expect the nature of hydrides is, if formed by elements of atomic numbers 15, 19, 23 and 44 with dihydrogen? Compare their behaviour towards water.

9.34 Do you expect different products in solution when aluminium(III) chloride and potassium chloride treated separately with (i) normal water (ii) acidified water, and (iii) alkaline water? Write equations wherever necessary.

9.35 How does H_2O_2 behave as a bleaching agent?

9.36 What do you understand by the terms:

(i) hydrogen economy (ii) hydrogenation (iii) ‘syngas’ (iv) water-gas shift reaction (v) fuel-cell ?

UNIT 10

THE *s*-BLOCK ELEMENTS

> ***The first element of alkali and alkaline earth metals differs in many respects from the other members of the group***

Objectives

After studying this unit, you will be able to

- describe the general characteristics of the alkali metals and their compounds;
- explain the general characteristics of the alkaline earth metals and their compounds;
- describe the manufacture, properties and uses of industrially important sodium and calcium compounds including Portland cement;
- appreciate the biological significance of sodium, potassium, magnesium and calcium.

The *s*-block elements of the Periodic Table are those in which the last electron enters the outermost *s*-orbital. As the *s*-orbital can accommodate only two electrons, two groups (1 & 2) belong to the s-block of the Periodic Table. Group 1 of the Periodic Table consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the *alkali metals*. These are so called because they form hydroxides on reaction with water which are strongly alkaline in nature. The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the *alkaline earth metals*. These are so called because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust*.

Among the alkali metals sodium and potassium are abundant and lithium, rubidium and caesium have much lower abundances (Table 10.1). Francium is highly radioactive; its longest-lived isotope ^{223}Fr has a half-life of only 21 minutes. Of the alkaline earth metals calcium and magnesium rank fifth and sixth in abundance respectively in the earth's crust. Strontium and barium have much lower abundances. Beryllium is rare and radium is the rarest of all comprising only 10^{-10} per cent of igneous rocks† (Table 10.2, page 299).

The general electronic configuration of *s*-block elements is [noble gas]ns^1 for alkali metals and [noble gas] ns^2 for alkaline earth metals.

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* *The thin, rocky outer layer of the Earth is crust.* † *A type of rock formed from magma (molten rock) that has cooled and hardened.*

Lithium and beryllium, the first elements of Group 1 and Group 2 respectively exhibit some properties which are different from those of the other members of the respective group. In these anomalous properties they resemble the second element of the following group. Thus, lithium shows similarities to magnesium and beryllium to aluminium in many of their properties. This type of diagonal similarity is commonly referred to as *diagonal relationship* in the periodic table. The diagonal relationship is due to the similarity in ionic sizes and /or charge/radius ratio of the elements. Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

10.1 GROUP 1 ELEMENTS: ALKALI METALS

The alkali metals show regular trends in their physical and chemical properties with the increasing atomic number. The atomic, physical and chemical properties of alkali metals are discussed below.

10.1.1 Electronic Configuration

All the alkali metals have one valence electron, ns^1 (Table 10.1) outside the noble gas core. The loosely held *s*-electron in the outermost valence shell of these elements makes them the most electropositive metals. They readily lose electron to give monovalent M^+ ions. Hence they are never found in free state in nature.

Element	Symbol	Electronic configuration
Lithium	Li	$1s^2 2s^1$
Sodium	Na	$1s^2 2s^2 2p^6 3s^1$
Potassium	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rubidium	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$
Caesium	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ or $[Xe]\, 6s^1$
Francium	Fr	$[Rn] 7s^1$

10.1.2 Atomic and Ionic Radii

The alkali metal atoms have the largest sizes in a particular period of the periodic table. With increase in atomic number, the atom becomes larger. The monovalent ions (M^+) are smaller than the parent atom. The atomic and ionic radii of alkali metals increase on moving down the group i.e., they increase in size while going from Li to Cs.

10.1.3 Ionization Enthalpy

The ionization enthalpies of the alkali metals are considerably low and decrease down the group from Li to Cs. This is because the effect of increasing size outweighs the increasing nuclear charge, and the outermost electron is very well screened from the nuclear charge.

10.1.4 Hydration Enthalpy

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Li^+ has maximum degree of hydration and for this reason lithium salts are mostly hydrated, e.g., $LiCl \cdot 2H_2O$

10.1.5 Physical Properties

All the alkali metals are silvery white, soft and light metals. Because of the large size, these elements have low density which increases down the group from Li to Cs. However, potassium is lighter than sodium. The melting and boiling points of the alkali metals are low indicating weak metallic bonding due to the presence of only a single valence electron in them. The alkali metals and their salts impart characteristic colour to an oxidizing flame. This is because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited electron comes back to the ground state, there is emission of radiation in the visible region of the spectrum as given below:

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Violet	Red violet	Blue
λ/nm	670.8	589.2	766.5	780.0	455.5

Alkali metals can therefore, be detected by the respective flame tests and can be determined by flame photometry or atomic absorption spectroscopy. These elements when irradiated with light, the light energy absorbed may be sufficient to make an atom lose electron.

Table 10.1 Atomic and Physical Properties of the Alkali Metals

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs	Francium Fr
Atomic number	3	11	19	37	55	87
Atomic mass (g mol^{-1})	6.94	22.99	39.10	85.47	132.91	(223)
Electronic configuration	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$	[Rn] $7s^1$
Ionization enthalpy / kJ mol^{-1}	520	496	419	403	376	~375
Hydration enthalpy/kJ mol^{-1}	–506	–406	–330	–310	–276	–
Metallic radius / pm	152	186	227	248	265	–
Ionic radius M^+ / pm	76	102	138	152	167	(180)
m.p. / K	454	371	336	312	302	–
b.p / K	1615	1156	1032	961	944	–
Density / g cm^{-3}	0.53	0.97	0.86	1.53	1.90	–
Standard potentials $E^\ominus$/ V for (M^+ / M)	–3.04	–2.714	–2.925	–2.930	–2.927	–
Occurrence in lithosphere†	18*	2.27**	1.84**	78-12*	2-6*	~ 10^{-18} *

**ppm (part per million), ** percentage by weight; † Lithosphere: The Earth's outer layer: its crust and part of the upper mantle*

This property makes caesium and potassium useful as electrodes in photoelectric cells.

10.1.6 Chemical Properties

The alkali metals are highly reactive due to their large size and low ionization enthalpy. The reactivity of these metals increases down the group.

(i) ***Reactivity towards air:*** The alkali metals tarnish in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxides. The superoxide O_2^- ion is stable only in the presence of large cations such as K, Rb, Cs.

$$4\,Li + O_2 \rightarrow 2\,Li_2O \text{ (oxide)}$$

$$2\,Na + O_2 \rightarrow Na_2O_2 \text{ (peroxide)}$$

$$M + O_2 \rightarrow MO_2 \text{ (superoxide)}$$

(M = K, Rb, Cs)

In all these oxides the oxidation state of the alkali metal is +1. Lithium shows exceptional behaviour in reacting directly with nitrogen of air to form the nitride, Li_3N as well. Because of their high reactivity towards air and water, alkali metals are normally kept in kerosene oil.

Problem 10.1

What is the oxidation state of K in KO_2?

Solution

The superoxide species is represented as O_2^-; since the compound is neutral, therefore, the oxidation state of potassium is +1.

(ii) Reactivity towards water: The alkali metals react with water to form hydroxide and dihydrogen.

$$2M + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2$$

(M = an alkali metal)

It may be noted that although lithium has most negative $E^{\ominus}$ value (Table 10.1), its reaction with water is less vigorous than that of sodium which has the least negative $E^{\ominus}$ value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. Other metals of the group react explosively with water.

They also react with proton donors such as alcohol, gaseous ammonia and alkynes.

(iii) Reactivity towards dihydrogen: The alkali metals react with dihydrogen at about 673K (lithium at 1073K) to form hydrides. All the alkali metal hydrides are ionic solids with high melting points.

$$2M + H_2 \rightarrow 2M^+H^-$$

(iv) Reactivity towards halogens : The alkali metals readily react vigorously with halogens to form ionic halides, M^+X^-. However, lithium halides are somewhat covalent. It is because of the high polarisation capability of lithium ion (The distortion of electron cloud of the anion by the cation is called polarisation). The Li^+ ion is very small in size and has high tendency to distort electron cloud around the negative halide ion. Since anion with large size can be easily distorted, among halides, lithium iodide is the most covalent in nature.

(v) Reducing nature: The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful (Table 10.1). The standard electrode potential ($E^{\ominus}$) which measures the reducing power represents the overall change :

$$M(s) \rightarrow M(g) \qquad \text{sublimation enthalpy}$$

$$M(g) \rightarrow M^+(g) + e^- \qquad \text{ionization enthalpy}$$

$$M^+(g) + H_2O \rightarrow M^+(aq) \qquad \text{hydration enthalpy}$$

With the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative $E^{\ominus}$ value and its high reducing power.

Problem 10.2

The $E^{\ominus}$ for Cl_2/Cl^- is +1.36, for I_2/I^- is + 0.53, for Ag^+/Ag is +0.79, Na^+/Na is –2.71 and for Li^+/Li is – 3.04. Arrange the following ionic species in decreasing order of reducing strength:

I^-, Ag, Cl^-, Li, Na

Solution

The order is Li > Na > I^- > Ag > Cl^-

(vi) Solutions in liquid ammonia: The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.

$$M + (x + y)NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of amide.

$$M^+_{(am)} + e^- + NH_3(l) \rightarrow MNH_{2(am)} + ½H_2(g)$$

(where 'am' denotes solution in ammonia.)

In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

10.1.7 Uses

Lithium metal is used to make useful alloys, for example with lead to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions. Lithium is also used to make electrochemical cells. Sodium is used to make a Na/Pb alloy needed to make $PbEt_4$ and $PbMe_4$. These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays vehicles use lead-free petrol. Liquid sodium metal is used as a coolant in fast breeder nuclear reactors. Potassium has a vital role in biological systems. Potassium chloride is used as a fertilizer. Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide. Caesium is used in devising photoelectric cells.

10.2 GENERAL CHARACTERISTICS OF THE COMPOUNDS OF THE ALKALI METALS

All the common compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are discussed here.

10.2.1 Oxides and Hydroxides

On combustion in excess of air, lithium forms mainly the oxide, Li_2O (plus some peroxide Li_2O_2), sodium forms the peroxide, Na_2O_2 (and some superoxide NaO_2) whilst potassium, rubidium and caesium form the superoxides, MO_2. Under appropriate conditions pure compounds M_2O, M_2O_2 and MO_2 may be prepared. The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilisation of large anions by larger cations through lattice energy effects. These oxides are easily hydrolysed by water to form the hydroxides according to the following reactions :

$$M_2O + H_2O \rightarrow 2M^+ + 2OH^-$$

$$M_2O_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2$$

$$2MO_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$

The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The superoxides are also paramagnetic. Sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

Problem 10.3

Why is KO_2 paramagnetic ?

Solution

The superoxide O_2^- is paramagnetic because of one unpaired electron in π^*2p molecular orbital.

The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat on account of intense hydration.

10.2.2 Halides

The alkali metal halides, MX, (X=F,Cl,Br,I) are all high melting, colourless crystalline solids. They can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). All of these halides have high negative enthalpies of formation; the $\Delta_f H^\ominus$ values for fluorides become less negative as we go down the group, whilst the reverse is true for $\Delta_f H^\ominus$ for chlorides, bromides and iodides. For a given metal $\Delta_f H^\ominus$ always becomes less negative from fluoride to iodide.

The melting and boiling points always follow the trend: fluoride > chloride > bromide > iodide. All these halides are soluble in water. The low solubility of LiF in water is due to its high lattice enthalpy whereas the low solubility of CsI is due to smaller hydration enthalpy of its two ions. Other halides of lithium are soluble in ethanol, acetone and ethylacetate; LiCl is soluble in pyridine also.

10.2.3 Salts of Oxo-Acids

Oxo-acids are those in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom e.g., carbonic acid, H_2CO_3 ($OC(OH)_2$; sulphuric acid, H_2SO_4 ($O_2S(OH)_2$). The alkali metals form salts with all the oxo-acids. They are generally soluble in water and thermally stable. Their carbonates (M_2CO_3) and in most cases the hydrogencarbonates ($MHCO_3$) also are highly stable to heat. As the electropositive character increases down the group, the stability of the carbonates and hydorgencarbonates increases. Lithium carbonate is not so stable to heat; lithium being very small in size polarises a large CO_3^{2-} ion leading to the formation of more stable Li_2O and CO_2. Its hydrogencarbonate does not exist as a solid.

10.3 ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behaviour of lithium is due to the : (i) exceptionally small size of its atom and ion, and (ii) high polarising power (i.e., charge/ radius ratio). As a result, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents. Further, lithium shows diagonal relationship to magnesium which has been discussed subsequently.

10.3.1 Points of Difference between Lithium and other Alkali Metals

(i) Lithium is much harder. Its m.p. and b.p. are higher than the other alkali metals.

(ii) Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide, Li_2O and the nitride, Li_3N unlike other alkali metals.

(iii) LiCl is deliquescent and crystallises as a hydrate, $LiCl.2H_2O$ whereas other alkali metal chlorides do not form hydrates.

(iv) Lithium hydrogencarbonate is not obtained in the solid form while all other elements form solid hydrogencarbonates.

(v) Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.

(vi) Lithium nitrate when heated gives lithium oxide, Li_2O, whereas other alkali metal nitrates decompose to give the corresponding nitrite.

$$4LiNO_3 \rightarrow 2\,Li_2O + 4\,NO_2 + O_2$$

$$2\,NaNO_3 \rightarrow 2\,NaNO_2 + O_2$$

(vii) LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

10.3.2 Points of Similarities between Lithium and Magnesium

The similarity between lithium and magnesium is particularly striking and arises because of their similar sizes : atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii : Li^+ = 76 pm, Mg^{2+}= 72 pm. The main points of similarity are:

(i) Both lithium and magnesium are harder and lighter than other elements in the respective groups.

(ii) Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride, Li_3N and Mg_3N_2, by direct combination with nitrogen.

(iii) The oxides, Li_2O and MgO do not combine with excess oxygen to give any superoxide.

(iv) The carbonates of lithium and magnesium decompose easily on heating to form the oxides and CO_2. Solid hydrogencarbonates are not formed by lithium and magnesium.

(v) Both LiCl and $MgCl_2$ are soluble in ethanol.

(vi) Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl{\cdot}2H_2O$ and $MgCl_2{\cdot}8H_2O$.

10.4 SOME IMPORTANT COMPOUNDS OF SODIUM

Industrially important compounds of sodium include sodium carbonate, sodium hydroxide, sodium chloride and sodium bicarbonate. The large scale production of these compounds and their uses are described below:

Sodium Carbonate (Washing Soda), $Na_2CO_3{\cdot}10H_2O$

Sodium carbonate is generally prepared by Solvay Process. In this process, advantage is taken of the low solubility of sodium hydrogencarbonate whereby it gets precipitated in the reaction of sodium chloride with ammonium hydrogencarbonate. The latter is prepared by passing CO_2 to a concentrated solution of sodium chloride saturated with ammonia, where ammonium carbonate followed by ammonium hydrogencarbonate are formed. The equations for the complete process may be written as :

$$2\,NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2\,CO_3$$

$$(NH_4)_2\,CO_3 + H_2O + CO_2 \rightarrow 2\,NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$$

Sodium hydrogencarbonate crystal separates. These are heated to give sodium carbonate.

$$2\,NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

In this process NH_3 is recovered when the solution containing NH_4Cl is treated with $Ca(OH)_2$. Calcium chloride is obtained as a by-product.

$$2\,NH_4Cl + Ca(OH)_2 \rightarrow 2\,NH_3 + CaCl_2 + H_2O$$

It may be mentioned here that Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogencarbonate is too soluble to be precipitated by the addition of ammonium hydrogencarbonate to a saturated solution of potassium chloride.

Properties : Sodium carbonate is a white crystalline solid which exists as a decahydrate, $Na_2CO_3{\cdot}10H_2O$. This is also called washing soda. It is readily soluble in water. On heating, the decahydrate loses its water of crystallisation to form monohydrate. Above 373K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.

$$Na_2CO_3{\bullet}10H_2O \xrightarrow{375K} Na_2CO_3{\bullet}H_2O + 9H_2O$$

$$Na_2CO_3{\bullet}H_2O \xrightarrow{>373K} Na_2CO_3 + H_2O$$

Carbonate part of sodium carbonate gets hydrolysed by water to form an alkaline solution.

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$$

Uses:

(i) It is used in water softening, laundering and cleaning.

(ii) It is used in the manufacture of glass, soap, borax and caustic soda.

(iii) It is used in paper, paints and textile industries.

(iv) It is an important laboratory reagent both in qualitative and quantitative analysis.

Sodium Chloride, NaCl

The most abundant source of sodium chloride is sea water which contains 2.7 to 2.9% by mass of the salt. In tropical countries like India, common salt is generally obtained by evaporation of sea water. Approximately 50 lakh tons of salt are produced annually in India by solar evaporation. Crude sodium chloride, generally obtained by crystallisation of brine solution, contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Calcium chloride, $CaCl_2$, and magnesium chloride, $MgCl_2$ are impurities because they are deliquescent (absorb moisture easily from the atmosphere). To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride gas. Crystals of pure sodium chloride separate out. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

Sodium chloride melts at 1081K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

Uses :

(i) It is used as a common salt or table salt for domestic purpose.

(ii) It is used for the preparation of Na_2O_2, NaOH and Na_2CO_3.

Sodium Hydroxide (Caustic Soda), NaOH

Sodium hydroxide is generally prepared commercially by the electrolysis of sodium chloride in Castner-Kellner cell. A brine solution is electrolysed using a mercury cathode and a carbon anode. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode.

$$\text{Cathode}: Na^+ + e^- \xrightarrow{Hg} Na - \text{amalgam}$$

$$\text{Anode}: Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$$

The amalgam is treated with water to give sodium hydroxide and hydrogen gas.

$$2\text{Na-amalgam} + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$$

Sodium hydroxide is a white, translucent solid. It melts at 591 K. It is readily soluble in water to give a strong alkaline solution. Crystals of sodium hydroxide are deliquescent. The sodium hydroxide solution at the surface reacts with the CO_2 in the atmosphere to form Na_2CO_3.

Uses: It is used in (i) the manufacture of soap, paper, artificial silk and a number of chemicals, (ii) in petroleum refining, (iii) in the purification of bauxite, (iv) in the textile industries for mercerising cotton fabrics, (v) for the preparation of pure fats and oils, and (vi) as a laboratory reagent.

Sodium Hydrogencarbonate (Baking Soda), $NaHCO_3$

Sodium hydrogencarbonate is known as baking soda because it decomposes on heating to generate bubbles of carbon dioxide (leaving holes in cakes or pastries and making them light and fluffy).

Sodium hydrogencarbonate is made by saturating a solution of sodium carbonate with carbon dioxide. The white crystalline powder of sodium hydrogencarbonate, being less soluble, gets separated out.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2\,NaHCO_3$$

Sodium hydrogencarbonate is a mild antiseptic for skin infections. It is used in fire extinguishers.

10.5 BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM

A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper.

Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes. Thus, potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

There is a very considerable variation in the concentration of sodium and potassium ions found on the opposite sides of cell membranes. As a typical example, in blood plasma, sodium is present to the extent of 143 $mmolL^{-1}$, whereas the potassium level is only 5 $mmolL^{-1}$ within the red blood cells. These concentrations change to 10 $mmolL^{-1}$ (Na^+) and 105 $mmolL^{-1}$ (K^+). These ionic gradients demonstrate that a discriminatory mechanism, called the sodium-potassium pump, operates across the cell membranes which consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human.

10.6 GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The group 2 elements comprise beryllium, magnesium, calcium, strontium, barium and radium. They follow alkali metals in the periodic table. These (except beryllium) are known as alkaline earth metals. The first element beryllium differs from the rest of the members and shows diagonal relationship to aluminium. The atomic and physical properties of the alkaline earth metals are shown in Table 10.2.

10.6.1 Electronic Configuration

These elements have two electrons in the *s*-orbital of the valence shell (Table 10.2). Their general electronic configuration may be represented as [noble gas] ns^2. Like alkali metals, the compounds of these elements are also predominantly ionic.

Element	Symbol	Electronic configuration
Beryllium	Be	$1s^2 2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ or $[Xe]6s^2$
Radium	Ra	$[Rn]7s^2$

10.6.2 Atomic and Ionic Radii

The atomic and ionic radii of the alkaline earth metals are smaller than those of the

Table 10.2 Atomic and Physical Properties of the Alkaline Earth Metals

Property	**Beryllium Be**	**Magnesium Mg**	**Calcium Ca**	**Strontium Sr**	**Barium Ba**	**Radium Ra**
Atomic number	4	12	20	38	56	88
Atomic mass (g mol^{-1})	9.01	24.31	40.08	87.62	137.33	226.03
Electronic configuration	[He] $2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$	[Rn] $7s^2$
Ionization enthalpy (I) / kJ mol^{-1}	899	737	590	549	503	509
Ionization enthalpy (II) /kJ mol^{-1}	1757	1450	1145	1064	965	979
Hydration enthalpy (kJ/mol)	– 2494	– 1921	–1577	– 1443	– 1305	–
Metallic radius / pm	111	160	197	215	222	–
Ionic radius M^{2+} / pm	31	72	100	118	135	148
m.p. / K	1560	924	1124	1062	1002	973
b.p / K	2745	1363	1767	1655	2078	(1973)
Density / g cm^{-3}	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard potential $E^\ominus$ / V for (M^{2+}/ M)	–1.97	–2.36	–2.84	–2.89	– 2.92	–2.92
Occurrence in lithosphere	2*	2.76**	4.6**	384*	390 *	10^{-6}*

**ppm (part per million); ** percentage by weight*

corresponding alkali metals in the same periods. This is due to the increased nuclear charge in these elements. Within the group, the atomic and ionic radii increase with increase in atomic number.

10.6.3 Ionization Enthalpies

The alkaline earth metals have low ionization enthalpies due to fairly large size of the atoms. Since the atomic size increases down the group, their ionization enthalpy decreases (Table 10.2). The first ionisation enthalpies of the alkaline earth metals are higher than those of the corresponding Group 1 metals. This is due to their small size as compared to the corresponding alkali metals. It is interesting to note that the second ionisation enthalpies of the alkaline earth metals are smaller than those of the corresponding alkali metals.

10.6.4 Hydration Enthalpies

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.

$$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g., $MgCl_2$ and $CaCl_2$ exist as $MgCl_2.6H_2O$ and $CaCl_2 \cdot 6H_2O$ while NaCl and KCl do not form such hydrates.

10.6.5 Physical Properties

The alkaline earth metals, in general, are silvery white, lustrous and relatively soft but harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish. The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller sizes. The trend is, however, not systematic. Because of the low ionisation enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba. Calcium, strontium and barium impart characteristic brick red, crimson and apple green colours respectively to the flame. In flame the electrons are excited to higher energy levels and when they drop back to the ground state, energy is emitted in the form of visible light. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence, these elements do not impart any colour to the flame. The flame test for Ca, Sr and Ba is helpful in their detection in qualitative analysis and estimation by flame photometry. The alkaline earth metals like those of alkali metals have high electrical and thermal conductivities which are typical characteristics of metals.

10.6.6 Chemical Properties

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

(i) Reactivity towards air and water: Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give BeO and Be_3N_2. Magnesium is more electropositive and burns with dazzling brilliance in air to give MgO and Mg_3N_2. Calcium, strontium and barium are readily attacked by air to form the oxide and nitride. They also react with water with increasing vigour even in cold to form hydroxides.

(ii) Reactivity towards the halogens: All the alkaline earth metals combine with halogen at elevated temperatures forming their halides.

$$\mathrm{M + X_2 \rightarrow MX_2\ (X = F,\ Cl,\ Br,\ l)}$$

Thermal decomposition of $(NH_4)_2BeF_4$ is the best route for the preparation of BeF_2, and $BeCl_2$ is conveniently made from the oxide.

$$\mathrm{BeO + C + Cl_2 \xrightleftharpoons{600-800\,K} BeCl_2 + CO}$$

(iii) Reactivity towards hydrogen: All the elements except beryllium combine with hydrogen upon heating to form their hydrides, MH_2.

BeH_2, however, can be prepared by the reaction of $BeCl_2$ with $LiAlH_4$.

$$\mathrm{2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3}$$

(iv) Reactivity towards acids: The alkaline earth metals readily react with acids liberating dihydrogen.

$$\mathrm{M + 2HCl \rightarrow MCl_2 + H_2}$$

(v) Reducing nature: Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials (Table 10.2). However their reducing power is less than those of their corresponding alkali metals. Beryllium has less negative value compared to other alkaline earth metals. However, its reducing nature is due to large hydration energy associated with the small size of Be^{2+} ion and relatively large value of the atomization enthalpy of the metal.

(vi) Solutions in liquid ammonia: Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.

$$\mathrm{M + (x + y)NH_3 \rightarrow \left[M(NH_3)_x\right]^{2+} + 2\left[e(NH_3)_y\right]^{-}}$$

From these solutions, the ammoniates, $[M(NH_3)_6]^{2+}$ can be recovered.

10.6.7 Uses

Beryllium is used in the manufacture of alloys. Copper-beryllium alloys are used in the preparation of high strength springs. Metallic beryllium is used for making windows of X-ray tubes. Magnesium forms alloys with aluminium, zinc, manganese and tin. Magnesium-aluminium alloys being light in mass are used in air-craft construction. Magnesium (powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals. A suspension of magnesium hydroxide in water (called *milk of magnesia*) is used as antacid in medicine. Magnesium carbonate is an ingredient of toothpaste. Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon. Calcium and barium metals, owing to their reactivity with oxygen and nitrogen at elevated temperatures, have often been used to remove air from vacuum tubes. Radium salts are used in radiotherapy, for example, in the treatment of cancer.

10.7 GENERAL CHARACTERISTICS OF COMPOUNDS OF THE ALKALINE EARTH METALS

The dipositive oxidation state (M^{2+}) is the predominant valence of Group 2 elements. The alkaline earth metals form compounds which are predominantly ionic but less ionic than the corresponding compounds of alkali metals. This is due to increased nuclear charge and smaller size. The oxides and other compounds of beryllium and magnesium are more covalent than those formed by the heavier and large sized members (Ca, Sr, Ba). The general characteristics of some of the compounds of alkali earth metals are described below.

(i) Oxides and Hydroxides: The alkaline earth metals burn in oxygen to form the monoxide, MO which, except for BeO, have rock-salt structure. The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat. BeO is amphoteric while oxides of other elements are ionic in nature. All these oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides.

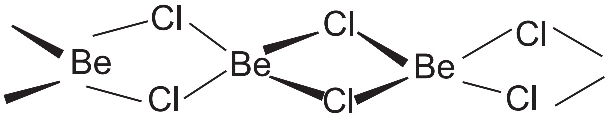
$$MO + H_2O \rightarrow M(OH)_2$$

The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from $Mg(OH)_2$ to $Ba(OH)_2$. The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with acid and alkali both.

$$Be(OH)_2 + 2OH^- \rightarrow \underset{\text{Beryllate ion}}{[Be(OH)_4]^{2-}}$$

$$Be(OH)_2 + 2HCl + 2H_2O \rightarrow [Be(OH)_4]Cl_2$$

(ii) Halides: Except for beryllium halides, all other halides of alkaline earth metals are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents. Beryllium chloride has a chain structure in the solid state as shown below:



In the vapour phase $BeCl_2$ tends to form a chloro-bridged dimer which dissociates into the linear monomer at high temperatures of the order of 1200 K. The tendency to form halide hydrates gradually decreases (for example, $MgCl_2 \cdot 8H_2O$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$) down the group. The dehydration of hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be achieved on heating; however, the corresponding hydrated halides of Be and Mg on heating suffer hydrolysis. The fluorides are relatively less soluble than the chlorides owing to their high lattice energies.

(iii) Salts of Oxoacids: The alkaline earth metals also form salts of oxoacids. Some of these are :

Carbonates: Carbonates of alkaline earth metals are insoluble in water and can be precipitated by addition of a sodium or ammonium carbonate solution to a solution of a soluble salt of these metals. The solubility of carbonates in water decreases as the atomic number of the metal ion increases. All the carbonates decompose on heating to give carbon dioxide and the oxide. Beryllium carbonate is unstable and can be kept only in the atmosphere of CO_2. The thermal stability increases with increasing cationic size.

Sulphates: The sulphates of the alkaline earth metals are all white solids and stable to heat. $BeSO_4$, and $MgSO_4$ are readily soluble in water; the solubility decreases from $CaSO_4$ to $BaSO_4$. The greater hydration enthalpies of Be^{2+} and Mg^{2+} ions overcome the lattice enthalpy factor and therefore their sulphates are soluble in water.

Nitrates: The nitrates are made by dissolution of the carbonates in dilute nitric acid. Magnesium nitrate crystallises with six molecules of water, whereas barium nitrate crystallises as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size and decreasing hydration enthalpy. All of them decompose on heating to give the oxide like lithium nitrate.

$$2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$$

(M = Be, Mg, Ca, Sr, Ba)

Problem 10.4

Why does the solubility of alkaline earth metal hydroxides in water increase down the group?

Solution

Among alkaline earth metal hydroxides, the anion being common the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size, the solubility increases as we go down the group.

Problem 10.5

Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?

Solution

The size of anions being much larger compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

10.8 ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium, the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium which is discussed subsequently.

(i) Beryllium has exceptionally small atomic and ionic sizes and thus does not compare well with other members of the group. Because of high ionisation enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.

(ii) Beryllium does not exhibit coordination number more than four as in its valence shell there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of *d*-orbitals.

(iii) The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.

10.8.1 Diagonal Relationship between Beryllium and Aluminium

The ionic radius of Be^{2+} is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in some ways. Some of the similarities are:

(i) Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.

(ii) Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, $[Be(OH)_4]^{2-}$ just as aluminium hydroxide gives aluminate ion, $[Al(OH)_4]^-$.

(iii) The chlorides of both beryllium and aluminium have Cl^- bridged chloride structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts.

(iv) Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{2-}, AlF_6^{3-}.

10.9 SOME IMPORTANT COMPOUNDS OF CALCIUM

Important compounds of calcium are calcium oxide, calcium hydroxide, calcium sulphate, calcium carbonate and cement. These are industrially important compounds. The large scale preparation of these compounds and their uses are described below.

Calcium Oxide or Quick Lime, CaO

It is prepared on a commercial scale by heating limestone ($CaCO_3$) in a rotary kiln at 1070-1270 K.

$$CaCO_3 \overset{\text{heat}}{\rightleftharpoons} CaO + CO_2$$

The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion.

Calcium oxide is a white amorphous solid. It has a melting point of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$CaO + CO_2 \rightarrow CaCO_3$$

The addition of limited amount of water breaks the lump of lime. This process is called *slaking of lime*. Quick lime slaked with soda gives solid sodalime. Being a basic oxide, it combines with acidic oxides at high temperature.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

$$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$$

Uses:

(i) It is an important primary material for manufacturing cement and is the cheapest form of alkali.

(ii) It is used in the manufacture of sodium carbonate from caustic soda.

(iii) It is employed in the purification of sugar and in the manufacture of dye stuffs.

Calcium Hydroxide (Slaked lime), $Ca(OH)_2$

Calcium hydroxide is prepared by adding water to quick lime, CaO.

It is a white amorphous powder. It is sparingly soluble in water. The aqueous solution is known as *lime water* and a suspension of slaked lime in water is known as *milk of lime*.

When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogencarbonate.

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow CaCl_2 + \underbrace{Ca(OCl)_2}_{\text{Bleaching powder}} + 2H_2O$$

Uses:

(i) It is used in the preparation of mortar, a building material.

(ii) It is used in white wash due to its disinfectant nature.

(iii) It is used in glass making, in tanning industry, for the preparation of bleaching powder and for purification of sugar.

Calcium Carbonate, $CaCO_3$

Calcium carbonate occurs in nature in several forms like limestone, chalk, marble etc. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$$

Excess of carbon dioxide should be avoided since this leads to the formation of water soluble calcium hydrogencarbonate.

Calcium carbonate is a white fluffy powder. It is almost insoluble in water. When heated to 1200 K, it decomposes to evolve carbon dioxide.

$$CaCO_3 \xrightarrow{1200\,K} CaO + CO_2$$

It reacts with dilute acid to liberate carbon dioxide.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

Uses:

It is used as a building material in the form of marble and in the manufacture of quick lime. Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron. Specially precipitated $CaCO_3$ is extensively used in the manufacture of high quality paper. It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, and a filler in cosmetics.

Calcium Sulphate (Plaster of Paris), $CaSO_4 \cdot ½\, H_2O$

It is a hemihydrate of calcium sulphate. It is obtained when gypsum, $CaSO_4 \cdot 2H_2O$, is heated to 393 K.

$$2(CaSO_4.2H_2O) \rightarrow 2(CaSO_4).H_2O + 3H_2O$$

Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, $CaSO_4$ is formed. This is known as 'dead burnt plaster'.

It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes.

Uses:

The largest use of Plaster of Paris is in the building industry as well as plasters. It is used for immoblising the affected part of organ where there is a bone fracture or sprain. It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

Cement: Cement is an important building material. It was first introduced in England in 1824 by Joseph Aspdin. It is also called Portland cement because it resembles with the natural limestone quarried in the Isle of Portland, England.

Cement is a product obtained by combining a material rich in lime, CaO with other material such as clay which contains silica, SiO_2 along with the oxides of aluminium, iron and magnesium. The average composition of Portland cement is : CaO, 50-60%; SiO_2, 20-25%; Al_2O_3, 5-10%; MgO, 2-3%; Fe_2O_3, 1-2% and SO_3, 1-2%. For a good quality cement, the ratio of silica (SiO_2) to alumina (Al_2O_3) should be between 2.5 and 4 and the ratio of lime (CaO) to the total of the oxides of silicon (SiO_2) aluminium (Al_2O_3) and iron (Fe_2O_3) should be as close as possible to 2.

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together they fuse and react to form 'cement clinker'. This clinker is mixed with 2-3% by weight of gypsum ($CaSO_4 \cdot 2H_2O$) to form cement. Thus important ingredients present in Portland cement are dicalcium silicate (Ca_2SiO_4) 26%, tricalcium silicate (Ca_3SiO_5) 51% and tricalcium aluminate ($Ca_3Al_2O_6$) 11%.

Setting of Cement: When mixed with water, the setting of cement takes place to give a hard mass. This is due to the hydration of the molecules of the constituents and their rearrangement. The purpose of adding gypsum is only to slow down the process of setting of the cement so that it gets sufficiently hardened.

Uses: Cement has become a commodity of national necessity for any country next to iron and steel. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

10.10 BIOLOGICAL IMPORTANCE OF MAGNESIUM AND CALCIUM

An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper. The daily requirement in the human body has been estimated to be 200 – 300 mg.

All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium. About 99 % of body calcium is present in bones and teeth. It also plays important roles in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation. The calcium concentration in plasma is regulated at about 100 mgL^{-1}. It is maintained by two hormones: calcitonin and parathyroid hormone. Do you know that bone is not an inert and unchanging substance but is continuously being solubilised and redeposited to the extent of 400 mg per day in man? All this calcium passes through the plasma.

SUMMARY

The ***s*-Block** of the periodic table constitutes **Group1** (alkali metals) and **Group 2** (alkaline earth metals). They are so called because their oxides and hydroxides are alkaline in nature. The alkali metals are characterised by one *s*-electron and the alkaline earth metals by two *s*-electrons in the valence shell of their atoms. These are highly reactive metals forming monopositive **(M^+)** and dipositve **(M^{2+})** ions respectively.

There is a regular trend in the physical and chemical properties of the alkali metal with increasing atomic numbers. The **atomic** and **ionic** sizes increase and the **ionization enthalpies** decrease systematically down the group. Somewhat similar trends are observed among the properties of the alkaline earth metals.

The first element in each of these groups, lithium in Group 1 and beryllium in Group 2 shows similarities in properties to the second member of the next group. Such similarities are termed as the **'diagonal relationship'** in the periodic table. As such these elements are anomalous as far as their group characteristics are concerned.

The alkali metals are silvery white, soft and low melting. They are highly reactive. The compounds of alkali metals are predominantly ionic. Their oxides and hydroxides are soluble in water forming strong alkalies. Important compounds of sodium includes sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogencarbonate. Sodium hydroxide is manufactured by **Castner-Kellner** process and sodium carbonate by **Solvay** process.

The chemistry of alkaline earth metals is very much like that of the alkali metals. However, some differences arise because of reduced atomic and ionic sizes and increased cationic charges in case of alkaline earth metals. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides. Industrially important compounds of calcium include calcium oxide (lime), calcium hydroxide (slaked lime), calcium sulphate **(Plaster of Paris),** calcium carbonate (limestone) and cement. **Portland cement** is an important constructional material. It is manufactured by heating a pulverised mixture of limestone and clay in a rotary kiln. The clinker thus obtained is mixed with some gypsum (2-3%) to give a fine powder of cement. All these substances find variety of uses in different areas.

Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in **biological fluids**. These ions perform important **biological functions** such as maintenance of ion balance and nerve impulse conduction.

EXERCISES

10.1 What are the common physical and chemical features of alkali metals ?

10.2 Discuss the general characteristics and gradation in properties of alkaline earth metals.

10.3 Why are alkali metals not found in nature ?

10.4 Find out the oxidation state of sodium in Na_2O_2.

10.5 Explain why is sodium less reactive than potassium.

10.6 Compare the alkali metals and alkaline earth metals with respect to (i) ionisation enthalpy (ii) basicity of oxides and (iii) solubility of hydroxides.

10.7 In what ways lithium shows similarities to magnesium in its chemical behaviour?

10.8 Explain why can alkali and alkaline earth metals not be obtained by chemical reduction methods?

10.9 Why are potassium and caesium, rather than lithium used in photoelectric cells?

10.10 When an alkali metal dissolves in liquid ammonia the solution can acquire different colours. Explain the reasons for this type of colour change.

10.11 Beryllium and magnesium do not give colour to flame whereas other alkaline earth metals do so. Why ?

10.12 Discuss the various reactions that occur in the Solvay process.

10.13 Potassium carbonate cannot be prepared by Solvay process. Why ?

10.14 Why is Li_2CO_3 decomposed at a lower temperature whereas Na_2CO_3 at higher temperature?

10.15 Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals. (a) Nitrates (b) Carbonates (c) Sulphates.

10.16 Starting with sodium chloride how would you proceed to prepare (i) sodium metal (ii) sodium hydroxide (iii) sodium peroxide (iv) sodium carbonate ?

10.17 What happens when (i) magnesium is burnt in air (ii) quick lime is heated with silica (iii) chlorine reacts with slaked lime (iv) calcium nitrate is heated ?

10.18 Describe two important uses of each of the following : (i) caustic soda (ii) sodium carbonate (iii) quicklime.

10.19 Draw the structure of (i) $BeCl_2$ (vapour) (ii) $BeCl_2$ (solid).

10.20 The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water. Explain.

10.21 Describe the importance of the following : (i) limestone (ii) cement (iii) plaster of paris.

10.22 Why are lithium salts commonly hydrated and those of the other alkali ions usually anhydrous?

10.23 Why is LiF almost insoluble in water whereas LiCl soluble not only in water but also in acetone ?

10.24 Explain the significance of sodium, potassium, magnesium and calcium in biological fluids.

10.25 What happens when

(i) sodium metal is dropped in water ?

(ii) sodium metal is heated in free supply of air ?

(iii) sodium peroxide dissolves in water ?

10.26 Comment on each of the following observations:

(a) The mobilities of the alkali metal ions in aqueous solution are $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

(b) Lithium is the only alkali metal to form a nitride directly.

(c) $E^\ominus$ for $M^{2+}(aq) + 2e^- \rightarrow M(s)$ (where M = Ca, Sr or Ba) is nearly constant.

10.27 State as to why

(a) a solution of Na_2CO_3 is alkaline ?

(b) alkali metals are prepared by electrolysis of their fused chlorides ?

(c) sodium is found to be more useful than potassium ?

10.28 Write balanced equations for reactions between

(a) Na_2O_2 and water

(b) KO_2 and water

(c) Na_2O and CO_2.

10.29 How would you explain the following observations?

(i) BeO is almost insoluble but $BeSO_4$ is soluble in water,

(ii) BaO is soluble but $BaSO_4$ is insoluble in water,

(iii) LiI is more soluble than KI in ethanol.

10.30 Which of the alkali metal is having least melting point ?

(a) Na (b) K (c) Rb (d) Cs

10.31 Which one of the following alkali metals gives hydrated salts ?

(a) Li (b) Na (c) K (d) Cs

10.32 Which one of the alkaline earth metal carbonates is thermally the most stable ?

(a) $MgCO_3$ (b) $CaCO_3$ (c) $SrCO_3$ (d) $BaCO_3$

UNIT 11

THE *p*-BLOCK ELEMENTS

Objectives

After studying this unit, you will be able to

- appreciate the general trends in the chemistry of *p*-block elements;
- describe the trends in physical and chemical properties of group 13 and 14 elements;
- explain anomalous behaviour of boron and carbon;
- describe allotropic forms of carbon;
- know the chemistry of some important compounds of boron, carbon and silicon;
- list the important uses of group 13 and 14 elements and their compounds.

> ***"The variation in properties of the p-block elements due to the influence of d and f electrons in the inner core of the heavier elements makes their chemistry interesting"***

In *p*-block elements the last electron enters the outermost *p* orbital. As we know that the number of *p* orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a set of *p* orbitals is six. Consequently there are six groups of *p*–block elements in the periodic table numbering from 13 to 18. Boron, carbon, nitrogen, oxygen, fluorine and helium head the groups. Their valence shell **electronic configuration is** ns^2np^{1-6} (except for He). The **inner core** of the electronic configuration may, however, differ. The difference in inner core of elements greatly influences their physical properties (such as atomic and ionic radii, ionisation enthalpy, etc.) as well as chemical properties. Consequently, a lot of variation in properties of elements in a group of *p*-block is observed. The *maximum oxidation state* shown by a *p*-block element is equal to the total number of valence electrons (*i.e.*, the sum of the *s*- and *p*-electrons). Clearly, the number of possible oxidation states increases towards the right of the periodic table. In addition to this so called *group oxidation state*, *p*-block elements may show other oxidation states which normally, but not necessarily, differ from the total number of valence electrons by unit of two. The important oxidation states exhibited by *p*-block elements are shown in Table 11.1. In boron, carbon and nitrogen families the group oxidation state is the most stable state for the lighter elements in the group. However, the oxidation state two unit less than the group oxidation state becomes progressively more stable for the heavier elements in each group. The occurrence of oxidation states two unit less than the group oxidation states are sometime attributed to the '**inert pair effect**'.

Table 11.1 General Electronic Configuration and Oxidation States of *p*-Block Elements

Group	13	14	15	16	17	18
General electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6 ($1s^2$ for He)
First member of the group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1	+2, – 4	+3, – 3	+4, +2, –2	+5, + 3, +1, –1	+6, +4, +2

The relative stabilities of these two oxidation states – group oxidation state and two unit less than the group oxidation state – may vary from group to group and will be discussed at appropriate places.

It is interesting to note that the *non-metals* and *metalloids* exist only in the *p*-block of the periodic table. The non-metallic character of elements decreases down the group. In fact the heaviest element in each *p*-block group is the most metallic in nature. This change from non-metallic to metallic character brings diversity in the chemistry of these elements depending on the group to which they belong.

In general, non-metals have higher ionisation enthalpies and higher electronegativities than the metals. Hence, in contrast to metals which readily form cations, non-metals readily form anions. The compounds formed by highly reactive non-metals with highly reactive metals are generally ionic because of large differences in their electronegativities. On the other hand, compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities. The change of non-metallic to metallic character can be best illustrated by the nature of oxides they form. The non-metal oxides are acidic or neutral whereas metal oxides are basic in nature.

The first member of p-block differs from the remaining members of their corresponding group in two major respects. First is the size and all other properties which depend on size. Thus, the lightest *p*-block elements show the same kind of differences as the lightest *s*-block elements, lithium and beryllium. The second important difference, which applies only to the *p*-block elements, arises from the effect of *d*-orbitals in the valence shell of heavier elements (starting from the third period onwards) and their lack in second period elements. The second period elements of *p*-groups starting from boron are restricted to a maximum covalence of four (using 2*s* and three 2*p* orbitals). In contrast, the third period elements of *p*-groups with the electronic configuration $3s^23p^n$ have the vacant 3*d* orbitals lying between the 3*p* and the 4*s* levels of energy. Using these *d*-orbitals the third period elements can expand their covalence above four. For example, while boron forms only $[BF_4]^-$, aluminium gives $[AlF_6]^{3-}$ ion. The presence of these *d*-orbitals influences the chemistry of the heavier elements in a number of other ways. The combined effect of size and availability of *d* orbitals considerably influences the ability of these elements to form π bonds. The first member of a group differs from the heavier members in its ability to form $p\pi$ - $p\pi$ multiple bonds to itself (e.g., C=C, C≡C, N≡N) and to other second row elements (e.g., C=O, C=N, C≡N, N=O). This type of π - bonding is not particularly strong for the heavier *p*-block elements. The heavier elements do form π bonds but this involves *d* orbitals ($d\pi - p\pi$ or $d\pi - d\pi$). As the *d* orbitals are of higher energy than the *p* orbitals, they contribute less to the overall stability of molecules than does $p\pi$ - $p\pi$ bonding of the second row elements. However, the coordination number in species of heavier elements may be higher than for the first element in the same oxidation state. For example, in +5 oxidation state both N and P form oxoanions : NO_3^- (three-coordination with π – bond involving one nitrogen *p*-orbital) and PO_4^{3-} (four-coordination involving *s*, *p* and *d* orbitals contributing to the π – bond). In this unit we will study the chemistry of group 13 and 14 elements of the periodic table.

11.1 GROUP 13 ELEMENTS: THE BORON FAMILY

This group elements show a wide variation in properties. Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium, thallium and nihonium are almost exclusively metallic in character.

Boron is a fairly rare element, mainly occurs as orthoboric acid, (H_3BO_3), borax, $Na_2B_4O_7 \cdot 10H_2O$, and kernite, $Na_2B_4O_7 \cdot 4H_2O$. In India borax occurs in Puga Valley (Ladakh) and Sambhar Lake (Rajasthan). The abundance of boron in earth crust is less than 0.0001% by mass. There are two isotopic forms of boron ^{10}B (19%) and ^{11}B (81%). Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%). Bauxite, Al_2O_3. $2H_2O$ and cryolite, Na_3AlF_6 are the important minerals of aluminium. In India it is found as mica in Madhya Pradesh, Karnataka, Orissa and Jammu. Gallium, indium and thallium are less abundant elements in nature. Nihonium has symbol Nh, atomic number 113, atomic mass 286 g mol^{-1} and electronic configuration [Rn] $5f^{14}\,6d^{10}\,7s^2\,7p^2$. So far it has been prepared in small amount and half life of its most stable isotope is 20 seconds. Due to these reasons its chemistry has not been established.

Nihonium is a synthetically prepared radioactive element. Here atomic, physical and chemical properties of elements of this group leaving nihonium are discussed below.

11.1.1 Electronic Configuration

The outer electronic configuration of these elements is ns^2np^1. A close look at the electronic configuration suggests that while boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 *d*-electrons, and thallium has noble gas plus 14 *f*- electrons plus 10 *d*-electron cores. Thus, the electronic structures of these elements are more complex than for the first two groups of elements discussed in unit 10. This difference in electronic structures affects the other properties and consequently the chemistry of all the elements of this group.

11.1.2 Atomic Radii

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen. Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 *d*-electrons offer only poor screening effect (Unit 2) for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

11.1.3 Ionization Enthalpy

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group. The decrease from B to Al is associated with increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of *d*- and *f*-electrons ,which have low screening effect, to compensate the increase in nuclear charge.

The order of ionisation enthalpies, as expected, is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$. The sum of the first three ionisation enthalpies for each of the elements is very high. Effect of this will be apparent when you study their chemical properties.

11.1.4 Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases marginally (Table 11.2). This is because of the discrepancies in atomic size of the elements.

11.1.5 Physical Properties

Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point. Rest of the members are soft metals with low melting point and high electrical conductivity. It is worthwhile to note that gallium with unusually low melting point (303 K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures. Density of the elements increases down the group from boron to thallium.

11.1.6 Chemical Properties

Oxidation state and trends in chemical reactivity

Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al^{3+} ions. In fact, aluminium is a highly electropositive metal. However, down the group, due to poor shielding effect of intervening *d* and *f* orbitals, the increased effective nuclear charge holds *ns* electrons tightly (responsible for *inert pair effect*) and thereby, restricting their participation in bonding. As a result of this, only *p*-orbital electron may be involved in bonding. In fact in Ga, In and Tl, both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements: Al<Ga<In<Tl. In thallium +1 oxidation state is predominant

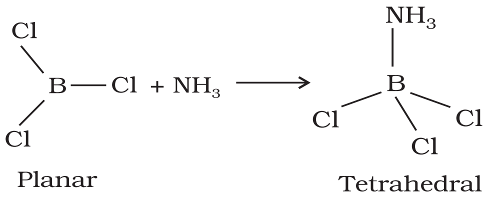
Table 11.2 Atomic and Physical Properties of Group 13 Elements

Property	Element				
	Boron B	Aluminium Al	Gallium Ga	Indium In	Thallium Tl
Atomic number	5	13	31	49	81
Atomic mass(g mol^{-1})	10.81	26.98	69.72	114.82	204.38
Electronic Configuration	[He]$2s^2 2p^1$	[Ne]$3s^2 3p^1$	[Ar]$3d^{10} 4s^2 4p^1$	[Kr]$4d^{10} 5s^2 5p^1$	[Xe]$4f^{14} 5d^{10} 6s^2 6p^1$
Atomic radius/pm^a	(88)	143	135	167	170
Ionic radius M^{3+}/pm^b	(27)	53.5	62.0	80.0	88.5
Ionic radius M^+/pm	-	-	120	140	150
Ionization enthalpy (kJ mol^{-1}) $\Delta_i H_1$	801	577	579	558	589
$\Delta_i H_2$	2427	1816	1979	1820	1971
$\Delta_i H_3$	3659	2744	2962	2704	2877
Electronegativity^c	2.0	1.5	1.6	1.7	1.8
Density /g cm^{-3} at 298 K	2.35	2.70	5.90	7.31	11.85
Melting point / K	2453	933	303	430	576
Boiling point / K	3923	2740	2676	2353	1730
$E^\ominus$/ V for (M^{3+}/M)	-	–1.66	–0.56	–0.34	+1.26
$E^\ominus$ / V for (M^+/M)	-	+0.55	-0.79(acid) –1.39(alkali)	–0.18	–0.34

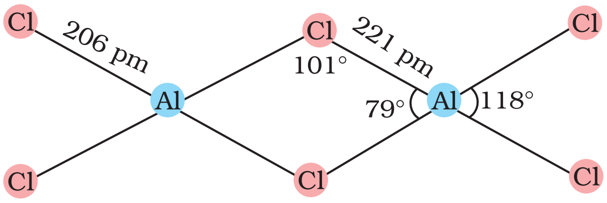
^{a}Metallic radius, ^{b} 6-coordination, ^{c} Pauling scale,

whereas the +3 oxidation state is highly oxidising in character. The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.

In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in BF_3) will be only six. Such **electron deficient** molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group. BCl_3 easily accepts a lone pair of electrons from ammonia to form $BCl_3 \cdot NH_3$.



$AlCl_3$ achieves stability by forming a dimer



Tetrahedral

In trivalent state most of the compounds being covalent are hydrolysed in water. For example, the trichlorides on hyrolysis in water form tetrahedral $\left[M(OH)_4\right]^-$ species; the hybridisation state of element M is sp^3. Aluminium chloride in acidified aqueous solution forms octahedral $\left[Al(H_2O)_6\right]^{3+}$ ion. In this complex ion, the 3*d* orbitals of Al are involved and the hybridisation state of Al is sp^3d^2.

Problem 11.1

Standard electrode potential values, $E^\ominus$ for Al^{3+}/Al is –1.66 V and that of Tl^{3+}/Tl is +1.26 V. Predict about the formation of M^{3+} ion in solution and compare the electropositive character of the two metals.

Solution

Standard electrode potential values for two half cell reactions suggest that aluminium has high tendency to make Al^{3+}(aq) ions, whereas Tl^{3+} is not only unstable in solution but is a powerful oxidising agent also. Thus Tl^+ is more stable in solution than Tl^{3+}. Aluminium being able to form +3 ions easily, is more electropositive than thallium.

(i) Reactivity towards air

Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.

$$2E(s) + 3O_2(g) \xrightarrow{\Delta} 2E_2O_3(s)$$

$$2E(s) + N_2(g) \xrightarrow{\Delta} 2EN(s)$$

(E = element)

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

(ii) Reactivity towards acids and alkalies

Boron does not react with acids and alkalies even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.

Aluminium dissolves in dilute HCl and liberates dihydrogen.

$$2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$$

However, concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface.

Aluminium also reacts with aqueous alkali and liberates dihydrogen.

$$\begin{array}{c} 2Al(s) + 2NaOH(aq) + 6H_2O(l) \\ \downarrow \\ 2\,Na^+[Al(OH)_4]^-(aq) \quad + \quad 3H_2(g) \end{array}$$

Sodium tetrahydroxoaluminate(III)

(iii) Reactivity towards halogens

These elements react with halogens to form trihalides (except TlI_3).

$$2E(s) + 3X_2(g) \rightarrow 2EX_3(s) \qquad (X = F, Cl, Br, I)$$

Problem 11.2

White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

Solution

Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.

11.2 IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

Certain important trends can be observed in the chemical behaviour of group 13 elements. The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$, except in boron, exist in aqueous medium.

The monomeric trihalides, being electron deficient, are strong Lewis acids. Boron trifluoride easily reacts with Lewis bases such as NH_3 to complete octet around boron.

$$F_3B + :NH_3 \rightarrow F_3B \leftarrow NH_3$$

It is due to the absence of *d* orbitals that the maximum covalence of B is 4. Since the *d* orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4. Most of the other metal halides (*e.g.*, $AlCl_3$) are dimerised through halogen bridging (*e.g.*, Al_2Cl_6). The metal species completes its octet by accepting electrons from halogen in these halogen bridged molecules.

Problem 11.3

Boron is unable to form BF_6^{3-} ion. Explain.

Solution

Due to non-availability of *d* orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4.

11.3 SOME IMPORTANT COMPOUNDS OF BORON

Some useful compounds of boron are borax, orthoboric acid and diborane. We will briefly study their chemistry.

11.3.1 Borax

It is the most important compound of boron. It is a white crystalline solid of formula $Na_2B_4O_7 \cdot 10H_2O$. In fact it contains the tetranuclear units $\left[B_4O_5(OH)_4\right]^{2-}$ and correct formula; therefore, is $Na_2[B_4O_5(OH)_4].8H_2O$. Borax dissolves in water to give an alkaline solution.

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + \underset{\text{Orthoboric acid}}{4H_3BO_3}$$

On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $Co(BO_2)_2$ bead is formed.

11.3.2 Orthoboric acid

Orthoboric acid, H_3BO_3 is a white crystalline solid, with soapy touch. It is sparingly soluble in water but highly soluble in hot water. It can be prepared by acidifying an aqueous solution of borax.

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$$

It is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.). It has a layer structure in which planar BO_3 units are joined by hydrogen bonds as shown in Fig. 11.1.

Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion:

$$B(OH)_3 + 2HOH \rightarrow [B(OH)_4]^- + H_3O^+$$

On heating, orthoboric acid above 370K forms metaboric acid, HBO_2 which on further heating yields boric oxide, B_2O_3.

$$H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$$

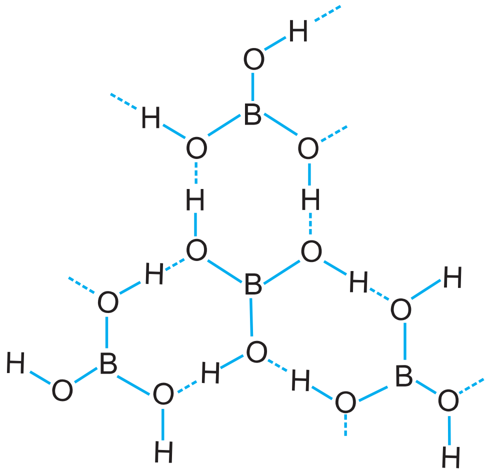


Fig. 11. 1 *Structure of boric acid; the dotted lines represent hydrogen bonds*

Problem 11.4

Why is boric acid considered as a weak acid?

Solution

Because it is not able to release H^+ ions on its own. It receives OH^- ions from water molecule to complete its octet and in turn releases H^+ ions.

11.3.3 Diborane, B_2H_6

The simplest boron hydride known, is diborane. It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.

$$4BF_3 + 3\ LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

A convenient laboratory method for the preparation of diborane involves the oxidation of sodium borohydride with iodine.

$$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$$

Diborane is produced on an industrial scale by the reaction of BF_3 with sodium hydride.

$$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$$

Diborane is a colourless, highly toxic gas with a b.p. of 180 K. Diborane catches fire spontaneously upon exposure to air. It burns in oxygen releasing an enormous amount of energy.

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O; \qquad \Delta_c H^{\ominus} = -1976\ \text{kJ mol}^{-1}$$

Most of the higher boranes are also spontaneously flammable in air. Boranes are readily hydrolysed by water to give boric acid.

$$B_2H_6(g) + 6H_2O(l) \rightarrow 2B(OH)_3(aq) + 6H_2(g)$$

Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts, $BH_3{\cdot}L$

$$B_2H_6 + 2\ NMe_3 \rightarrow 2BH_3{\cdot}NMe_3$$

$$B_2H_6 + 2\ CO \rightarrow 2BH_3{\cdot}CO$$

Reaction of ammonia with diborane gives initially $B_2H_6.2NH_3$ which is formulated as $[BH_2(NH_3)_2]^+ [BH_4]^-$; further heating gives borazine, $B_3N_3H_6$ known as "inorganic benzene" in view of its ring structure with alternate BH and NH groups.

$$3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{Heat} 2B_3N_3H_6 + 12H_2$$

The structure of diborane is shown in Fig.11.2(a). The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three

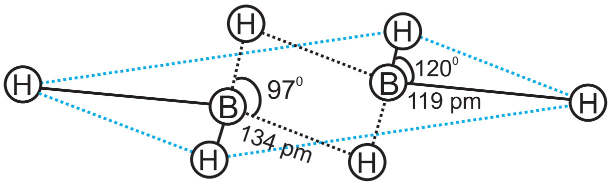


Fig.11.2(a) *The structure of diborane, B_2H_6*

centre–two electron bonds shown in Fig.11.2 (b).

Boron also forms a series of hydridoborates; the most important one is the tetrahedral $[BH_4]^-$ ion. Tetrahydridoborates of several metals are known. Lithium and sodium tetrahydridoborates, also known as ***borohydrides***, are prepared by the reaction of metal hydrides with B_2H_6 in diethyl ether.

$$2MH + B_2H_6 \rightarrow 2\ M^+\ [BH_4]^- \qquad (M = Li\ or\ Na)$$

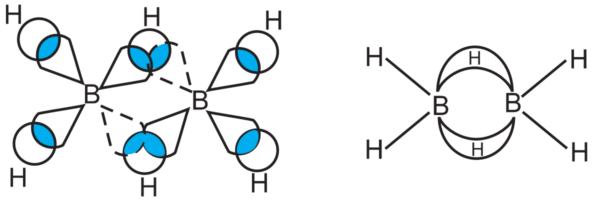


Fig.11.2(b) *Bonding in diborane. Each B atom uses sp^3 hybrids for bonding. Out of the four sp^3 hybrids on each B atom, one is without an electron shown in broken lines. The terminal B-H bonds are normal 2-centre-2-electron bonds but the two bridge bonds are 3-centre-2-electron bonds. The 3-centre-2-electron bridge bonds are also referred to as banana bonds.*

Both $LiBH_4$ and $NaBH_4$ are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

11.4 USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS

Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity, finds many applications. Boron fibres are used in making bullet-proof vest and light composite material for aircraft. The boron-10 (^{10}B) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods. The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses (e.g., Pyrex), glass-wool and fibreglass. Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as constituent of medicinal soaps. An aqueous solution of orthoboric acid is generally used as a mild antiseptic.

Aluminium is a bright silvery-white metal, with high tensile strength. It has a high electrical and thermal conductivity. On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper. Aluminium is used extensively in industry and everyday life. It forms alloys with Cu, Mn, Mg, Si and Zn. Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry. The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

11.5 GROUP 14 ELEMENTS: THE CARBON FAMILY

Carbon, silicon, germanium, tin lead and flerovium are the members of group 14. Carbon is the seventeenth most abundant element by mass in the earth's crust. It is widely distributed in nature in free as well as in the combined state. In elemental state it is available as coal, graphite and diamond; however, in combined state it is present as metal carbonates, hydrocarbons and carbon dioxide gas (0.03%) in air. One can emphatically say that carbon is the most versatile element in the world. Its combination with other elements such as dihydrogen, dioxygen, chlorine and sulphur provides an astonishing array of materials ranging from living tissues to drugs and plastics. Organic chemistry is devoted to carbon containing compounds. It is an essential constituent of all living organisms. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C. In addition to these, third isotope, ^{14}C is also present. It is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is the second (27.7 % by mass) most abundant element on the earth's crust and is present in nature in the form of silica and silicates. Silicon is a very important component of ceramics, glass and cement. Germanium exists only in traces. Tin occurs mainly as cassiterite, SnO_2 and lead as galena, PbS. Flerovium is synthetically prepared radioactive element

Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

Symbol of Flerovium is Fl. It has atomic number 114, atomic mass 289 g mol^{-1} and electronic configuration $[\text{Rn}]\,5f^{14}6d^{10}7s^2\,7p^2$. It has been prepared only in small amount. Its half life is short and its chemistry has not been established yet. The important atomic and physical properties along with their electronic configuration of the elements of group 14 leaving flerovium are given in Table 11.3. Some of the atomic, physical and chemical properties are discussed below:

11.5.1 Electronic Configuration

The valence shell electronic configuration of these elements is ns^2np^2. The inner core of the electronic configuration of elements in this group also differs.

11.5.2 Covalent Radius

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled *d* and *f* orbitals in heavier members.

11.5.3 Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general the ionisation enthalpy decreases down the group. Small decrease in Δ_iH from Si to Ge to Sn and slight increase in Δ_iH from Sn to Pb is the consequence of poor shielding effect of intervening *d* and *f* orbitals and increase in size of the atom.

11.5.4 Electronegativity

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

Table 11.3 Atomic and Physical Properties of Group 14 Elements

Property		**Element**				
		Carbon C	**Silicon Si**	**Germanium Ge**	**Tin Sn**	**Lead Pb**
Atomic Number		6	14	32	50	82
Atomic mass (g mol^{-1})		12.01	28.09	72.60	118.71	207.2
Electronic configuration		$[\text{He}]2s^22p^2$	$[\text{Ne}]3s^23p^2$	$[\text{Ar}]3d^{10}4s^24p^2$	$[\text{Kr}]4d^{10}5s^2\,5p^2$	$[\text{Xe}]4f^{14}5d^{10}6s^26p^2$
Covalent radius/pm[a]		77	118	122	140	146
Ionic radius M^{4+}/pm[b]		–	40	53	69	78
Ionic radius M^{2+}/pm[b]		–	–	73	118	119
Ionization enthalpy/ kJ mol^{-1}	Δ_iH_1	1086	786	761	708	715
	Δ_iH_2	2352	1577	1537	1411	1450
	Δ_iH_3	4620	3228	3300	2942	3081
	Δ_iH_4	6220	4354	4409	3929	4082
Electronegativity[c]		2.5	1.8	1.8	1.8	1.9
Density[d]/g cm^{-3}		3.51[e]	2.34	5.32	7.26[f]	11.34
Melting point/K		4373	1693	1218	505	600
Boiling point/K		–	3550	3123	2896	2024
Electrical resistivity/ ohm cm (293 K)		10^{14}–10^{16}	50	50	10^{-5}	2×10^{-5}

[a] for M^{IV} oxidation state; [b] 6–coordination; [c] Pauling scale; [d] 293 K; [e] for diamond; for graphite, density is 2.22; [f] β-form (stable at room temperature)

11.5.5 Physical Properties

All members of group 14 are solids. Carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

11.5.6 Chemical Properties

Oxidation states and trends in chemical reactivity

The group 14 elements have four electrons in outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge<Sn<Pb. It is due to the inability of ns^2 electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group. Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 state and only few compounds in +2 state. Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent). Lead compounds in +2 state are stable and in +4 state are strong oxidising agents. In tetravalent state the number of electrons around the central atom in a molecule (*e.g.*, carbon in CCl_4) is eight. Being *electron precise* molecules, they are normally not expected to act as electron acceptor or electron donor species. Although carbon cannot exceed its covalence more than 4, other elements of the group can do so. It is because of the presence of *d* orbital in them. Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like, SiF_6^{2-}, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ exist where the hybridisation of the central atom is sp^3d^2.

(i) Reactivity towards oxygen

All members when heated in oxygen form oxides. There are mainly two types of oxides, *i.e.*, monoxide and dioxide of formula MO and MO_2 respectively. SiO only exists at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states. The dioxides — CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

Problem 11.5

Select the member(s) of group 14 that (i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state, (iii) used as semiconductor.

Solution

(i) carbon (ii) lead
(iii) silicon and germanium

(ii) Reactivity towards water

Carbon, silicon and germanium are not affected by water. Tin decomposes steam to form dioxide and dihydrogen gas.

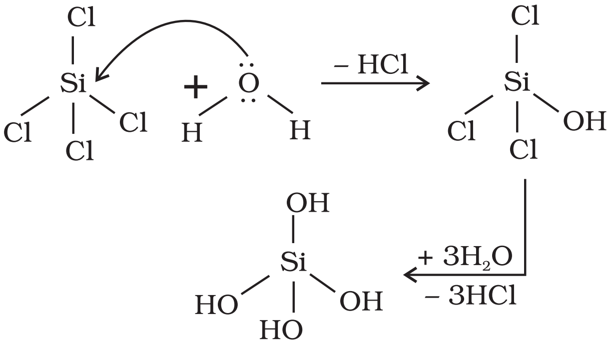
$$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$$

Lead is unaffected by water, probably because of a protective oxide film formation.

(iii) Reactivity towards halogen

These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl, Br, I). Except carbon, all other members react directly with halogen under suitable condition to make halides. Most of the MX_4 are covalent in nature. The central metal atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape. Exceptions are SnF_4 and PbF_4, which are ionic in nature. PbI_4 does not exist because Pb—I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom. Heavier members Ge to Pb are able to make halides of formula MX_2. Stability of dihalides increases down the group. Considering the thermal and chemical stability, GeX_4 is more stable than GeX_2, whereas PbX_2 is more than PbX_4. Except CCl_4, other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in *d* orbital.

Hydrolysis can be understood by taking the example of $SiCl_4$. It undergoes hydrolysis by initially accepting lone pair of electrons from water molecule in *d* orbitals of Si, finally leading to the formation of $Si(OH)_4$ as shown below :



Silicic acid

Problem 11. 6

$[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ not. Give possible reasons.

Solution

The main reasons are :

(i) six large chloride ions cannot be accommodated around Si^{4+} due to limitation of its size.

(ii) interaction between lone pair of chloride ion and Si^{4+} is not very strong.

11.6 IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of *d* orbitals.

In carbon, only *s* and *p* orbitals are available for bonding and, therefore, it can accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of *d* orbitals.

Carbon also has unique ability to form $p\pi-p\pi$ multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are: C=C, C≡C, C=O, C=S, and C≡N. Heavier elements do not form $p\pi-p\pi$ bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called **catenation**. This is because C—C bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is C >> Si > Ge ≈ Sn. Lead does not show catenation.

Bond	**Bond enthalpy / kJ mol $^{-1}$**
C—C	348
Si—Si	297
Ge—Ge	260
Sn—Sn	240

Due to property of catenation and $p\pi-p\pi$ bond formation, carbon is able to show allotropic forms.

11.7 ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as **fullerenes** was discovered by H.W.Kroto, E.Smalley and R.F.Curl. For this discovery they were awarded the Nobel Prize in 1996.

11.7.1 Diamond

It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C–C bond length is 154 pm. The structure extends in space and produces a rigid three-dimensional network of carbon atoms. In this

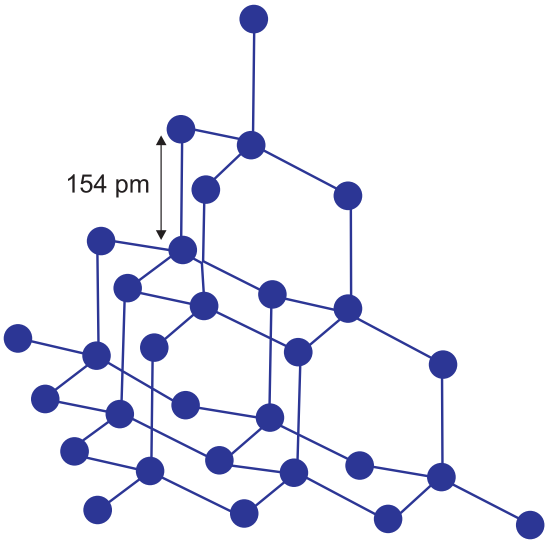


Fig. 11.3 *The structure of diamond*

structure (Fig. 11.3) directional covalent bonds are present throughout the lattice.

It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

Problem 11.7

Diamond is covalent, yet it has high melting point. Why ?

Solution

Diamond has a three-dimensional network involving strong C—C bonds, which are very difficult to break and, in turn has high melting point.

11.7.2 Graphite

Graphite has layered structure (Fig.11.4). Layers are held by van der Waals forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

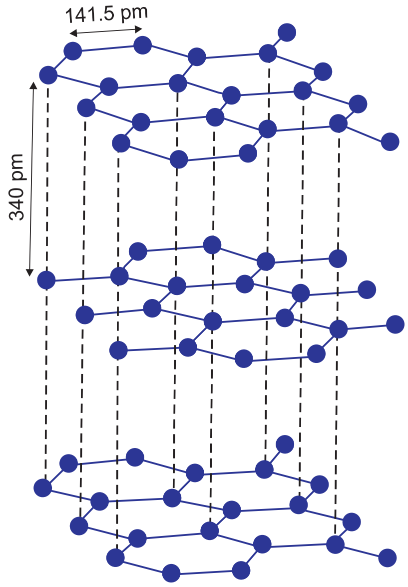


Fig 11.4 *The structure of graphite*

11.7.3 Fullerenes

Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised C^n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called **Buckminsterfullerene** (Fig. 11.5).

It contains twenty six- membered rings and twelve five-membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called *bucky balls* in short.

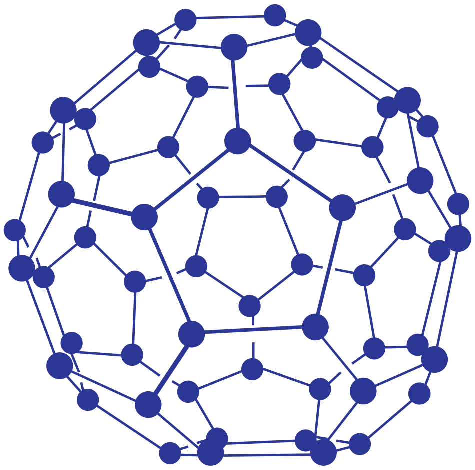


Fig.11.5 *The structure of C_{60}, Buckminsterfullerene : Note that molecule has the shape of a soccer ball (football).*

It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H^{\ominus}$ of graphite is taken as zero. $\Delta_f H^{\ominus}$ values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol^{-1}, respectively.

Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes. Carbon black is obtained by burning hydrocarbons in a limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

11.7.4 Uses of Carbon

Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalies. Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminators and in airconditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy. Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg).

11.8 SOME IMPORTANT COMPOUNDS OF CARBON AND SILICON

Oxides of Carbon

Two important oxides of carbon are carbon monoxide, CO and carbon dioxide, CO_2.

11.8.1 Carbon Monoxide

Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.

$$2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$$

On small scale pure CO is prepared by dehydration of formic acid with concentrated H_2SO_4 at 373 K

$$HCOOH \xrightarrow[\text{conc.}H_2SO_4]{373K} H_2O + CO$$

On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H_2 thus produced is known as **water gas** or **synthesis gas**.

$$C(s) + H_2O(g) \xrightarrow{473\text{–}1273K} \underbrace{CO(g) + H_2(g)}_{\text{Water gas}}$$

When air is used instead of steam, a mixture of CO and N_2 is produced, which is called **producer gas**.

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273K} \underbrace{2CO(g) + 4N_2(g)}_{\text{Producer gas}}$$

Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

Carbon monoxide is a colourless, odourless and almost water insoluble gas. It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals. This property of

CO is used in the extraction of many metals from their oxides ores.

$$Fe_2O_3\,(s) + 3CO\,(g) \xrightarrow{\Delta} 2Fe\,(s) + 3CO_2\,(g)$$

$$ZnO\,(s) + CO\,(g) \xrightarrow{\Delta} Zn\,(s) + CO_2\,(g)$$

In CO molecule, there are one sigma and two π bonds between carbon and oxygen, $:C \equiv O:$. Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated to form **metal carbonyls**. The highly poisonous nature of CO arises because of its ability to form a **complex with haemoglobin**, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

11.8.2 Carbon Dioxide

It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$$

$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$$

In the laboratory it is conveniently prepared by the action of dilute HCl on calcium carbonate.

$$CaCO_3(s) + 2HCl\,(aq) \rightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O(l)$$

On commercial scale it is obtained by heating limestone.

It is a colourless and odourless gas. Its low solubility in water makes it of immense biochemical and geo-chemical importance. With water, it forms carbonic acid, H_2CO_3 which is a weak dibasic acid and dissociates in two steps:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

$$HCO_3^-\,(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}\,(aq) + H_3O^+(aq)$$

H_2CO_3/HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42. Being acidic in nature, it combines with alkalies to form metal carbonates.

Carbon dioxide, which is normally present to the extent of ~ 0.03 % by volume in the atmosphere, is removed from it by the process known as **photosynthesis**. It is the process by which green plants convert atmospheric CO_2 into carbohydrates such as glucose. The overall chemical change can be expressed as:

$$6CO_2 + 12H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

By this process plants make food for themselves as well as for animals and human beings. Unlike CO, it is not poisonous. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO_2 content of the atmosphere. This may lead to increase in **green house effect** and thus, raise the temperature of the atmosphere which might have serious consequences.

Carbon dioxide can be obtained as a solid in the form of **dry ice** by allowing the liquified CO_2 to expand rapidly. Dry ice is used as a refrigerant for ice-cream and frozen food. Gaseous CO_2 is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher. A substantial amount of CO_2 is used to manufacture urea.

In CO_2 molecule carbon atom undergoes *sp* hybridisation. Two *sp* hybridised orbitals of carbon atom overlap with two *p* orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in $p\pi$– $p\pi$ bonding with oxygen atom. This results in its linear shape [with both C–O bonds of equal length (115 pm)] with no dipole moment. The resonance structures are shown below:

$$\overset{-}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-C\equiv\overset{+}{O}: \leftrightarrow :\overset{\cdot\cdot}{O}=C=\overset{\cdot\cdot}{O}: \leftrightarrow :\overset{+}{O}\equiv C-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\overset{-}{:}$$

Resonance structures of carbon dioxide

11.8.3 Silicon Dioxide, SiO_2

95% of the earth's crust is made up of silica and silicates. Silicon dioxide, commonly known as silica, occurs in several crystallographic forms. Quartz, cristobalite and tridymite are some of the crystalline forms of silica, and they are interconvertable at suitable temperature. Silicon dioxide is a covalent, three-dimensional network solid in which each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon atoms as shown in diagram (Fig 11.6). Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternate silicon and oxygen atoms.

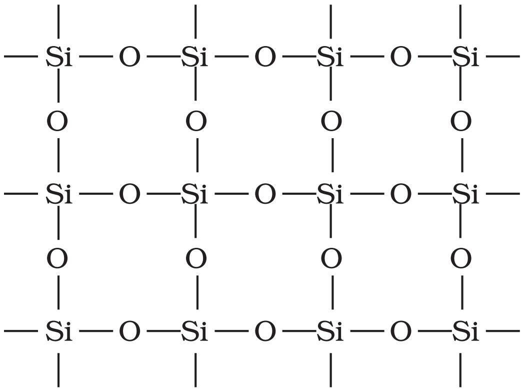


Fig. 11.6 *Three dimensional structure of* SiO_2

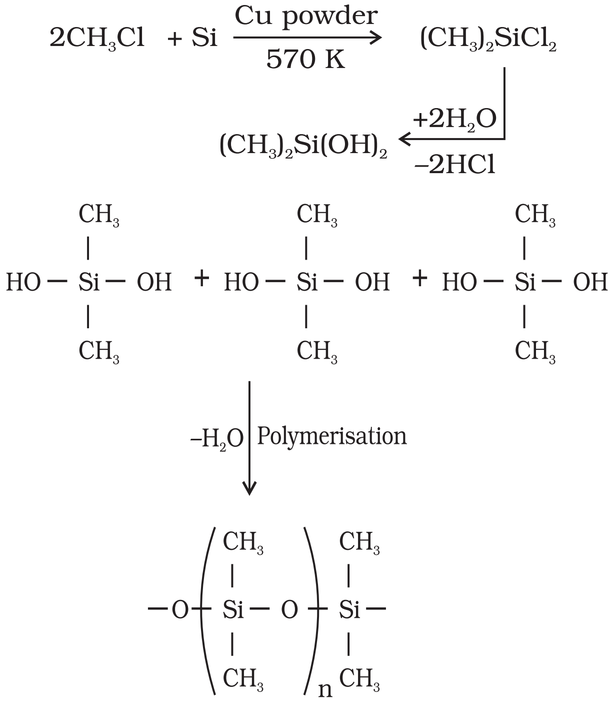
Silica in its normal form is almost non-reactive because of very high Si—O bond enthalpy. It resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures. However, it is attacked by HF and NaOH.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$
$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Quartz is extensively used as a piezoelectric material; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts. Kieselghur, an amorphous form of silica is used in filtration plants.

11.8.4 Silicones

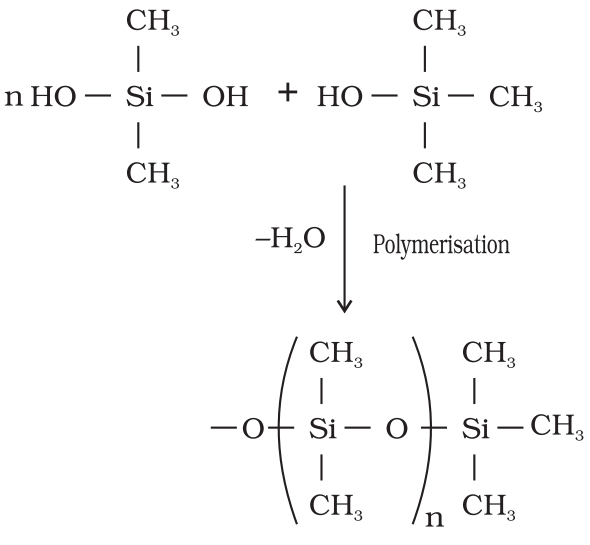
They are a group of organosilicon polymers, which have $\{R_2SiO\}$ as a repeating unit. The starting materials for the manufacture of silicones are alkyl or aryl substituted silicon chlorides, $R_nSiCl_{(4-n)}$, where R is alkyl or aryl group. When methyl chloride reacts with silicon in the presence of copper as a catalyst at a temperature 573K various types of methyl substituted chlorosilane of formula $MeSiCl_3$, Me_2SiCl_2, Me_3SiCl with small amount of Me_4Si are formed. Hydrolysis of dimethyldichlorosilane, $(CH_3)_2SiCl_2$ followed by condensation polymerisation yields straight chain polymers.



$$2CH_3Cl + Si \xrightarrow[570\ K]{Cu\ powder} (CH_3)_2SiCl_2 \xrightarrow[-2HCl]{+2H_2O} (CH_3)_2Si(OH)_2$$

Silicone

The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ which blocks the ends as shown below :



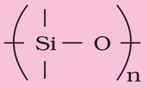
Silicone

Silicones being surrounded by non-polar alkyl groups are water repelling in nature. They have in general high thermal stability, high dielectric strength and resistance to oxidation and chemicals. They have wide applications. They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic plants.

Problem: 11.8

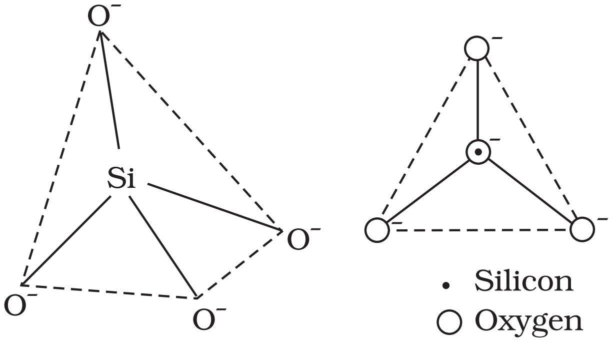
What are silicones ?

Solution

Simple silicones consist of  $\left(-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\right)_n$ chains in which alkyl or phenyl groups occupy the remaining bonding positions on each silicon. They are hydrophobic (water repellant) in nature.

11.8.5 Silicates

A large number of silicates minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. The basic structural unit of silicates is SiO_4^{4-} (Fig.11.7) in which silicon atom is bonded to four oxygen atoms in tetrahedron fashion. In silicates either the discrete unit is present or a number of such units are joined together via corners by sharing 1,2,3 or 4 oxygen atoms per silicate units. When silicate units are linked together, they form chain, ring, sheet or three-dimensional structures. Negative charge on silicate structure is neutralised by positively charged metal ions. If all the four corners are shared with other tetrahedral units, three-dimensional network is formed.



(a) (b)

Fig. 11.7 *(a) Tetrahedral structure of* SiO_4^{4-} *anion; (b) Representation of* SiO_4^{4-} *unit*

Two important man-made silicates are glass and cement.

11.8.6 Zeolites

If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as Na^+, K^+ or Ca^{2+} balance the negative charge. Examples are feldspar and zeolites. Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of “hard” water.

SUMMARY

p*-Block** of the periodic table is unique in terms of having all types of elements – **metals, non-metals** and **metalloids**. There are six groups of *p*-block elements in the periodic table numbering from 13 to 18. Their valence shell electronic configuration is ns^2np^{1-6} (except for He). Differences in the **inner core** of their electronic configuration greatly influence their physical and chemical properties. As a consequence of this, a lot of variation in properties among these elements is observed. In addition to the *group oxidation state*, these elements show other oxidation states differing from the total number of valence electrons by unit of two. While the group oxidation state is the most stable for the lighter elements of the group, lower oxidation states become progressively more stable for the heavier elements. The combined effect of size and availability of *d* orbitals considerably influences the ability of these elements to form π-bonds. While the lighter elements form ***pπ–pπ bonds, the heavier ones form ***dπ–pπ*** or ***dπ–dπ*** bonds. Absence of *d* orbital in second period elements limits their maximum covalence to 4 while heavier ones can exceed this limit.

Boron is a typical non-metal and the other members are metals. The availability of 3 valence electrons ($2s^22p^1$) for covalent bond formation using four orbitals ($2s$, $2p_x$, $2p_y$ and $2p_z$) leads to the so called **electron deficiency** in boron compounds. This deficiency makes them good electron acceptor and thus boron compounds behave as **Lewis acids**. Boron forms covalent molecular compounds with dihydrogen as boranes, the simplest of which is **diborane**, B_2H_6. Diborane contains two bridging hydrogen atoms between two boron atoms; these bridge bonds are considered to be **three-centre two-electron bonds**. The important compounds of boron with dioxygen are **boric acid** and **borax**. Boric acid, $B(OH)_3$ is a weak monobasic acid; it acts as a Lewis acid by accepting electrons from hydroxyl ion. Borax is a white crystalline solid of formula $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$. The **borax bead test** gives characteristic colours of transition metals.

Aluminium exhibits +3 oxidation state. With heavier elements +1 oxidation state gets progressively stabilised on going down the group. This is a consequence of the so called **inert pair effect**.

Carbon is a typical non-metal forming covalent bonds employing all its four valence electrons ($2s^22p^2$). It shows the property of **catenation**, the ability to form chains or rings, not only with C–C single bonds but also with multiple bonds (C=C or C≡C). The tendency to catenation decreases as $C >> Si > Ge \simeq Sn > Pb$. Carbon provides one of the best examples of **allotropy**. Three important allotropes of carbon are **diamond**, **graphite** and **fullerenes**. The members of the carbon family mainly exhibit +4 and +2 oxidation states; compouds in +4 oxidation states are generally covalent in nature. The tendency to show +2 oxidation state increases among heavier elements. Lead in +2 state is stable whereas in +4 oxidation state it is a strong oxidising agent. Carbon also exhibits negative oxidation states. It forms two important oxides: CO and CO_2. Carbon monoxide is neutral whereas CO_2 is acidic in nature. Carbon monoxide having lone pair of electrons on C forms metal **carbonyls**. It is deadly poisonous due to higher stability of its **haemoglobin complex** as compared to that of oxyhaemoglobin complex. Carbon dioxide as such is not toxic. However, increased content of CO_2 in atmosphere due to combustion of fossil fuels and decomposition of limestone is feared to cause increase in '**green house effect**'. This, in turn, raises the temperature of the atmosphere and causes serious complications. **Silica**, **silicates** and **silicones** are important class of compounds and find applications in industry and technology.

EXERCISES

11.1 Discuss the pattern of variation in the oxidation states of
(i) B to Tl and (ii) C to Pb.

11.2 How can you explain higher stability of BCl_3 as compared to $TlCl_3$?

11.3 Why does boron triflouride behave as a Lewis acid ?

11.4 Consider the compounds, BCl_3 and CCl_4. How will they behave with water ? Justify.

11.5 Is boric acid a protic acid ? Explain.

11.6 Explain what happens when boric acid is heated .

11.7 Describe the shapes of BF_3 and BH_4^-. Assign the hybridisation of boron in these species.

11.8 Write reactions to justify amphoteric nature of aluminium.

11.9 What are electron deficient compounds ? Are BCl_3 and $SiCl_4$ electron deficient species ? Explain.

11.10 Write the resonance structures of CO_3^{2-} and HCO_3^- .

11.11 What is the state of hybridisation of carbon in (a) CO_3^{2-} (b) diamond (c) graphite?

11.12 Explain the difference in properties of diamond and graphite on the basis of their structures.

11.13 Rationalise the given statements and give chemical reactions :

- Lead(II) chloride reacts with Cl_2 to give $PbCl_4$.
- Lead(IV) chloride is highly unstable towards heat.
- Lead is known not to form an iodide, PbI_4.

11.14 Suggest reasons why the B–F bond lengths in BF_3 (130 pm) and BF_4^- (143 pm) differ.

11.15 If B–Cl bond has a dipole moment, explain why BCl_3 molecule has zero dipole moment.

11.16 Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF. Aluminium trifluoride precipitates out of the resulting solution when gaseous BF_3 is bubbled through. Give reasons.

11.17 Suggest a reason as to why CO is poisonous.

11.18 How is excessive content of CO_2 responsible for global warming ?

11.19 Explain structures of diborane and boric acid.

11.20 What happens when

(a) Borax is heated strongly,
(b) Boric acid is added to water,
(c) Aluminium is treated with dilute NaOH,
(d) BF_3 is reacted with ammonia ?

11.21 Explain the following reactions

(a) Silicon is heated with methyl chloride at high temperature in the presence of copper;
(b) Silicon dioxide is treated with hydrogen fluoride;
(c) CO is heated with ZnO;
(d) Hydrated alumina is treated with aqueous NaOH solution.

11.22 Give reasons :

(i) Conc. HNO_3 can be transported in aluminium container.
(ii) A mixture of dilute NaOH and aluminium pieces is used to open drain.
(iii) Graphite is used as lubricant.
(iv) Diamond is used as an abrasive.
(v) Aluminium alloys are used to make aircraft body.
(vi) Aluminium utensils should not be kept in water overnight.
(vii) Aluminium wire is used to make transmission cables.

11.23 Explain why is there a phenomenal decrease in ionization enthalpy from carbon to silicon ?

11.24 How would you explain the lower atomic radius of Ga as compared to Al ?

11.25 What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes?

11.26 (a) Classify following oxides as neutral, acidic, basic or amphoteric:
CO, B_2O_3, SiO_2, CO_2, Al_2O_3, PbO_2, Tl_2O_3
(b) Write suitable chemical equations to show their nature.

11.27 In some of the reactions thallium resembles aluminium, whereas in others it resembles with group I metals. Support this statement by giving some evidences.

11.28 When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities.

11.29 What do you understand by (a) inert pair effect (b) allotropy and (c) catenation?

11.30 A certain salt X, gives the following results.

(i) Its aqueous solution is alkaline to litmus.
(ii) It swells up to a glassy material Y on strong heating.
(iii) When conc. H_2SO_4 is added to a hot solution of X,white crystal of an acid Z separates out.

Write equations for all the above reactions and identify X, Y and Z.

11.31 Write balanced equations for:

(i) $BF_3 + LiH \rightarrow$
(ii) $B_2H_6 + H_2O \rightarrow$
(iii) $NaH + B_2H_6 \rightarrow$
(iv) $H_3BO_3 \xrightarrow{\Delta}$
(v) $Al + NaOH \rightarrow$
(vi) $B_2H_6 + NH_3 \rightarrow$

11.32. Give one method for industrial preparation and one for laboratory preparation of CO and CO_2 each.

11.33 An aqueous solution of borax is

(a) neutral (b) amphoteric
(c) basic (d) acidic

11.34 Boric acid is polymeric due to

(a) its acidic nature (b) the presence of hydrogen bonds
(c) its monobasic nature (d) its geometry

11.35 The type of hybridisation of boron in diborane is

(a) *sp* (b) sp^2 (c) sp^3 (d) dsp^2

11.36 Thermodynamically the most stable form of carbon is

(a) diamond (b) graphite
(c) fullerenes (d) coal

11.37 Elements of group 14

(a) exhibit oxidation state of +4 only
(b) exhibit oxidation state of +2 and +4
(c) form M^{2-} and M^{4+} ions
(d) form M^{2+} and M^{4+} ions

11.38 If the starting material for the manufacture of silicones is $RSiCl_3$, write the structure of the product formed.

UNIT 12

ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

Objectives

After studying this unit, you will be able to

- understand reasons for tetravalence of carbon and shapes of organic molecules;
- write structures of organic molecules in various ways;
- classify the organic compounds;
- name the compounds according to IUPAC system of nomenclature and also derive their structures from the given names;
- understand the concept of organic reaction mechanism;
- explain the influence of electronic displacements on structure and reactivity of organic compounds;
- recognise the types of organic reactions;
- learn the techniques of purification of organic compounds;
- write the chemical reactions involved in the qualitative analysis of organic compounds;
- understand the principles involved in quantitative analysis of organic compounds.

In the previous unit you have learnt that the element carbon has the unique property called **catenation** due to which it forms covalent bonds with other carbon atoms. It also forms covalent bonds with atoms of other elements like hydrogen, oxygen, nitrogen, sulphur, phosphorus and halogens. The resulting compounds are studied under a separate branch of chemistry called **organic chemistry**. This unit incorporates some basic principles and techniques of analysis required for understanding the formation and properties of organic compounds.

12.1 GENERAL INTRODUCTION

Organic compounds are vital for sustaining life on earth and include complex molecules like genetic information bearing deoxyribonucleic acid (DNA) and proteins that constitute essential compounds of our blood, muscles and skin. Organic compounds appear in materials like clothing, fuels, polymers, dyes and medicines. These are some of the important areas of application of these compounds.

Science of organic chemistry is about two hundred years old. Around the year 1780, chemists began to distinguish between organic compounds obtained from plants and animals and inorganic compounds prepared from mineral sources. Berzilius, a Swedish chemist proposed that a 'vital force' was responsible for the formation of organic compounds. However, this notion was rejected in 1828 when F. Wohler synthesised an organic compound, urea from an inorganic compound, ammonium cyanate.

$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2}$$

The pioneering synthesis of acetic acid by Kolbe (1845) and that of methane by Berthelot (1856) showed conclusively that organic compounds could be synthesised from inorganic sources in a laboratory.

The development of electronic theory of covalent bonding ushered organic chemistry into its modern shape.

12.2 TETRAVALENCE OF CARBON: SHAPES OF ORGANIC COMPOUNDS

12.2.1 The Shapes of Carbon Compounds

The knowledge of fundamental concepts of molecular structure helps in understanding and predicting the properties of organic compounds. You have already learnt theories of valency and molecular structure in Unit 4. Also, you already know that tetravalence of carbon and the formation of covalent bonds by it are explained in terms of its electronic configuration and the hybridisation of *s* and *p* orbitals. It may be recalled that formation and the shapes of molecules like methane (CH_4), ethene (C_2H_4), ethyne (C_2H_2) are explained in terms of the use of sp^3, sp^2 and *sp* hybrid orbitals by carbon atoms in the respective molecules.

Hybridisation influences the bond length and bond enthalpy (strength) in compounds. The *sp* hybrid orbital contains more *s* character and hence it is closer to its nucleus and forms shorter and stronger bonds than the sp^3 hybrid orbital. The sp^2 hybrid orbital is intermediate in *s* character between *sp* and sp^3 and, hence, the length and enthalpy of the bonds it forms, are also intermediate between them. The change in hybridisation affects the electronegativity of carbon. The greater the *s* character of the hybrid orbitals, the greater is the electronegativity. Thus, a carbon atom having an *sp* hybrid orbital with 50% *s* character is more electronegative than that possessing sp^2 or sp^3 hybridised orbitals. This relative electronegativity is reflected in several physical and chemical properties of the molecules concerned, about which you will learn in later units.

12.2.2 Some Characteristic Features of π Bonds

In a π (pi) bond formation, parallel orientation of the two *p* orbitals on adjacent atoms is necessary for a proper sideways overlap. Thus, in $H_2C=CH_2$ molecule all the atoms must be in the same plane. The *p* orbitals are mutually parallel and both the *p* orbitals are perpendicular to the plane of the molecule. Rotation of one CH_2 fragment with respect to other interferes with maximum overlap of *p* orbitals and, therefore, such rotation about carbon-carbon double bond (C=C) is restricted. The electron charge cloud of the π bond is located above and below the plane of bonding atoms. This results in the electrons being easily available to the attacking reagents. In general, π bonds provide the most reactive centres in the molecules containing multiple bonds.

Problem 12.1

How many σ and π bonds are present in each of the following molecules?

(a) $HC{\equiv}CCH{=}CHCH_3$ (b) $CH_2{=}C{=}CHCH_3$

Solution

(a) σ_{C-C}: 4; σ_{C-H} : 6; $\pi_{C=C}$:1; π C≡C:2

(b) σ_{C-C}: 3; σ_{C-H}: 6; $\pi_{C=C}$: 2.

Problem 12.2

What is the type of hybridisation of each carbon in the following compounds?

(a) CH_3Cl, (b) $(CH_3)_2CO$, (c) CH_3CN,

(d) $HCONH_2$, (e) $CH_3CH{=}CHCN$

Solution

(a) sp^3, (b) sp^3, sp^2, (c) sp^3, *sp*, (d) sp^2, (e) sp^3, sp^2, sp^2, *sp*

Problem 12.3

Write the state of hybridisation of carbon in the following compounds and shapes of each of the molecules.

(a) $H_2C{=}O$, (b) CH_3F, (c) $HC{\equiv}N$.

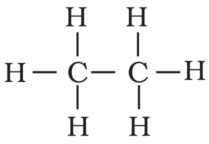
Solution

(a) sp^2 hybridised carbon, trigonal planar; (b) sp^3 hybridised carbon, tetrahedral; (c) *sp* hybridised carbon, linear.

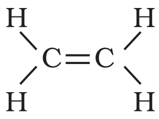
12.3 STRUCTURAL REPRESENTATIONS OF ORGANIC COMPOUNDS

12.3.1 Complete, Condensed and Bond-line Structural Formulas

Structures of organic compounds are represented in several ways. The *Lewis structure* or dot structure, dash structure, condensed structure and bond line structural formulas are some of the specific types. The Lewis structures, however, can be simplified by representing the two-electron covalent bond by a dash (–). Such a structural formula focuses on the electrons involved in bond formation. A single dash represents a single bond, double dash is used for double bond and a triple dash represents triple bond. Lone-pairs of electrons on heteroatoms (*e.g.*, oxygen, nitrogen, sulphur, halogens etc.) may or may not be shown. Thus, ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2) and methanol (CH_3OH) can be represented by the following structural formulas. Such structural representations are called *complete structural formulas*.



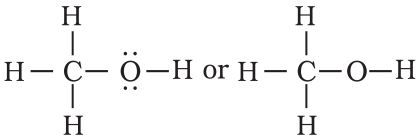
Ethane



Ethene

$H-C\equiv C-H$

Ethyne



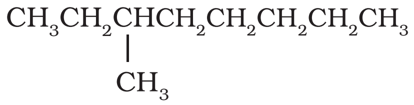
Methanol

These structural formulas can be further abbreviated by omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a *condensed structural formula*. Thus, ethane, ethene, ethyne and methanol can be written as:

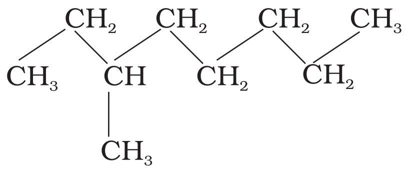
CH_3CH_3	$H_2C{=}CH_2$	$HC\equiv CH$	CH_3OH
Ethane	*Ethene*	*Ethyne*	*Methanol*

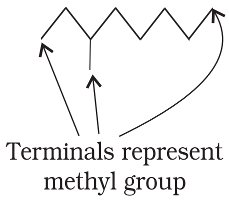
Similarly, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ can be further condensed to $CH_3(CH_2)_6CH_3$. For further simplification, organic chemists use another way of representing the structures, in which only lines are used. In this *bond-line structural* representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a *zig-zag* fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc. The terminals denote methyl ($-CH_3$) groups (unless indicated otherwise by a functional group), while the line junctions denote carbon atoms bonded to appropriate number of hydrogens required to satisfy the valency of the carbon atoms. Some of the examples are represented as follows:

(i) 3-Methyloctane can be represented in various forms as:

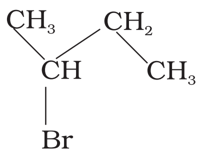
(a) 

$CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_2CH_2CH_3$

(b) 

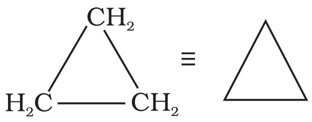
(c) 

(ii) Various ways of representing 2-bromo butane are:

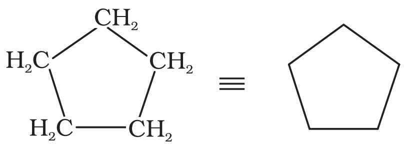
(a) $CH_3CHBrCH_2CH_3$ (b) 

(c) 

In cyclic compounds, the bond-line formulas may be given as follows:



Cyclopropane



Cyclopentane

chlorocyclohexane

Problem 12.4

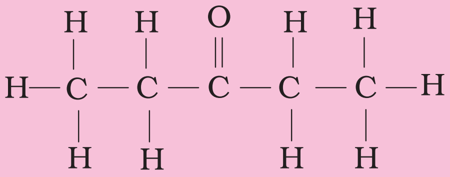
Expand each of the following condensed formulas into their complete structural formulas.

(a) $CH_3CH_2COCH_2CH_3$

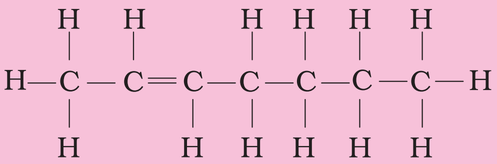
(b) $CH_3CH=CH(CH_2)_3CH_3$

Solution

(a)



(b)

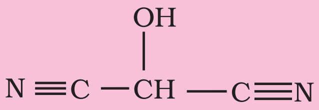


Problem 12.5

For each of the following compounds, write a condensed formula and also their bond-line formula.

(a) $HOCH_2CH_2CH_2CH(CH_3)CH(CH_3)CH_3$

(b)



$$\mathrm{N{\equiv}C-\overset{\overset{\displaystyle OH}{|}}{C}H-C{\equiv}N}$$

Solution

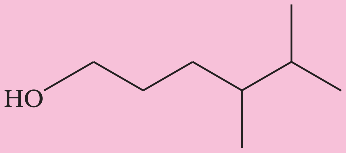
Condensed formula:

(a) $HO(CH_2)_3CH(CH_3)CH(CH_3)_2$

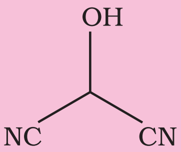
(b) $HOCH(CN)_2$

Bond-line formula:

(a)



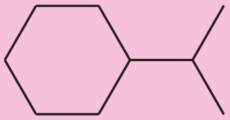
(b)



Problem 12.6

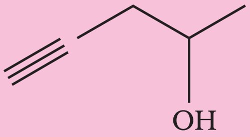
Expand each of the following bond-line formulas to show all the atoms including carbon and hydrogen

(a)

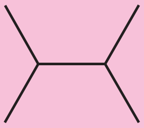


(b)

(c)

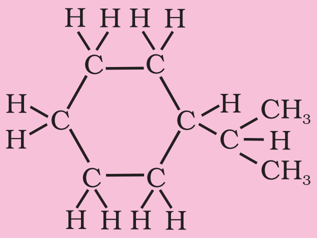


(d)

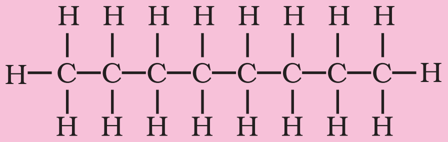


Solution

(a)

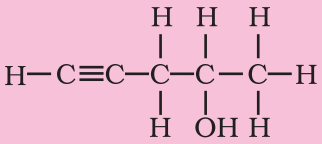


(b)



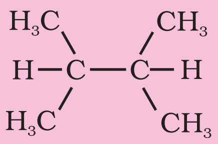
$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$$

(c)



$$\mathrm{H-C{\equiv}C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-H}$$

(d)



12.3.2 Three-Dimensional Representation of Organic Molecules

The three-dimensional (3-D) structure of organic molecules can be represented on paper by using certain conventions. For example, by using solid (◀) and dashed (⋯⋯) wedge formula, the 3-D image of a molecule from a two-dimensional picture can be perceived. In these formulas the solid-wedge is used to indicate a bond projecting out of the plane of paper, towards the observer. The dashed-wedge is used to depict the bond projecting out of the plane of the paper and away from the observer. Wedges are shown in such a way that the broad end of the wedge is towards the observer. The bonds lying in plane of the paper are depicted by using a normal line (—). 3-D representation of methane molecule on paper has been shown in Fig. 12.1.

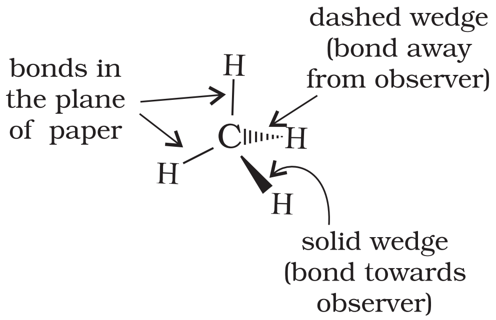
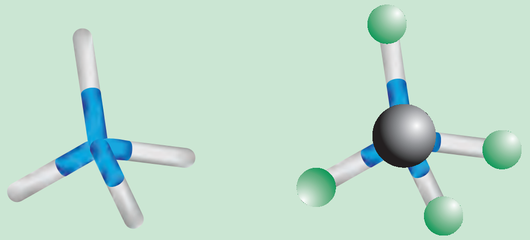


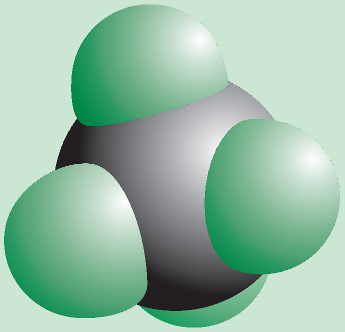
Fig. 12.1 *Wedge-and-dash representation of CH_4*

Molecular Models

Molecular models are physical devices that are used for a better visualisation and perception of three-dimensional shapes of organic molecules. These are made of wood, plastic or metal and are commercially available. Commonly three types of molecular models are used: (1) *Framework model,* (2) *Ball-and-stick model,* and (3) *Space filling model.* In the *framework model* only the bonds connecting the atoms of a molecule and not the atoms themselves are shown. This model emphasizes the pattern of bonds of a molecule while ignoring the size of atoms. In the *ball-and-stick model,* both the atoms and the bonds are shown. Balls represent atoms and the stick denotes a bond. Compounds containing C=C (e.g., ethene) can best be represented by using springs in place of sticks. These models are referred to as *ball-and-spring model.* The *space-filling model* emphasises the relative size of each atom based on its van der Waals radius. Bonds are not shown in this model. It conveys the volume occupied by each atom in the molecule. In addition to these models, computer graphics can also be used for molecular modelling.



Framework model *Ball and stick model*

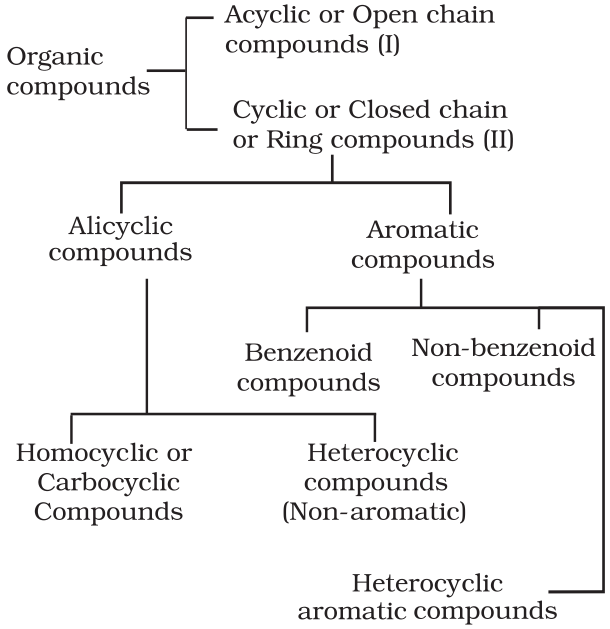


Space filling model

Fig. 12.2

12.4 CLASSIFICATION OF ORGANIC COMPOUNDS

The existing large number of organic compounds and their ever-increasing numbers has made it necessary to classify them on the basis of their structures. Organic compounds are broadly classified as follows:

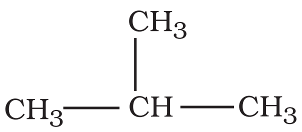


I. *Acyclic or open chain compounds*

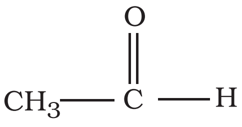
These compounds are also called as **aliphatic** compounds and consist of straight or branched chain compounds, for example:

CH_3CH_3

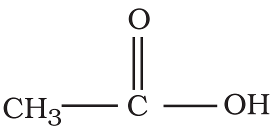
Ethane



Isobutane



Acetaldehyde

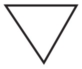


Acetic acid

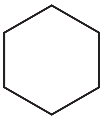
II *Cyclic or closed chain or ring compounds*

(a) Alicyclic compounds

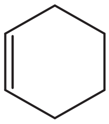
Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring (homocyclic).



Cyclopropane

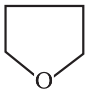


Cyclohexane



Cyclohexene

Sometimes atoms other than carbon are also present in the ring (heterocylic). Tetrahydrofuran given below is an example of this type of compound:



Tetrahydrofuran

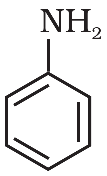
These exhibit some of the properties similar to those of aliphatic compounds.

(b) Aromatic compounds

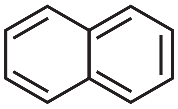
Aromatic compounds are special types of compounds. You will learn about these compounds in detail in Unit 13. These include benzene and other related ring compounds (benzenoid). Like alicyclic compounds, aromatic comounds may also have hetero atom in the ring. Such compounds are called hetrocyclic aromatic compounds. Some of the examples of various types of aromatic compounds are:

Benzenoid aromatic compounds

Benzene

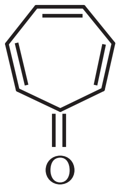


Aniline



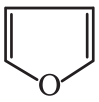
Naphthalene

Non-benzenoid compound

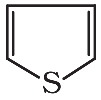


Tropone

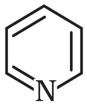
Heterocyclic aromatic compounds



Furan



Thiophene



Pyridine

Organic compounds can also be classified on the basis of functional groups, into *families* or *homologous series.*

12.4.1 Functional Group

The functional group is an atom or a group of atoms joined to the carbon chain which is responsible for the characteristic chemical properties of the organic compounds. The examples are hydroxyl group (–OH), aldehyde group (–CHO) and carboxylic acid group (–COOH) etc.

12.4.2 Homologous Series

A group or a series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called *homologues*. The members of a homologous series can be represented by general molecular formula and the successive members differ from each other in molecular formula by a $–CH_2$ unit. There are a number of homologous series of organic compounds. Some of these are alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals, alkanones, alkanoic acids, amines etc.

It is also possible that a compound contains two or more identical or different functional groups. This gives rise to polyfunctional compounds.

12.5 NOMENCLATURE OF ORGANIC COMPOUNDS

Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming has been developed and is known as the **IUPAC (International Union of Pure and Applied Chemistry)** system of nomenclature. In this systematic nomenclature, the names are correlated with the structure such that the reader or listener can deduce the structure from the name.

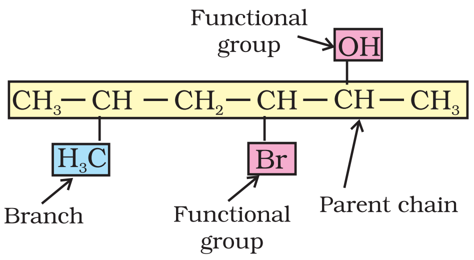
Before the IUPAC system of nomenclature, however, organic compounds were assigned names based on their origin or certain properties. For instance, citric acid is named so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is *formica*. These names are traditional and are considered as *trivial* or *common names*. Some common names are followed even today. For example, Buckminsterfullerene is a common name given to the newly discovered C_{60} cluster (a form of carbon) noting its structural similarity to the geodesic domes popularised by the famous architect R. Buckminster Fuller. Common names are useful and in many cases indispensable, particularly when the alternative systematic names are lengthy and complicated. Common names of some organic compounds are given in Table 12.1.

Table 12.1 Common or Trivial Names of Some Organic Compounds

Compound	Common name
CH_4	Methane
$H_3CCH_2CH_2CH_3$	*n*-Butane
$(H_3C)_2CHCH_3$	Isobutane
$(H_3C)_4C$	Neopentane
$H_3CCH_2CH_2OH$	*n*-Propyl alcohol
HCHO	Formaldehyde
$(H_3C)_2CO$	Acetone
$CHCl_3$	Chloroform
CH_3COOH	Acetic acid
C_6H_6	Benzene
$C_6H_5OCH_3$	Anisole
$C_6H_5NH_2$	Aniline
$C_6H_5COCH_3$	Acetophenone
$CH_3OCH_2CH_3$	Ethyl methyl ether

12.5.1 The IUPAC System of Nomenclature

A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it. See the example given below.



By further using *prefixes* and *suffixes*, the parent name can be modified to obtain the actual name. Compounds containing carbon and hydrogen only are called hydrocarbons. A hydrocarbon is termed saturated if it contains only carbon-carbon single bonds. The IUPAC name for a homologous series of such compounds is *alkane*. Paraffin (Latin: little affinity) was the earlier name given to these compounds. Unsaturated hydrocarbons are those, which contain at least one carbon-carbon double or triple bond.

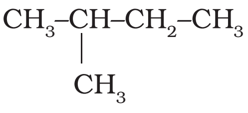
12.5.2 IUPAC Nomenclature of Alkanes

***Straight chain hydrocarbons*:** The names of such compounds are based on their chain structure, and end with suffix '-*ane*' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH_4 to C_4H_{10}, where the prefixes are derived from trivial names). The IUPAC names of some straight chain saturated hydrocarbons are given in Table 12.2. The alkanes in Table 12.2 differ from each other by merely the number of $-CH_2$ groups in the chain. They are homologues of alkane series.

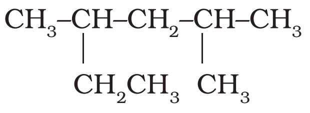
Table 12.2 IUPAC Names of Some Unbranched Saturated Hydrocarbons

Name	Molecular formula	Name	Molecular formula
Methane	CH_4	Heptane	C_7H_{16}
Ethane	C_2H_6	Octane	C_8H_{18}
Propane	C_3H_8	Nonane	C_9H_{20}
Butane	C_4H_{10}	Decane	$C_{10}H_{22}$
Pentane	C_5H_{12}	Icosane	$C_{20}H_{42}$
Hexane	C_6H_{14}	Triacontane	$C_{30}H_{62}$

***Branched chain hydrocarbons*:** In a branched chain compound small chains of carbon atoms are attached at one or more carbon atoms of the parent chain. The small carbon chains (branches) are called alkyl groups. For example:


$CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2{-}CH_3$

(a)


$CH_3{-}\underset{\underset{CH_2CH_3}{|}}{CH}{-}CH_2{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_3$

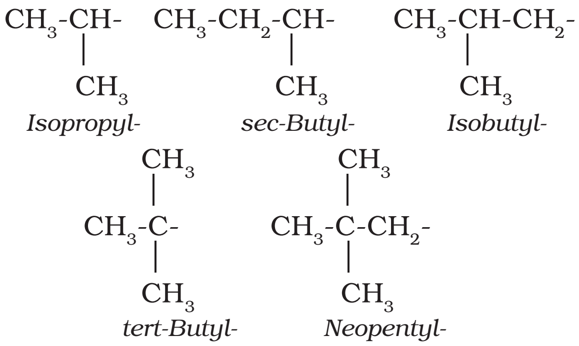
(b)

In order to name such compounds, the names of alkyl groups are prefixed to the name of parent alkane. An alkyl group is derived from a saturated hydrocarbon by removing a hydrogen atom from carbon. Thus, CH_4 becomes $-CH_3$ and is called *methyl group*. An alkyl group is named by substituting '*yl*' for '*ane*' in the corresponding alkane. Some alkyl groups are listed in Table 12.3.

Table 12.3 Some Alkyl Groups

Alkane		Alkyl group	
Molecular formula	**Name of alkane**	**Structural formula**	**Name of alkyl group**
CH_4	Methane	$-CH_3$	Methyl
C_2H_6	Ethane	$-CH_2CH_3$	Ethyl
C_3H_8	Propane	$-CH_2CH_2CH_3$	Propyl
C_4H_{10}	Butane	$-CH_2CH_2CH_2CH_3$	Butyl
$C_{10}H_{22}$	Decane	$-CH_2(CH_2)_8CH_3$	Decyl

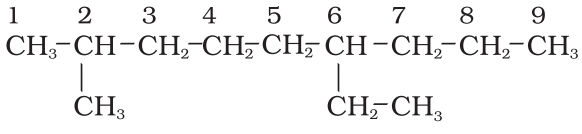
Abbreviations are used for some alkyl groups. For example, methyl is abbreviated as Me, ethyl as Et, propyl as Pr and butyl as Bu. The alkyl groups can be branched also. Thus, propyl and butyl groups can have branched structures as shown below.



Common branched groups have specific trivial names. For example, the propyl groups can either be *n*-propyl group or isopropyl group. The branched butyl groups are called *sec*-butyl, isobutyl and *tert*-butyl group. We also encounter the structural unit, $-CH_2C(CH_3)_3$, which is called neopentyl group.

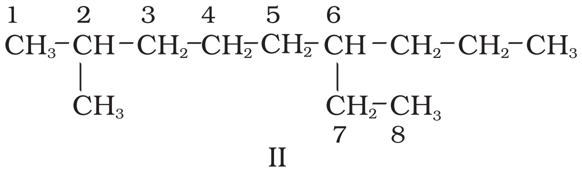
Nomenclature of branched chain alkanes: We encounter a number of branched chain alkanes. The rules for naming them are given below.

1. First of all, the **longest carbon chain in the molecule is identified**. In the example (I) given below, the longest chain has nine carbons and it is considered as the *parent* or *root* chain. Selection of parent chain as shown in (II) is not correct because it has only eight carbons.



$$\overset{1}{CH_3}-\underset{CH_3}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_2}-\underset{CH_2-CH_3}{\overset{6}{CH}}-\overset{7}{CH_2}-\overset{8}{CH_2}-\overset{9}{CH_3}$$

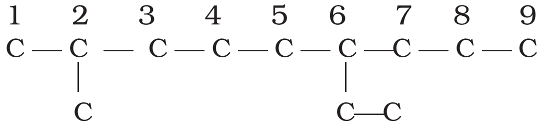
I



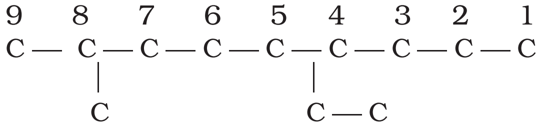
$$\overset{1}{CH_3}-\underset{CH_3}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_2}-\underset{\underset{7\quad 8}{CH_2-CH_3}}{\overset{6}{CH}}-CH_2-CH_2-CH_3$$

II

2. The carbon atoms of the parent chain are numbered to identify the parent alkane and to locate the positions of the carbon atoms at which branching takes place due to the substitution of alkyl group in place of hydrogen atoms. **The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers.** Thus, the numbering in the above example should be from left to right (branching at carbon atoms 2 and 6) and not from right to left (giving numbers 4 and 8 to the carbon atoms at which branches are attached).



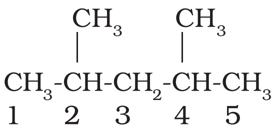
$$\overset{1}{C}-\underset{C}{\overset{2}{C}}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\underset{C-C}{\overset{6}{C}}-\overset{7}{C}-\overset{8}{C}-\overset{9}{C}$$



$$\overset{9}{C}-\underset{C}{\overset{8}{C}}-\overset{7}{C}-\overset{6}{C}-\overset{5}{C}-\underset{C-C}{\overset{4}{C}}-\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$

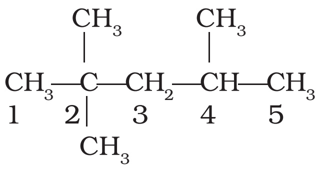
3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. Thus, name for the compound shown above is: 6-ethyl-2-methylnonane. [Note: the numbers are separated from the groups by hyphens and there is no break between methyl and nonane.]

4. If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however, are not considered. Thus, the following compounds are named as:



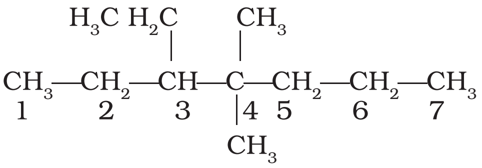
$$\underset{1}{CH_3}-\underset{2}{\overset{CH_3}{CH}}-\underset{3}{CH_2}-\underset{4}{\overset{CH_3}{CH}}-\underset{5}{CH_3}$$

2,4-Dimethylpentane



$$\underset{1}{CH_3}-\underset{\underset{CH_3}{2}}{\overset{CH_3}{C}}-\underset{3}{CH_2}-\underset{4}{\overset{CH_3}{CH}}-\underset{5}{CH_3}$$

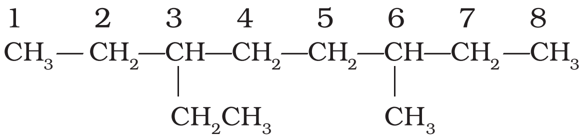
2,2,4-Trimethylpentane



$$\underset{1}{CH_3}-\underset{2}{CH_2}-\underset{3}{\overset{H_3C\ H_2C}{CH}}-\underset{\underset{CH_3}{4}}{\overset{CH_3}{C}}-\underset{5}{CH_2}-\underset{6}{CH_2}-\underset{7}{CH_3}$$

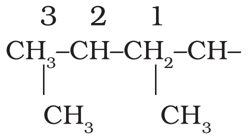
3-Ethyl-4,4-dimethylheptane

5. If the two substituents are found in equivalent positions, the **lower number is given to the one coming first in the alphabetical listing**. Thus, the following compound is 3-ethyl-6-methyloctane and not 6-ethyl-3-methyloctane.



$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{CH_2CH_3}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_2}-\underset{CH_3}{\overset{6}{CH}}-\overset{7}{CH_2}-\overset{8}{CH_3}$$

6. The branched alkyl groups can be named by following the above mentioned procedures. However, the **carbon atom of the branch that attaches to the root alkane** is numbered 1 as exemplified below.

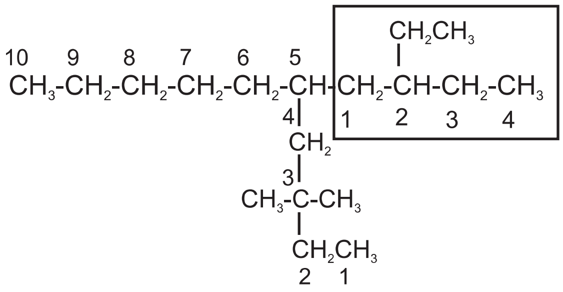


$$\overset{4}{CH_3}-\underset{CH_3}{\overset{3}{CH}}-\overset{2}{CH_2}-\underset{CH_3}{\overset{1}{CH}}-$$

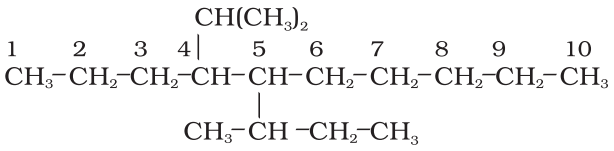
1,3-Dimethylbutyl-

The name of such branched chain alkyl group is placed in parenthesis while naming the compound. While writing the trivial names of substituents' **in alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes *sec*- and *tert*- are not** considered to be the part of the fundamental name. The use of *iso* and related common prefixes for naming alkyl groups is also allowed by the IUPAC nomenclature as long as these are not further substituted. In multi-substituted compounds, the following rules may aso be remembered:

- If there happens to be two chains of equal size, then that chain is to be selected which contains more number of side chains.
- After selection of the chain, numbering is to be done from the end closer to the substituent.

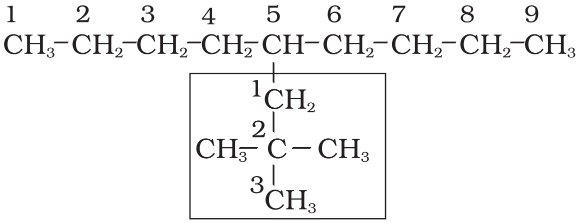


5-(2-Ethylbutyl)-3,3-dimethyldecane
[and not 5-(2,2-Dimethylbutyl)-3-ethyldecane]



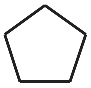
$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{\displaystyle CH(CH_3)_2}{\overset{4\,|}{CH}}-\underset{\displaystyle CH_3-CH-CH_2-CH_3}{\underset{|}{\overset{5}{CH}}}-\overset{6}{CH_2}-\overset{7}{CH_2}-\overset{8}{CH_2}-\overset{9}{CH_2}-\overset{10}{CH_3}$$

5-sec-Butyl-4-isopropyldecane

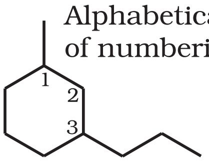


5-(2,2-Dimethylpropyl)nonane

***Cyclic Compounds*:** A saturated monocyclic compound is named by prefixing '*cyclo*' to the corresponding straight chain alkane. If side chains are present, then the rules given above are applied. Names of some cyclic compounds are given below.

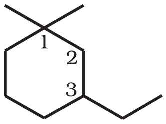


Cyclopentane



Alphabetical order of numbering

1-Methyl-3-propylcyclohexane



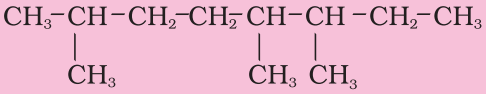
More branched carbon gets lower number

3-Ethyl-1,1-dimethylcyclohexane
(not 1-ethyl-3,3-dimethylcyclohexane)

Problem 12.7

Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parentheses are incorrect.

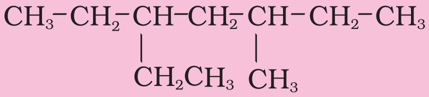
(a)



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

2,5,6- Trimethyloctane
[and not 3,4,7-Trimethyloctane]

(b)



$$CH_3-CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

3-Ethyl-5-methylheptane
[and not 5-Ethyl-3-methylheptane]

Solution

(a) Lowest locant number, 2,5,6 is lower than 3,5,7, (b) substituents are in equivalent position; lower number is given to the one that comes first in the name according to alphabetical order.

12.5.3 Nomenclature of Organic Compounds having Functional Group(s)

A functional group, as defined earlier, is an atom or a group of atoms bonded together in a unique manner which is usually the site of chemical reactivity in an organic molecule. Compounds having the same functional group undergo similar reactions. For example, CH_3OH, CH_3CH_2OH, and $(CH_3)_2CHOH$ — all having -OH functional group liberate hydrogen on reaction with sodium metal. The presence of functional groups enables systematisation of organic compounds into different classes. Examples of some functional groups with their prefixes and suffixes along with some examples of organic compounds possessing these are given in Table 12.4.

First of all, the functional group present in the molecule is identified which determines the choice of appropriate suffix. **The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain**. By using the suffix as given in Table 12.4, the name of the compound is arrived at.

In the case of polyfunctional compounds, one of the functional groups is chosen as the *principal functional group* and the compound is then named on that basis. The remaining functional groups, which are subordinate functional groups, are named as substituents using the appropriate prefixes. The choice of principal functional group is made on the basis of order of preference. **The order of decreasing priority for some functional groups is:**

-COOH, $–SO_3H$, -COOR (R=alkyl group), COCl, $-CONH_2$, -CN,-HC=O, >C=O, -OH, $-NH_2$, >C=C<, -C≡C- .

The –R, C_6H_5-, halogens (F, Cl, Br, I), $–NO_2$, alkoxy (–OR) etc. are always prefix substituents. Thus, a compound containing both an alcohol and a keto group is named as hydroxyalkanone since the keto group is preferred to the hydroxyl group.

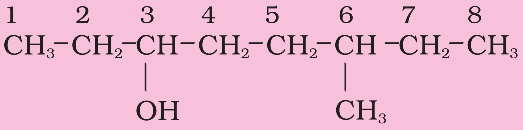
For example, $HOCH_2(CH_2)_3CH_2COCH_3$ will be named as 7-hydroxyheptan-2-one and not as 2-oxoheptan -7-ol. Similarly, $BrCH_2CH=CH_2$ is named as 3-bromoprop-1-ene and not 1-bromoprop-2-ene.

If more than one functional group of the same type are present, their number is indicated by adding di, tri, etc. before the class suffix. In such cases the full name of the parent alkane is written before the class suffix. For example $CH_2(OH)CH_2(OH)$ is named as ethane–1,2–diol. However, the ending – ne of the parent alkane is dropped in the case of compounds having more than one double or triple bond; for example, $CH_2=CH-CH=CH_2$ is named as buta–1,3–diene.

Problem 12.8

Write the IUPAC names of the compounds i-iv from their given structures.

(i)

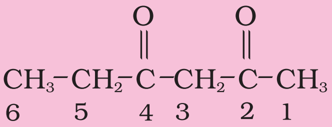


$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{OH}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_2}-\underset{CH_3}{\overset{6}{CH}}-\overset{7}{CH_2}-\overset{8}{CH_3}$$

Solution

- The functional group present is an alcohol (OH). Hence the suffix is '-ol'.
- The longest chain containing -OH has eight carbon atoms. Hence the corresponding saturated hydrocarbon is octane.
- The -OH is on carbon atom 3. In addition, a methyl group is attached at 6th carbon.
  Hence, the systematic name of this compound is 6-Methyloctan-3-ol.

(ii)

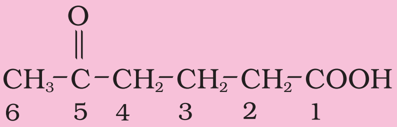


$$\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{\overset{\overset{O}{\|}}{C}}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{1}{CH_3}$$

Solution

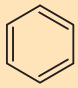
The functional group present is ketone (>C=O), hence suffix '-one'. Presence of two keto groups is indicated by 'di', hence suffix becomes 'dione'. The two keto groups are at carbons 2 and 4. The longest chain contains 6 carbon atoms, hence, parent hydrocarbon is hexane. Thus, the systematic name is Hexane-2,4-dione.

(iii)



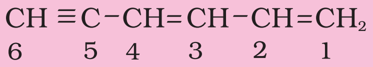
$$\underset{6}{CH_3}-\underset{5}{\overset{\overset{O}{\|}}{C}}-\underset{4}{CH_2}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{COOH}$$

Table 12.4 Some Functional Groups and Classes of Organic Compounds

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Alkanes	-	-	-ane	Butane, $CH_3(CH_2)_2CH_3$
Alkenes	>C=C<	-	-ene	But-1-ene, $CH_2=CHCH_2CH_3$
Alkynes	-C≡C-	-	-yne	But-1-yne, $CH≡CCH_2CH_3$
Arenes	-	-	-	Benzene, 
Halides	-X (X=F,Cl,Br,I)	halo-	-	1-Bromobutane, $CH_3(CH_2)_2CH_2Br$
Alcohols	-OH	hydroxy-	-ol	Butan-2-ol, $CH_3CH_2CHOHCH_3$
Aldehydes	-CHO	formyl, or oxo	-al	Butanal, $CH_3(CH_2)_2CHO$
Ketones	>C=O	oxo-	-one	Butan-2-one, $CH_3CH_2COCH_3$
Nitriles	-C≡N	cyano	nitrile	Pentanenitrile, $CH_3CH_2CH_2CH_2CN$
Ethers	-R-O-R-	alkoxy-	-	Ethoxyethane, $CH_3CH_2OCH_2CH_3$
Carboxylic acids	-COOH	carboxy	-oic acid	Butanoic acid, $CH_3(CH_2)_2CO_2H$
Carboxylate ions	$-COO^-$	-	-oate	Sodium butanoate, $CH_3(CH_2)_2CO_2^-\ Na^+$
Esters	-COOR	alkoxycarbonyl	-oate	Methyl propanoate, $CH_3CH_2COOCH_3$
Acyl halides	-COX (X=F,Cl,Br,I)	halocarbonyl	-oyl halide	Butanoyl chloride, $CH_3(CH_2)_2COCl$
Amines	$-NH_2$, >NH,>N-	amino-	-amine	Butan -2-amine , $CH_3CHNH_2CH_2CH_3$
Amides	$-CONH_2$, -CONHR, $-CONR_2$	-carbamoyl	-amide	Butanamide, $CH_3(CH_2)_2CONH_2$
Nitro compounds	$-NO_2$	nitro	-	1-Nitrobutane, $CH_3(CH_2)_3NO_2$
Sulphonic acids	$–SO_3H$	sulpho	sulphonic acid	Methylsulphonic acid CH_3SO_3H

Solution

Here, two functional groups namely ketone and carboxylic acid are present. The principal functional group is the carboxylic acid group; hence the parent chain will be suffixed with 'oic' acid. Numbering of the chain starts from carbon of – COOH functional group. The keto group in the chain at carbon 5 is indicated by 'oxo'. The longest chain including the principal functional group has 6 carbon atoms; hence the parent hydrocarbon is hexane. The compound is, therefore, named as 5-Oxohexanoic acid.

(iv)

$$\underset{6}{CH} \equiv \underset{5}{C} - \underset{4}{CH} = \underset{3}{CH} - \underset{2}{CH} = \underset{1}{CH_2}$$

Solution

The two C=C functional groups are present at carbon atoms 1 and 3, while the C≡C functional group is present at carbon 5. These groups are indicated by suffixes 'diene' and 'yne' respectively. The longest chain containing the functional groups has 6 carbon atoms; hence the parent hydrocarbon is hexane. The name of compound, therefore, is Hexa-1,3-dien-5-yne.

Problem 12.9

Derive the structure of (i) 2-Chlorohexane, (ii) Pent-4-en-2-ol, (iii) 3- Nitrocyclohexene, (iv) Cyclohex-2-en-1-ol, (v) 6-Hydroxy-heptanal.

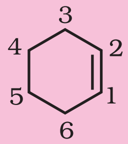
Solution

(i) 'hexane' indicates the presence of 6 carbon atoms in the chain. The functional group chloro is present at carbon 2. Hence, the structure of the compound is $CH_3CH_2CH_2CH_2CH(Cl)CH_3$.

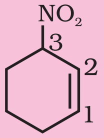
(ii) 'pent' indicates that parent hydrocarbon contains 5 carbon atoms in the chain. 'en' and 'ol' correspond to the functional groups C=C and -OH at carbon atoms 4 and 2 respectively. Thus, the structure is

CH_2=$CHCH_2CH\ (OH)CH_3$.

(iii) Six membered ring containing a carbon-carbon double bond is implied by cyclohexene, which is numbered as shown in (I). The prefix 3-nitro means that a nitro group is present on C-3. Thus, complete structural formula of the compound is (II). Double bond is suffixed functional group whereas NO_2 is prefixed functional group therefore double bond gets preference over $–NO_2$ group:



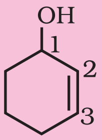
I



II

(iv) '1-ol' means that a -OH group is present at C-1. OH is suffixed functional group and gets preference over C=C bond. Thus the structure is as shown in (II):

I

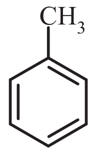


II

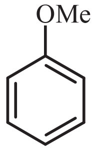
(v) 'heptanal' indicates the compound to be an aldehyde containing 7 carbon atoms in the parent chain. The '6-hydroxy' indicates that -OH group is present at carbon 6. Thus, the structural formula of the compound is: $CH_3CH(OH)CH_2CH_2CH_2CH_2CHO$. Carbon atom of –CHO group is included while numbering the carbon chain.

12.5.4 Nomenclature of Substituted Benzene Compounds

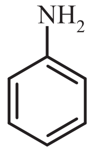
For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word *benzene* as shown in the following examples. However, common names (written in bracket below) of many substituted benzene compounds are also universally used.



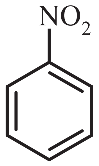
Methylbenzene
(Toluene)



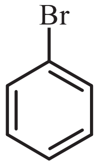
Methoxybenzene
(Anisole)



Aminobenzene
(Aniline)

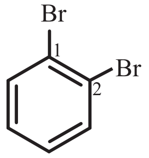


Nitrobenzene



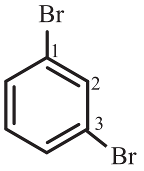
Bromobenzene

If benzene ring is disubstituted, the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible.For example, the compound(b) is named as 1,3-dibromobenzene and not as 1,5-dibromobenzene.



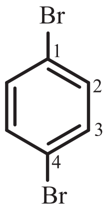
(a)

1,2-Dibromo-benzene



(b)

1,3-Dibromo-benzene



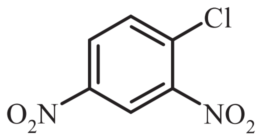
(c)

1,4-Dibromo-benzene

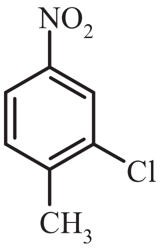
In the trivial system of nomenclature the terms *ortho* (*o*), *meta* (*m*) and *para* (*p*) are used as prefixes to indicate the relative positions 1,2;1,3 and 1,4 respectively. Thus, 1,3-dibromobenzene (b) is named as *m*-dibromobenzene (*meta* is abbreviated as *m*-) and the other isomers of dibromobenzene 1,2-(a) and 1,4-(c), are named as *ortho* (or just *o*-) and *para* (or just *p*-)-dibromobenzene, respectively.

For tri - or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound.

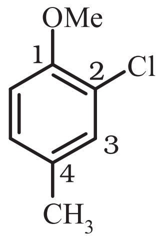
Substituent of the base compound is assigned number1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents appear in the name in alphabetical order. Some examples are given below.



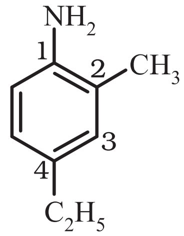
1-Chloro-2,4-dinitrobenzene
(not 4-chloro,1,3-dinitrobenzene)



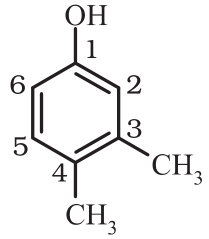
2-Chloro-1-methyl-4-nitrobenzene
(not 4-methyl-5-chloro-nitrobenzene)



2-Chloro-4-methylanisole



4-Ethyl-2-methylaniline



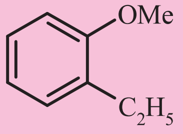
3,4-Dimethylphenol

When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is *phenyl* (C_6H_5-, also abbreviated as Ph).

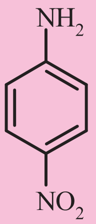
Problem 12.10

Write the structural formula of:
(a) *o*-Ethylanisole, (b) *p*-Nitroaniline,
(c) 2,3 - Dibromo -1 - phenylpentane,
(d) 4-Ethyl-1-fluoro-2-nitrobenzene.

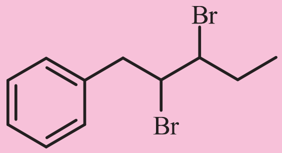
Solution



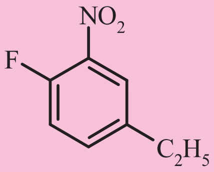
(a)



(b)



(c)



(d)

12.6 ISOMERISM

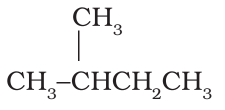
The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers. The following flow chart shows different types of isomerism.

12.6.1 Structural Isomerism

Compounds having the same molecular formula but different structures (manners in which atoms are linked) are classified as structural isomers. Some typical examples of different types of structural isomerism are given below:

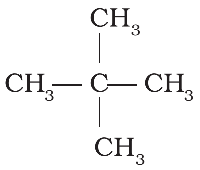
(i) Chain isomerism: When two or more compounds have similar molecular formula but different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example, C_5H_{12} represents three compounds:

$CH_3CH_2CH_2CH_2CH_3$
Pentane



$$CH_3\text{–}\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$$

Isopentane
(2-Methylbutane)

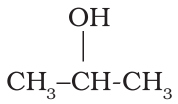


$$CH_3\text{—}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\text{—}CH_3$$

Neopentane
(2,2-Dimethylpropane)

(ii) Position isomerism: When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. For example, the molecular formula C_3H_8O represents two alcohols:

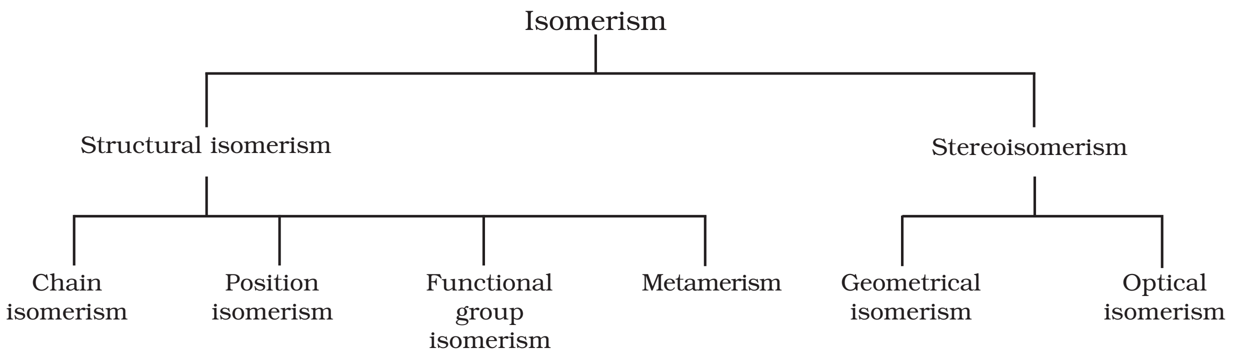
$CH_3CH_2CH_2OH$
Propan-1-ol

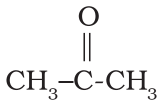


$$CH_3\text{–}\overset{\overset{\displaystyle OH}{|}}{C}H\text{-}CH_3$$

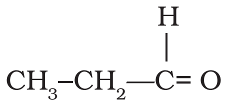
Propan-2-ol

(iii) Functional group isomerism: Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group isomerism. For example, the molecular formula C_3H_6O represents an aldehyde and a ketone:




$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

Propanone


$CH_3-CH_2-\overset{\overset{\displaystyle H}{|}}{C}=O$

Propanal

(iv) Metamerism: It arises due to different alkyl chains on either side of the functional group in the molecule. For example, $C_4H_{10}O$ represents methoxypropane ($CH_3OC_3H_7$) and ethoxyethane ($C_2H_5OC_2H_5$).

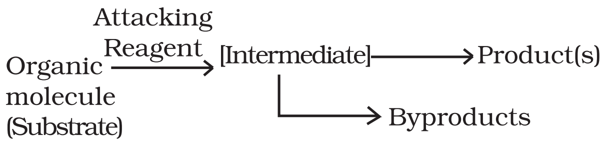
12.6.2 Stereoisomerism

The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. This special type of isomerism is called as stereoisomerism and can be classified as *geometrical* and optical *isomerism.*

12.7 FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

In an organic reaction, the organic molecule (also referred to as a substrate) reacts with an appropriate attacking reagent and leads to the formation of one or more intermediate(s) and finally product(s)

The general reaction is depicted as follows :



Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both the reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called *substrate.*

In such a reaction a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed. **A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism.** The knowledge of reaction mechanism helps in understanding the reactivity of organic compounds and in planning strategy for their synthesis.

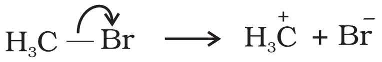
In the following sections, we shall learn some of the principles that explain how these reactions take place.

12.7.1 Fission of a Covalent Bond

A covalent bond can get cleaved either by : (i) ***heterolytic cleavage,*** or by (ii) ***homolytic cleavage.***

In ***heterolytic cleavage***, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

After heterolysis, one atom has a sextet electronic structure and a positive charge and the other, a valence octet with at least one lone pair and a negative charge. Thus, heterolytic cleavage of bromomethane will give $\overset{+}{C}H_3$ and Br^- as shown below.


$$H_3C-Br \longrightarrow H_3\overset{+}{C} + \overset{-}{Br}$$

A species having a carbon atom possessing sextext of electrons and a positive charge is called a *carbocation* (earlier called *carbonium ion).* The $\overset{+}{C}H_3$ ion is known as a methyl cation or methyl carbonium ion. Carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon. Some other examples of carbocations are: $CH_3\overset{+}{C}H_2$ (ethyl cation, a primary carbocation), $(CH_3)_2\overset{+}{C}H$ (isopropyl cation, a secondary carbocation), and $(CH_3)_3\overset{+}{C}$ (*tert*-butyl cation, a tertiary carbocation). Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects, which you will be studying in the sections 12.7.5 and 12.7.9. The observed order of carbocation stability is: $\overset{+}{C}H_3 < CH_3\overset{+}{C}H_2 < (CH_3)_2\overset{+}{C}H < (CH_3)_3\overset{+}{C}$. These carbocations have trigonal planar shape with positively charged carbon being sp^2 hybridised. Thus, the shape of $\overset{+}{C}H_3$ may be considered as being derived from the overlap of three equivalent C(sp^2) hybridised orbitals with 1*s* orbital of each of the three hydrogen atoms. Each bond may be represented as C(*sp*^{2})–H(1*s*) sigma bond. The remaining carbon orbital is perpendicular to the molecular plane and contains no electrons. [Fig. 12.3(a)].

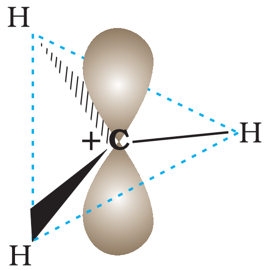


Fig. 12.3(a) *Shape of methyl carbocation*

The heterolytic cleavage can also give a species in which carbon gets the shared pair of electrons. For example, when group Z attached to the carbon leaves without

$$\overset{\curvearrowleft}{CH_3 - Z} \longrightarrow H_3\overset{-}{C}: + \overset{+}{Z}$$

electron pair, the methyl anion $\left(H_3\overset{-}{C}:\right)$ is formed. Such a carbon species carrying a negative charge on carbon atom is called *carbanion.* Carbon in carbanion is generally sp^3 hybridised and its structure is distorted tetrahedron as shown in Fig. 12.3(b).

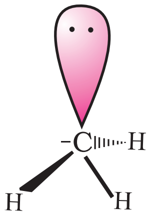


Fig. 12.3(b) *Shape of methyl carbanion*

Carbanions are also unstable and reactive species. The organic reactions which proceed through heterolytic bond cleavage are called **ionic** or **heteropolar** or just polar reactions.

In ***homolytic cleavage***, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Thus, in homolytic cleavage, the movement of a single electron takes place instead of an electron pair. The single electron movement is shown by 'half-headed' (fish hook: $\curvearrowright$) curved arrow. Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called *free radicals*. Like carbocations and carbanions, free radicals are also very reactive. A homolytic cleavage can be shown as:

$$\overset{\frown\,\frown}{R - X} \xrightarrow{\text{Heat or Light}} \underset{\substack{\text{Alkyl}\\ \text{free radical}}}{\dot{R}} + \dot{X}$$

Alkyl radicals are classified as *primary*, *secondary*, or *tertiary*. Alkyl radical stability increases as we proceed from primary to tertiary:

$$\dot{C}H_3 < \dot{C}H_2CH_3 < \dot{C}H(CH_3)_2 < \dot{C}(CH_3)_3,$$

Methyl free radical	Ethyl free radical	Isopropyl free radical	Tert-butyl free radical

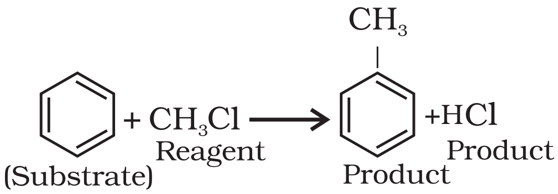
Organic reactions, which proceed by homolytic fission are called *free radical* or *homopolar* or *nonpolar* reactions.

12.7.2 Substrate and Reagent

Ions are generally not formed in the reactions of organic compounds. Molecules as such participate in the reaction. It is convenient to name one reagent as substrate and other as reagent. In general, a molecule whose carbon is involved in new bond formation is called substrate and the other one is called reagent. When carbon-carbon bond is formed, the choice of naming the reactants as substrate and reagent is arbitrary and depends on molecule under observation. Example:

(i) $\underset{\text{Substrate}}{CH_2 = CH_2} + \underset{\text{Reagent}}{Br_2} \longrightarrow \underset{\text{Product}}{CH_2Br - CH_2Br}$

(ii)



Nucleophiles and Electrophiles

Reagents attack the reactive site of the substrate. The reactive site may be electron deficient portion of the molecule (a positive reactive site) e.g., an atom with incomplete electron shell or the positive end of the dipole in the molecule. If the attacking species is electron rich, it attacks these sites. If attacking species is electron deficient, the reactive site for it is that part of the substrate molecule which can supply electrons, e.g., π electrons in a double bond.

A reagent that brings an electron pair to the reactive site is called a **nucleophile** (Nu:) i.e., nucleus seeking and the reaction is then called **nucleophilic**. A reagent that takes away an electron pair from reactive site is called **electrophile** (E^+) i.e., electron seeking and the reaction is called **electrophilic**.

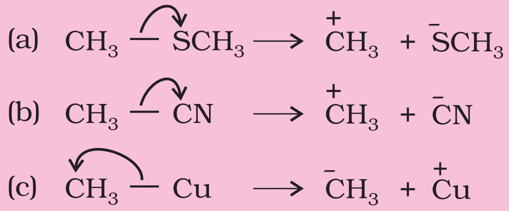
During a polar organic reaction, a nucleophile attacks an electrophilic centre of the substrate which is that specific atom or part of the substrate which is electron deficient. Similarly, the electrophiles attack at nucleophilic centre, which is the electron rich centre of the substrate. Thus, the electrophiles receive electron pair from the substrate when the two undergo bonding interaction. A curved-arrow notation is used to show the movement of an electron pair from the nucleophile to the electrophile. Some examples of nucleophiles are the negatively charged ions with lone pair of electrons such as hydroxide (HO^-), cyanide (NC^-) ions and carbanions ($R_3\ddot{C}:^-$). Neutral molecules such as $H_2\ddot{O}:$, $R_3N:$, $R_2\ddot{N}H$ etc., can also act as nucleophiles due to the presence of lone pair of electrons. Examples of electrophiles include carbocations ($\overset{+}{C}H_3$) and neutral molecules having functional groups like carbonyl group (>C=O) or alkyl halides (R_3C-X, where X is a halogen atom). The carbon atom in carbocations has sextet configuration; hence, it is electron deficient and can receive a pair of electrons from the nucleophiles. In neutral molecules such as alkyl halides, due to the polarity of the C-X bond a partial positive charge is generated on the carbon atom and hence the carbon atom becomes an electrophilic centre at which a nucleophile can attack.

Problem 12.11

Using curved-arrow notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage.

(a) CH_3–SCH_3, (b) CH_3–CN, (c) CH_3–Cu

Solution



(a) $CH_3-SCH_3 \longrightarrow \overset{+}{C}H_3 + \bar{S}CH_3$

(b) $CH_3-CN \longrightarrow \overset{+}{C}H_3 + \bar{C}N$

(c) $CH_3-Cu \longrightarrow \bar{C}H_3 + \overset{+}{Cu}$

Problem 12.12

Giving justification, categorise the following molecules/ions as nucleophile or electrophile:

$HS^-, BF_3, C_2H_5O^-, (CH_3)_3N:,$

$\overset{+}{Cl}, CH_3-\overset{+}{C}=O, H_2N:^-, \overset{+}{N}O_2$

Solution

Nucleophiles: $HS^-, C_2H_5O^-, (CH_3)_3N:, H_2N:^-$

These species have unshared pair of electrons, which can be donated and shared with an electrophile.

Electrophiles: $BF_3, \overset{+}{Cl}, CH_3-\overset{+}{C}=O, \overset{+}{N}O_2$.

Reactive sites have only six valence electrons; can accept electron pair from a nucleophile.

Problem 12.13

Identify electrophilic centre in the following: $CH_3CH=O$, CH_3CN, CH_3I.

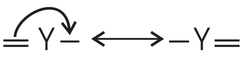
Solution

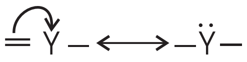
Among $CH_3H\overset{*}{C}=O$, $H_3C\overset{*}{C}\equiv N$, and $H_3\overset{*}{C}$–I, the starred carbon atoms are electrophilic centers as they will have partial positive charge due to polarity of the bond.

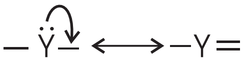
12.7.3 Electron Movement in Organic Reactions

The movement of electrons in organic reactions can be shown by curved-arrow notation. It shows how changes in bonding occur due to electronic redistribution during the reaction. To show the change in position of a pair of electrons, curved arrow starts from the point from where an electron pair is shifted and it ends at a location to which the pair of electron may move.

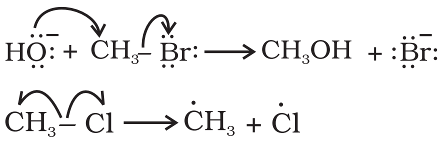
Presentation of shifting of electron pair is given below :

(i)  from π bond to adjacent bond position

(ii)  from π bond to adjacent atom

(iii)  from atom to adjacent bond position

Movement of single electron is indicated by a single barbed 'fish hooks' (i.e. half headed curved arrow). For example, in transfer of hydroxide ion giving ethanol and in the dissociation of chloromethane, the movement of electron using curved arrows can be depicted as follows:



12.7.4 Electron Displacement Effects in Covalent Bonds

The electron displacement in an organic molecule may take place either in the ground state under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent. The electron displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarlisation of the bond. Inductive effect and resonance effects are examples of this type of electron displacements. Temporary electron displacement effects are seen in a molecule when a reagent approaches to attack it. This type of electron displacement is called electromeric effect or polarisability effect. In the following sections we will learn about these types of electronic displacements.

12.7.5 Inductive Effect

When a covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom of the bond. Such a shift of electron density results in a polar covalent bond. Bond polarity leads to various electronic effects in organic compounds.

Let us consider cholorethane (CH_3CH_2Cl) in which the C–Cl bond is a polar covalent bond. It is polarised in such a way that the carbon-1 gains some positive charge (δ^+) and the chlorine some negative charge (δ^-). The fractional electronic charges on the two atoms in a polar covalent bond are denoted by symbol δ (delta) and the shift of electron density is shown by an arrow that points from δ^+ to δ^- end of the polar bond.

$$\underset{2}{\overset{\delta\delta^+}{CH_3}} \longrightarrow \underset{1}{\overset{\delta^+}{CH_2}} \longrightarrow \overset{\delta^-}{Cl}$$

In turn carbon-1, which has developed partial positive charge (δ^+) draws some electron density towards it from the adjacent C-C bond. Consequently, some positive charge ($\delta\delta^+$) develops on carbon-2 also, where $\delta\delta^+$ symbolises relatively smaller positive charge as compared to that on carbon – 1. In other words, the polar C – Cl bond induces polarity in the adjacent bonds. Such polarisation of σ-bond caused by the polarisation of adjacent σ-bond is referred to as the **inductive effect**. This effect is passed on to the subsequent bonds also but the effect decreases rapidly as the number of intervening bonds increases and becomes vanishingly small after three bonds. The inductive effect is related to the ability of substituent(s) to either withdraw or donate electron density to the attached carbon atom. Based on this ability, the substitutents can be classified as *electron-withdrawing* or *electron donating* groups relative to hydrogen. Halogens and many other groups such as nitro (- NO_2), cyano (- CN), carboxy (- COOH), ester (COOR), aryloxy (-OAr, e.g. – OC_6H_5), etc. are electron-withdrawing groups. On the other hand, the alkyl groups like methyl ($-CH_3$) and ethyl ($-CH_2-CH_3$) are usually considered as electron donating groups.

Problem 12.14

Which bond is more polar in the following pairs of molecules: (a) H_3C-H, H_3C-Br (b) H_3C-NH_2, H_3C-OH (c) H_3C-OH, H_3C-SH

Solution

(a) C–Br, since Br is more electronegative than H, (b) C–O, (c) C–O

Problem 12.15

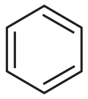
In which C–C bond of $CH_3CH_2CH_2Br$, the inductive effect is expected to be the least?

Solution

Magnitude of inductive effect diminishes as the number of intervening bonds increases. Hence, the effect is least in the bond between carbon-3 and hydrogen.

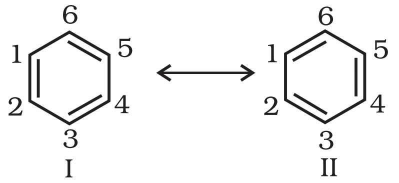
12.7.6 Resonance Structure

There are many organic molecules whose behaviour cannot be explained by a single Lewis structure. An example is that of benzene. Its cyclic structure containing alternating C–C single and C=C double bonds shown is inadequate for explaining its characteristic properties.



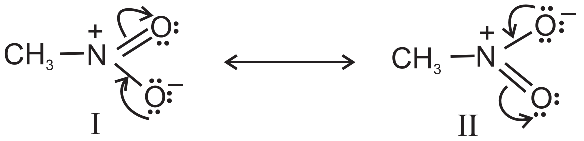
Benzene

As per the above representation, benzene should exhibit two different bond lengths, due to C–C single and C=C double bonds. However, as determined experimentally benzene has a uniform C–C bond distances of 139 pm, a value intermediate between the C–C single(154 pm) and C=C double (134 pm) bonds. Thus, the structure of benzene cannot be represented adequately by the above structure. Further, benzene can be represented equally well by the energetically identical structures I and II.



Therefore, according to the resonance theory (Unit 4) the actual structure of benzene cannot be adequately represented by any of these structures, rather it is a hybrid of the two structures (I and II) called *resonance structures*. **The resonance structures (canonical structures or contributing structures) are hypothetical and individually do not represent any real molecule.** They contribute to the actual structure in proportion to their stability.

Another example of resonance is provided by nitromethane (CH_3NO_2) which can be represented by two Lewis structures, (I and II). There are two types of N-O bonds in these structures.



However, it is known that the two N–O bonds of nitromethane are of the same length (intermediate between a N–O single bond and a N=O double bond). The actual structure of nitromethane is therefore a resonance hybrid of the two canonical forms I and II.

The energy of actual structure of the molecule (the resonance hybrid) is lower than that of any of the canonical structures. The difference in energy between the actual structure and the lowest energy resonance structure is called the ***resonance stabilisation energy*** or simply the ***resonance energy***. The more the number of important contributing structures, the more is the resonance energy. Resonance is particularly important when the contributing structures are equivalent in energy.

The following rules are applied while writing resonance structures:

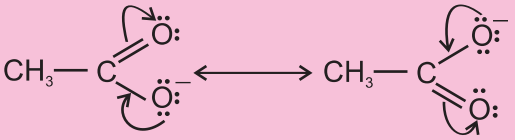
The resonance structures have (i) the same positions of nuclei and (ii) the same number of unpaired electrons. Among the resonance structures, the one which has more number of covalent bonds, all the atoms with octet of electrons (except hydrogen which has a duplet), less separation of opposite charges, (a negative charge if any on more electronegative atom, a positive charge if any on more electropositive atom) and more dispersal of charge, is more stable than others.

Problem 12.16

Write resonance structures of CH_3COO^- and show the movement of electrons by curved arrows.

Solution

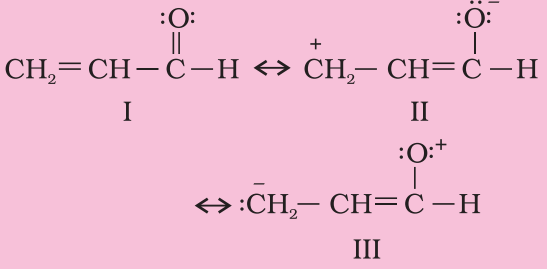
First, write the structure and put unshared pairs of valence electrons on appropriate atoms. Then draw the arrows one at a time moving the electrons to get the other structures.



Problem 12.17

Write resonance structures of $CH_2{=}CH{-}CHO$. Indicate relative stability of the contributing structures.

Solution



$$\underset{\text{I}}{CH_2{=}CH{-}\overset{:O:}{\overset{\|}{C}}{-}H} \leftrightarrow \underset{\text{II}}{\overset{+}{C}H_2{-}CH{=}\overset{:\ddot{O}:^-}{\overset{|}{C}}{-}H}$$

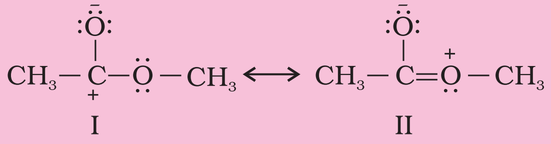
$$\leftrightarrow \underset{\text{III}}{:\overset{-}{C}H_2{-}CH{=}\overset{:O:^+}{\overset{|}{C}}{-}H}$$

Stability: I > II > III

[I: Most stable, more number of covalent bonds, each carbon and oxygen atom has an octet and no separation of opposite charge II: negative charge on more electronegative atom and positive charge on more electropositive atom; III: does not contribute as oxygen has positive charge and carbon has negative charge, hence least stable].

Problem 12.18

Explain why the following two structures, I and II cannot be the major contributors to the real structure of CH_3COOCH_3.



$$\underset{\text{I}}{CH_3{-}\underset{+}{\overset{:\bar{\ddot{O}}:}{\overset{|}{C}}}{-}\ddot{O}{-}CH_3} \longleftrightarrow \underset{\text{II}}{CH_3{-}\overset{:\bar{\ddot{O}}:}{\overset{|}{C}}{=}\overset{+}{\ddot{O}}{-}CH_3}$$

Solution

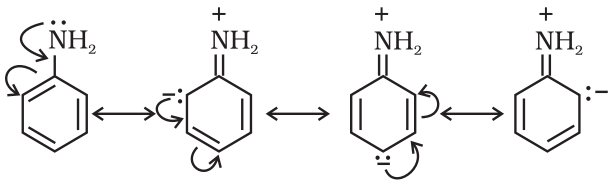
The two structures are less important contributors as they involve charge separation. Additionally, structure I contains a carbon atom with an incomplete octet.

12.7.7 Resonance Effect

The resonance effect is defined as 'the polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and lone pair of electrons present on an adjacent atom'. The effect is transmitted through the chain. There are two types of resonance or mesomeric effect designated as R or M effect.

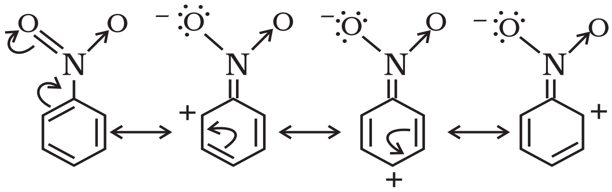
(i) Positive Resonance Effect (+R effect)

In this effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system. This electron displacement makes certain positions in the molecule of high electron densities. This effect in aniline is shown as :



(ii) Negative Resonance Effect (- R effect)

This effect is observed when the transfer of electrons is towards the atom or substituent group attached to the conjugated system. For example in nitrobenzene this electron displacement can be depicted as :



The atoms or substituent groups, which represent +R or –R electron displacement effects are as follows :

+R effect: – halogen, –OH, –OR, –OCOR, $–NH_2$, –NHR, $–NR_2$, –NHCOR,

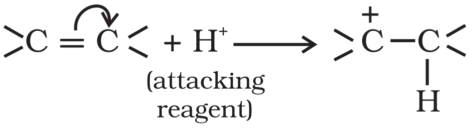
– R effect: – COOH, –CHO, >C=O, – CN, $–NO_2$

The presence of alternate single and double bonds in an open chain or cyclic system is termed as a conjugated system. These systems often show abnormal behaviour. The examples are 1,3- butadiene, aniline and nitrobenzene etc. In such systems, the π-electrons are delocalised and the system develops polarity.

12.7.8 Electromeric Effect (E effect)

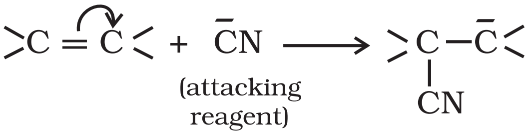
It is a temporary effect. The organic compounds having a **multiple bond** (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of π-electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction. It is represented by E and the shifting of the electrons is shown by a curved arrow (↷). There are two distinct types of electromeric effect.

(i) Positive Eelctromeric Effect (+E effect) In this effect the π–electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :



$$>C=C< + \underset{\text{(attacking reagent)}}{H^+} \longrightarrow >\overset{+}{C}-\underset{H}{\underset{|}{C}}<$$

(ii) Negative Electromeric Effect (–E effect) In this effect the π - electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example:



$$>C=C< + \underset{\text{(attacking reagent)}}{\overset{-}{C}N} \longrightarrow >\underset{CN}{\underset{|}{C}}-\overset{-}{C}<$$

When inductive and electromeric effects operate in opposite directions, the electomeric effect predominates.

12.7.9 Hyperconjugation

Hyperconjugation is a general stabilising interaction. It involves delocalisation of σ electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared *p* orbital. The σ electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared *p* orbital. Hyperconjugation is a permanent effect.

To understand hyperconjugation effect, let us take an example of $CH_3\overset{+}{C}H_2$ (ethyl cation) in which the positively charged carbon atom has an empty *p* orbital. One of the C-H bonds of the methyl group can align in the plane of this empty *p* orbital and the electrons constituting the C-H bond in plane with this *p* orbital can then be delocalised into the empty *p* orbital as depicted in Fig. 12.4 (a).

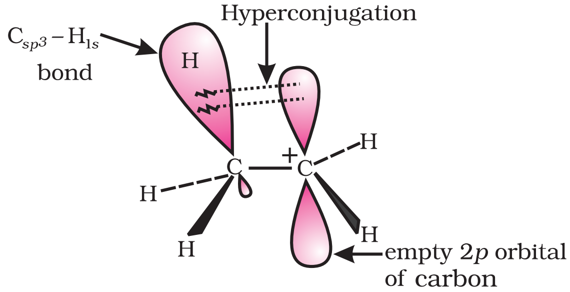
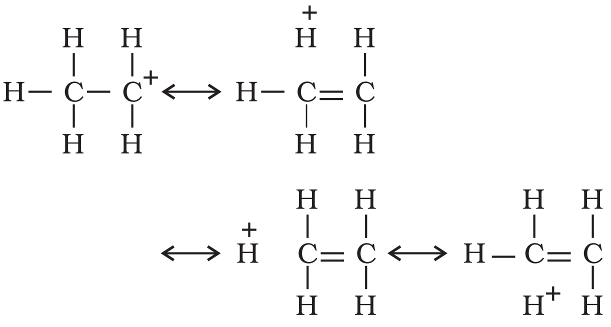


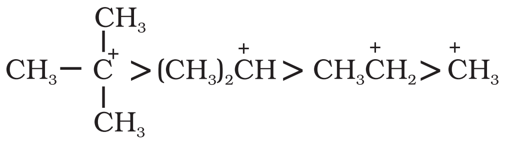
Fig. 12.4(a) *Orbital diagram showing hyperconjugation in ethyl cation*

This type of overlap stabilises the carbocation because electron density from the adjacent σ bond helps in dispersing the positive charge.



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C^+}} \longleftrightarrow H-\underset{H}{\overset{\overset{+}{H}}{C}}=\underset{H}{\overset{H}{C}} \longleftrightarrow \overset{+}{H}\ \ \underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}} \longleftrightarrow H-\underset{H^+}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}$$

In general, greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilisation of the cation. Thus, we have the following relative stability of carbocations :



$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{\overset{+}{C}}}}} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

Hyperconjugation is also possible in alkenes and alkylarenes.

Delocalisation of electrons by hyperconjugation in the case of alkene can be depicted as in Fig. 12.4(b).

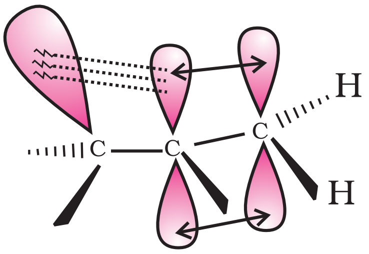
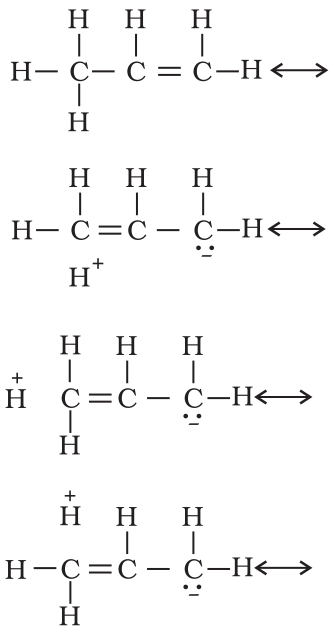


Fig. 12.4(b) *Orbital diagram showing hyperconjugation in propene*

There are various ways of looking at the hyperconjugative effect. One of the way is to regard C—H bond as possessing partial ionic character due to resonance.



The hyperconjugation may also be regarded as no bond resonance.

Problem 12.19

Explain why $(CH_3)_3\overset{+}{C}$ is more stable than $CH_3\overset{+}{C}H_2$ and $\overset{+}{C}H_3$ is the least stable cation.

Solution

Hyperconjugation interaction in $(CH_3)_3\overset{+}{C}$ is greater than in $CH_3\overset{+}{C}H_{2+}$ as the $(CH_3)_3\overset{+}{C}$ has nine C-H bonds. In $\overset{+}{C}H_3$, vacant *p* orbital is perpendicular to the plane in which C-H bonds lie; hence cannot overlap with it. Thus, $\overset{+}{C}H_3$ lacks hyperconjugative stability.

12.7.10 Types of Organic Reactions and Mechanisms

Organic reactions can be classified into the following categories:

(i) Substitution reactions
(ii) Addition reactions
(iii) Elimination reactions
(iv) Rearrangement reactions

You will be studying these reactions in Unit 13 and later in class XII.

12.8 METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

Once an organic compound is extracted from a natural source or synthesised in the laboratory, it is essential to purify it. Various methods used for the purification of organic compounds are based on the nature of the compound and the impurity present in it.

The common techniques used for purification are as follows :

(i) Sublimation
(ii) Crystallisation
(iii) Distillation
(iv) Differential extraction and
(v) Chromatography

Finally, the purity of a compound is ascertained by determining its melting or boiling point. Most of the pure compounds have sharp melting points and boiling points. New methods of checking the purity of an organic compound are based on different types of chromatographic and spectroscopic techniques.

12.8.1 Sublimation

You have learnt earlier that on heating, some solid substances change from solid to vapour state without passing through liquid state. The purification technique based on the above principle is known as sublimation and is used to separate sublimable compounds from non-sublimable impurities.

12.8.2 Crystallisation

This is one of the most commonly used techniques for the purification of solid organic compounds. It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. The impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to get a nearly saturated solution. On cooling the solution, pure compound crystallises out and is removed by filtration. The filtrate (mother liquor) contains impurities and small quantity of the compound. If the compound is highly soluble in one solvent and very little soluble in another solvent, crystallisation can be satisfactorily carried out in a mixture of these solvents. Impurities, which impart colour to the solution are removed by adsorbing over activated charcoal. Repeated crystallisation becomes necessary for the purification of compounds containing impurities of comparable solubilities.

12.8.3 Distillation

This important method is used to separate (i) volatile liquids from nonvolatile impurities and (ii) the liquids having sufficient difference in their boiling points. Liquids having different boiling points vaporise at different temperatures. The vapours are cooled and the liquids so formed are collected separately. Chloroform (b.p 334 K) and aniline (b.p. 457 K) are easily separated by the technique of distillation (Fig 12.5). The liquid mixture is taken in a round bottom flask and heated carefully. On boiling, the vapours of lower boiling component are formed first. The vapours are condensed by using a condenser and the liquid is collected in a receiver. The vapours of higher boiling component form later and the liquid can be collected separately.

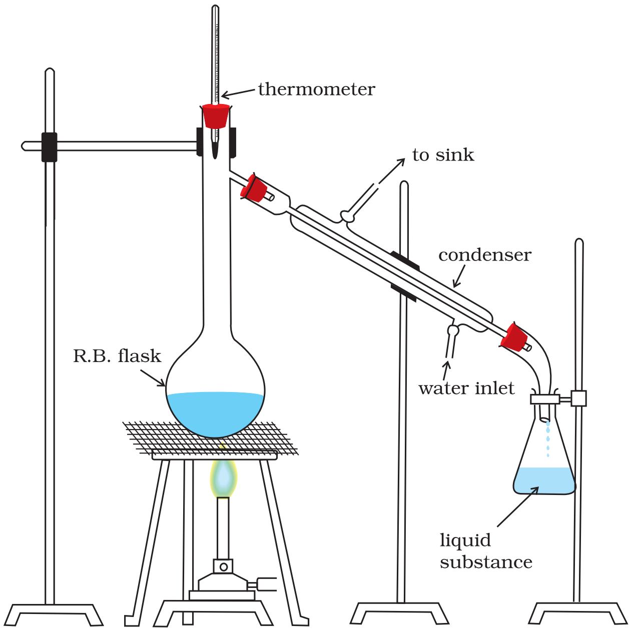


Fig.12.5 *Simple distillation. The vapours of a substance formed are condensed and the liquid is collected in conical flask.*

Fractional Distillation: If the difference in boiling points of two liquids is not much, simple distillation cannot be used to separate them. The vapours of such liquids are formed within the same temperature range and are condensed simultaneously. The technique of fractional distillation is used in such cases. In this technique, vapours of a liquid mixture are passed through a fractionating column before condensation. The fractionating column is fitted over the mouth of the round bottom flask (Fig.12.6, page 358).

Vapours of the liquid with higher boiling point condense before the vapours of the liquid with lower boiling point. The vapours rising up in the fractionating column become richer in more volatile component. By the time the

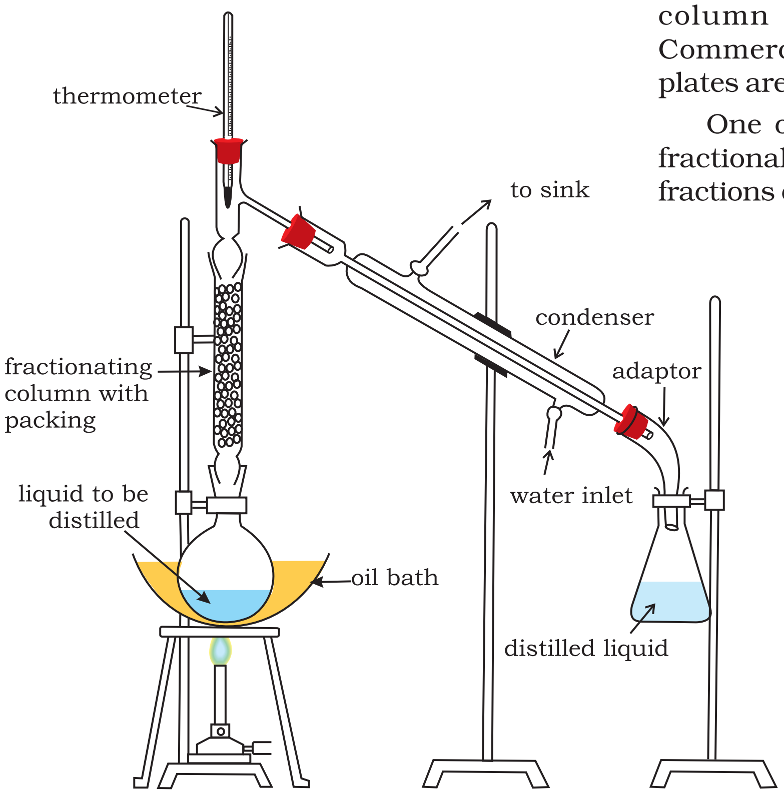


Fig.12.6 *Fractional distillation. The vapours of lower boiling fraction reach the top of the column first followed by vapours of higher boiling fractions.*

vapours reach to the top of the fractionating column, these are rich in the more volatile component. Fractionating columns are available in various sizes and designs as shown in Fig.12.7. A fractionating column provides many surfaces for heat exchange between the ascending vapours and the descending condensed liquid. Some of the condensing liquid in the fractionating column obtains heat from the ascending vapours and revaporises. The vapours thus become richer in low boiling component. The vapours of low boiling component ascend to the top of the column. On reaching the top, the vapours become pure in low boiling component and pass through the condenser and the pure liquid is collected in a receiver. After a series of successive distillations, the remaining liquid in the distillation flask gets enriched in high boiling component. Each successive condensation and vaporisation unit in the fractionating column is called a ***theoretical plate.*** Commercially, columns with hundreds of plates are available.

One of the technological applications of fractional distillation is to separate different fractions of ***crude oil in petroleum industry.***

Distillation under reduced pressure: This method is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Such liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surface. A liquid boils at a temperature at which its vapour pressure is equal to the external pressure. The pressure is reduced with the help of a water pump or vacuum pump (Fig.12.8). Glycerol can be separated from **spent-lye in soap industry** by using this technique.

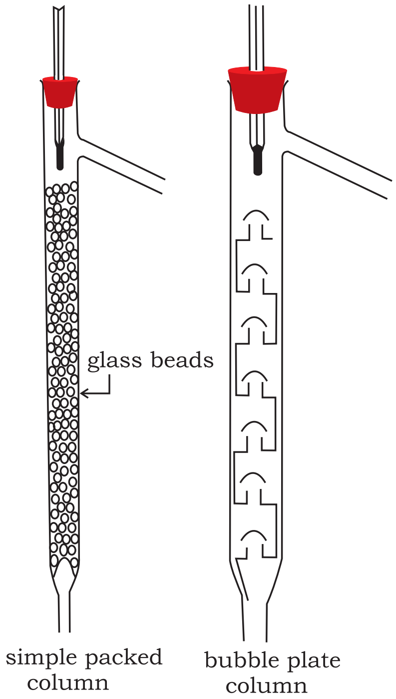


Fig.12.7 *Different types of fractionating columns.*

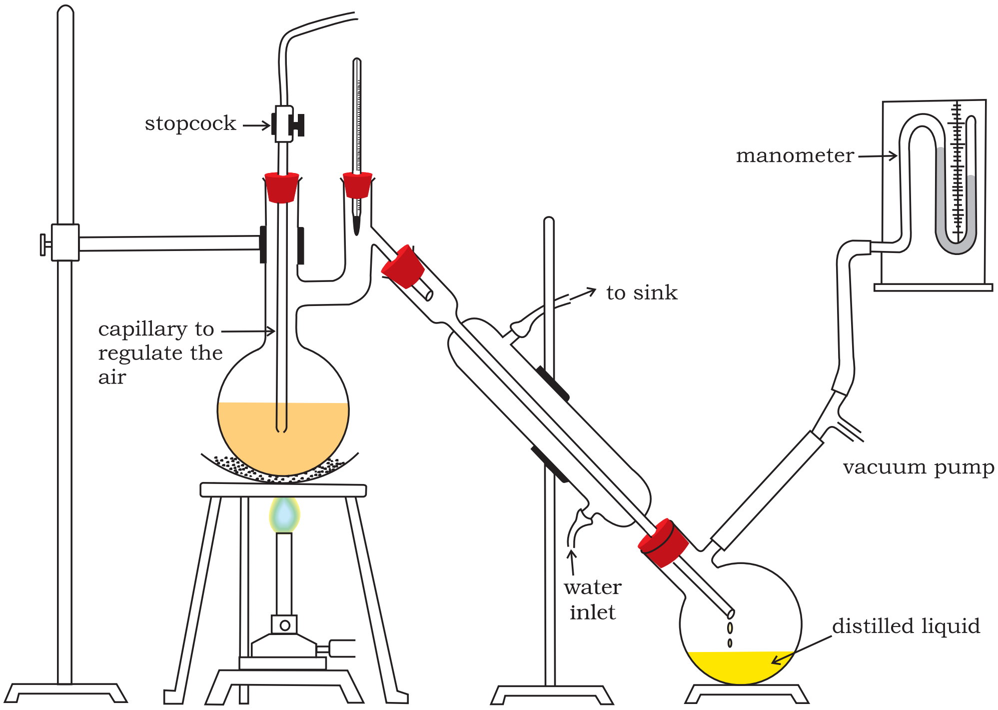


Fig.12.8 *Distillation under reduced pressure. A liquid boils at a temperature below its vapour pressure by reducing the pressure.*

Steam Distillation: This technique is applied to separate substances which are steam volatile and are immiscible with water. In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic compound is condensed and collected. The compound is later separated from water using a separating funnel. In steam distillation, the liquid boils when the sum of vapour pressures due to the organic liquid (p_1) and that due to water (p_2) becomes equal to the atmospheric pressure (p), i.e. $p = p_1 + p_2$. Since p_1 is lower than p, the organic liquid vaporises at lower temperature than its boiling point.

Thus, if one of the substances in the mixture is water and the other, a water insoluble substance, then the mixture will boil close to but below, 373K. A mixture of water and the substance is obtained which can be separated by using a separating funnel. Aniline is separated by this technique from aniline – water mixture (Fig.12.9, Page 360).

12.8.4 Differential Extraction

When an organic compound is present in an aqueous medium, it is separated by shaking it with an organic solvent in which it is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they form two distinct layers which can be separated by separatory funnel. The organic solvent is later removed by distillation or by evaporation to get back the compound. Differential extraction is carried out in a separatory funnel as shown in Fig. 12.10 (Page 360). If the organic compound is less soluble in the organic solvent, a very large quantity of solvent would be required to extract even a very small quantity of the compound. The technique of ***continuous extraction*** is employed in such cases. In this technique same solvent is repeatedly used for extraction of the compound.

12.8.5 Chromatography

Chromatography is an important technique extensively used to separate mixtures into their components, purify compounds and also to test the purity of compounds. The name

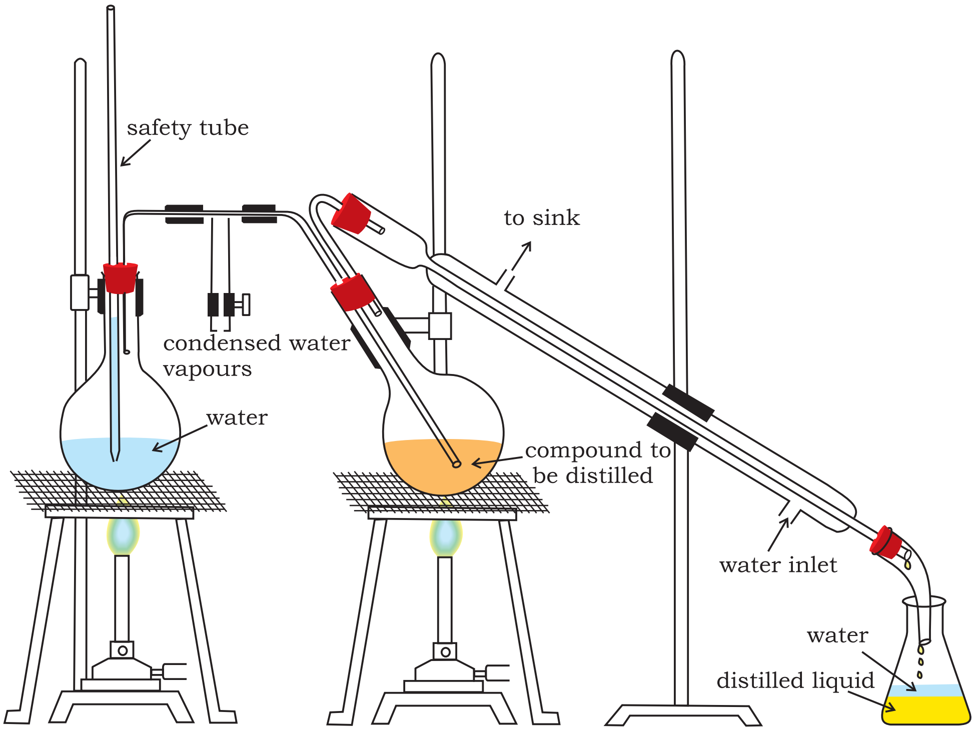


Fig.12.9 *Steam distillation. Steam volatile component volatilizes, the vapours con-*

chromatography is based on the Greek word *chroma*, for colour since the method was first used for the separation of coloured substances found in plants. In this technique, the mixture of substances is applied onto a stationary phase, which may be a solid or a liquid. A pure solvent, a mixture of solvents, or a gas is allowed to move slowly over the stationary phase. The components of the mixture get gradually separated from one another. The moving phase is called the mobile phase.

Based on the principle involved, chromatography is classified into different categories. Two of these are:

(a) Adsorption chromatography, and
(b) Partition chromatography.

***a) Adsorption Chromatography*:** Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential adsorption.

(a) Column chromatography, and
(b) Thin layer chromatography.

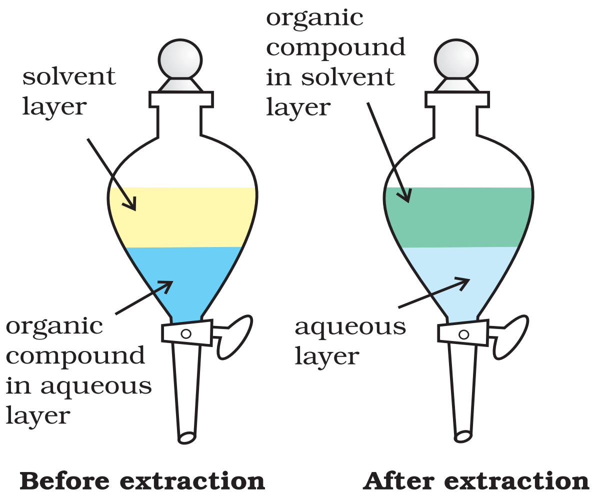


Fig.12.10 *Differential extraction. Extraction of compound takes place based on difference in solubility*

Column Chromatography: Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end (Fig. 12.11). The mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube. An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column (Fig.12.11).

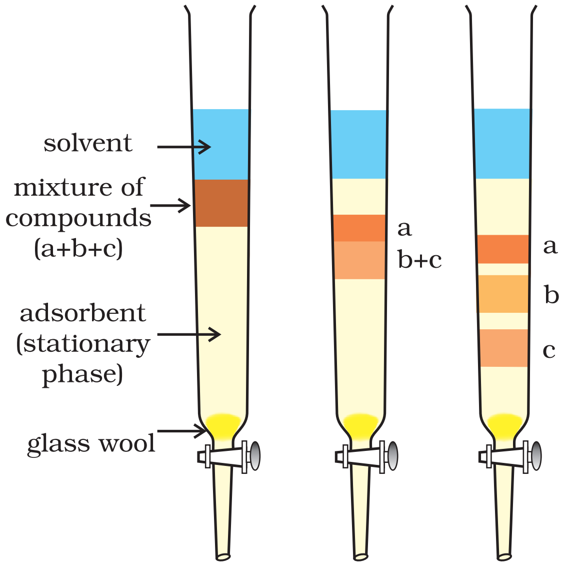


Fig.12.11 *Column chromatography. Different stages of separation of components of a mixture.*

Thin Layer Chromatography: Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate. A thin layer (about 0.2mm thick) of an adsorbent (silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as *thin layer chromatography plate or chromaplate*. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate. The glass plate is then placed in a closed jar containing the eluant (Fig. 12.12a). As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its **retardation factor** i.e. **R_f value** (Fig.12.12 b).

$$R_f = \frac{\text{Distance moved by the substance from base line } (x)}{\text{Distance moved by the solvent from base line } (y)}$$

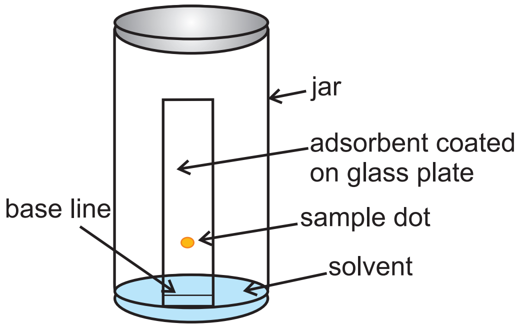


Fig.12.12 (a) *Thin layer chromatography. Chromatogram being developed.*

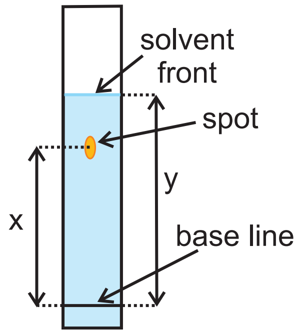


Fig.12.12 (b) *Developed chromatogram.*

The spots of coloured compounds are visible on TLC plate due to their original colour. The spots of colourless compounds, which are invisible to the eye but fluoresce in ultraviolet light, can be detected by putting the plate under ultraviolet light. Another detection technique is to place the plate in a covered jar containing a few crystals of iodine. Spots of compounds, which adsorb iodine, will show up as brown spots. Sometimes an appropriate reagent may also be sprayed on the plate. For example, amino acids may be detected by spraying the plate with ninhydrin solution (Fig.12.12b).

Partition Chromatography: Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper known as chromatography paper is used. Chromatography paper contains water trapped in it, which acts as the stationary phase.

A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents (Fig. 12.13). This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram. The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.

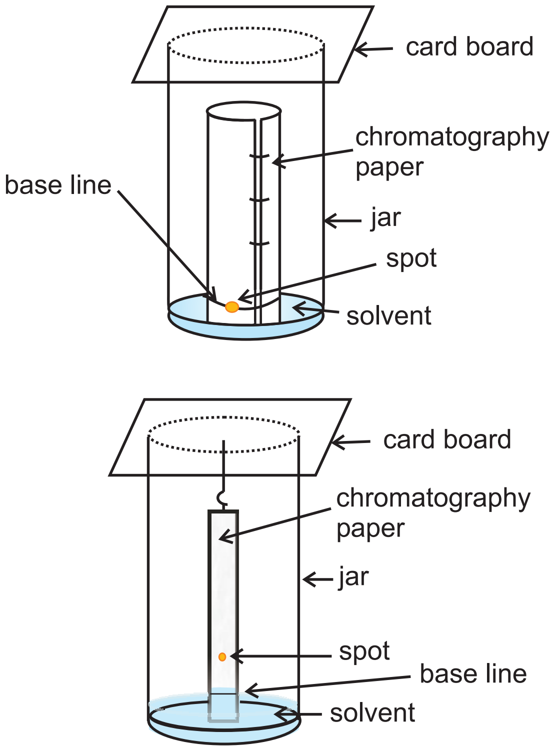


Fig.12.13 *Paper chromatography. Chromatography paper in two different shapes.*

12.9 QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The elements present in organic compounds are carbon and hydrogen. In addition to these, they may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

12.9.1 Detection of Carbon and Hydrogen

Carbon and hydrogen are detected by heating the compound with copper(II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O$$

$$\underset{\text{White}}{5H_2O + CuSO_4} \longrightarrow \underset{\text{Blue}}{CuSO_4.5H_2O}$$

12.9.2 Detection of Other Elements

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by **"Lassaigne's test"**. The elements present in the compound are converted from covalent form into the ionic form by fusing the compound with sodium metal. Following reactions take place:

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} Na\,X$$

(X = Cl, Br or I)

C, N, S and X come from organic compound.

Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract.

(A) Test for Nitrogen

The sodium fusion extract is boiled with iron(II) sulphate and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen. Sodium cyanide first reacts with iron(II) sulphate and forms sodium hexacyanidoferrate(II). On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanidoferrate(II) to produce iron(III) hexacyanidoferrate(II) (ferriferrocyanide) which is Prussian blue in colour.

$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3.xH_2O}$$

(B) Test for Sulphur

(a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$$S^{2-} + Pb^{2+} \longrightarrow \underset{\text{Black}}{PbS}$$

(b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur.

$$S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow \underset{\text{Violet}}{[Fe(CN)_5NOS]^{4-}}$$

In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no Prussian blue since there are no free cyanide ions.

$$Na + C + N + S \longrightarrow NaSCN$$

$$Fe^{3+} + SCN^- \longrightarrow \underset{\text{Blood red}}{[Fe(SCN)]^{2+}}$$

If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.

$$NaSCN + 2Na \longrightarrow NaCN + Na_2S$$

(C) Test for Halogens

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

$$X^- + Ag^+ \longrightarrow AgX$$

X represents a halogen – Cl, Br or I.

If nitrogen or sulphur is also present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens.

(D) Test for Phosphorus

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + \underset{\substack{\text{Ammonium}\\ \text{molybdate}}}{12(NH_4)_2MoO_4} + 21HNO_3 \longrightarrow$$

$$\underset{\substack{\text{Ammonium}\\ \text{phosphomolybdate}}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

12.10 QUANTITATIVE ANALYSIS

Quantitative analysis of compounds is very important in organic chemistry. It helps chemists in the determination of mass per cent of elements present in a compound. You have learnt in Unit-1 that mass per cent of elements is required for the determination of emperical and molecular formula.

The percentage composition of elements present in an organic compound is determined by the following methods:

12.10.1 Carbon and Hydrogen

Both carbon and hydrogen are estimated in one experiment. A known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide. Carbon and hydrogen in the compound are oxidised to carbon dioxide and water respectively.

$$C_xH_y + (x + y/4)\,O_2 \longrightarrow x\,CO_2 + (y/2)\,H_2O$$

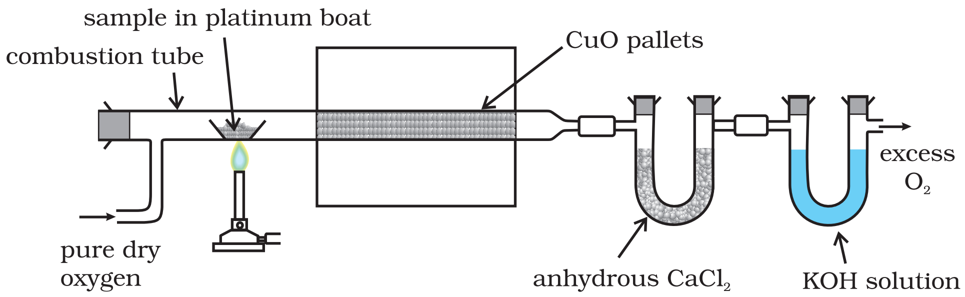


Fig.12.14 *Estimation of carbon and hydrogen. Water and carbon dioxide formed on oxidation of substance are absorbed in anhydrous calcium chloride and potassium hydroxide solutions respectively contained in U tubes.*

The mass of water produced is determined by passing the mixture through a weighed U-tube containing anhydrous calcium chloride. Carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide. These tubes are connected in series (Fig.12.14). The increase in masses of calcium chloride and potassium hydroxide gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated.

Let the mass of organic compound be m g, mass of water and carbon dioxide produced be m_1 and m_2 g respectively;

$$\text{Percentage of carbon} = \frac{12 \times m_2 \times 100}{44 \times m}$$

$$\text{Percentage of hydrogen} = \frac{2 \times m_1 \times 100}{18 \times m}$$

Problem 12.20

On complete combustion, 0.246 g of an organic compound gave 0.198g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound.

Solution

$$\text{Percentage of carbon} = \frac{12 \times 0.198 \times 100}{44 \times 0.246}$$

$$= 21.95\%$$

$$\text{Percentage of hydrogen} = \frac{2 \times 0.1014 \times 100}{18 \times 0.246}$$

$$= 4.58\%$$

12.10.2 Nitrogen

There are two methods for estimation of nitrogen: (i) Dumas method and (ii) Kjeldahl's method.

(i) Dumas method: The nitrogen containing organic compound, when heated with copper oxide in an atmosphere of carbon dioxide, yields free nitrogen in addition to carbon dioxide and water.

$$C_xH_yN_z + (2x + y/2)\,CuO \longrightarrow$$

$$x\,CO_2 + y/2\,H_2O + z/2\,N_2 + (2x + y/2)\,Cu$$

Traces of nitrogen oxides formed, if any, are reduced to nitrogen by passing the gaseous mixture over a heated copper gauze. The mixture of gases so produced is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide. Nitrogen is collected in the upper part of the graduated tube (Fig.12.15).

Let the mass of organic compound = m g

Volume of nitrogen collected = V_1 mL

Room temperature = T_1K

$$\text{Volume of nitrogen at STP} = \frac{p_1 V_1 \times 273}{760 \times T_1}$$

(Let it be V mL)

Where p_1 and V_1 are the pressure and volume of nitrogen, p_1 is different from the atmospheric pressure at which nitrogen gas is collected. The value of p_1 is obtained by the relation;

p_1= Atmospheric pressure – Aqueous tension

22400 mL N_2 at STP weighs 28 g.

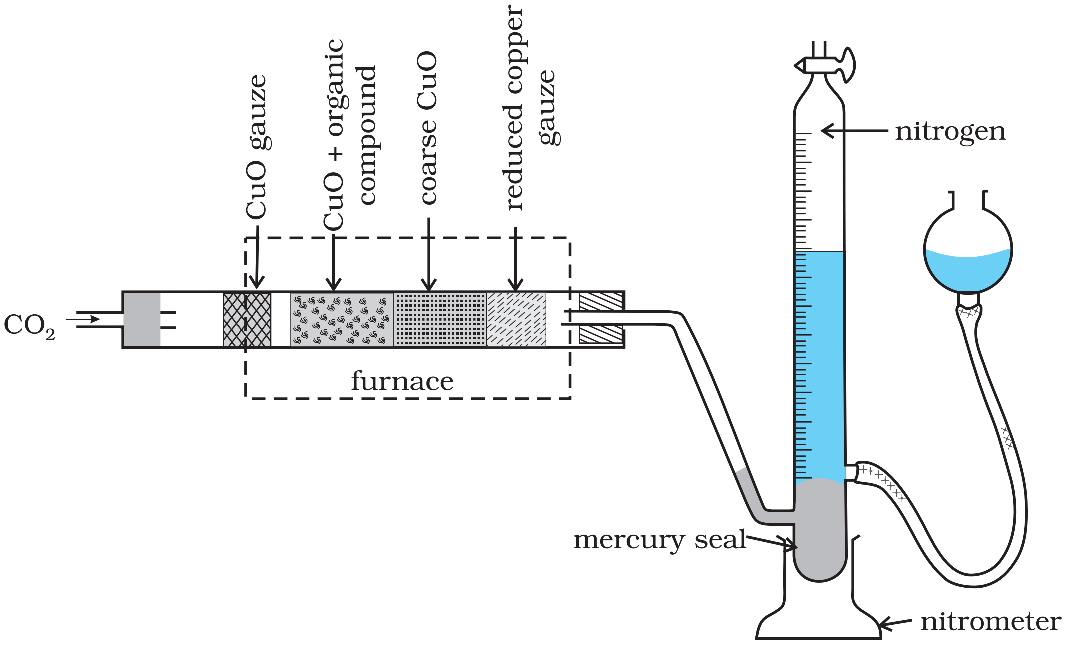


Fig.12.15 *Dumas method. The organic compound yields nitrogen gas on heating it with copper(II) oxide in the presence of CO_2 gas. The mixture of gases is collected over potassium hydroxide solution in which CO_2 is absorbed and volume of nitrogen gas is determined.*

$$V \text{ mL } N_2 \text{ at STP weighs} = \frac{28 \times V}{22400} \text{g}$$

$$\text{Percentage of nitrogen} = \frac{28 \times V \times 100}{22400 \times m}$$

Problem 12.21

In Dumas' method for estimation of nitrogen, 0.3g of an organic compound gave 50mL of nitrogen collected at 300K temperature and 715mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300K=15 mm)

Solution

Volume of nitrogen collected at 300K and 715mm pressure is 50 mL

Actual pressure = 715-15 =700 mm

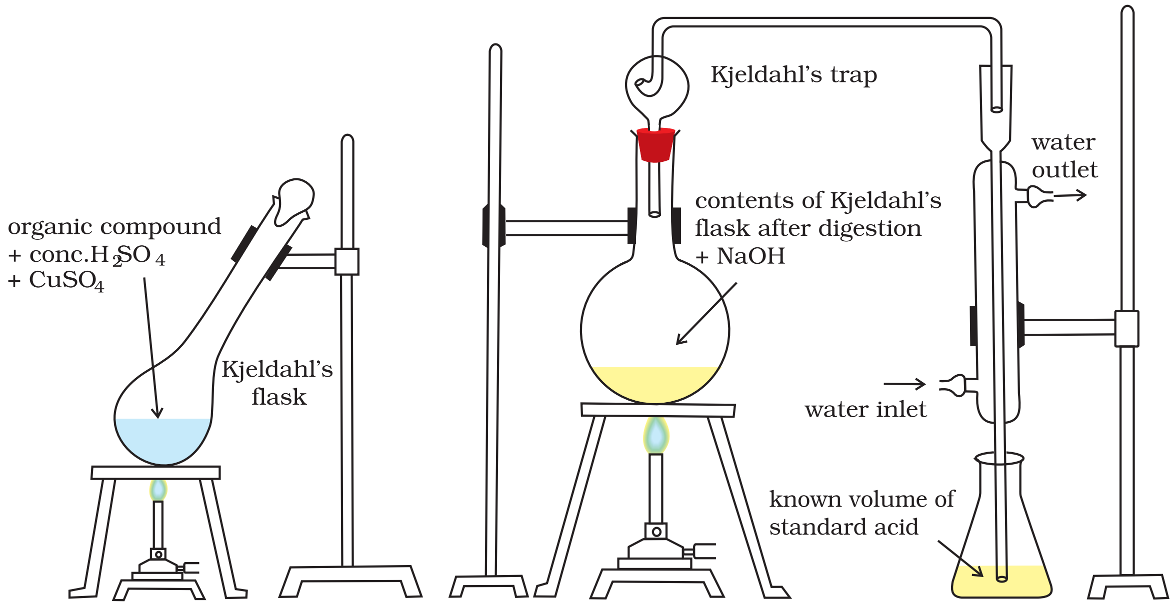
$$\text{Volume of nitrogen at STP} = \frac{273 \times 700 \times 50}{300 \times 760} = 41.9 \text{ mL}$$

22,400 mL of N_2 at STP weighs = 28 g

$$41.9 \text{ mL of nitrogen weighs} = \frac{28 \times 41.9}{22400} \text{g}$$

$$\text{Percentage of nitrogen} = \frac{28 \times 41.9 \times 100}{22400 \times 0.3} = 17.46\%$$

(ii) Kjeldahl's method: The compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate (Fig. 12.16). The resulting acid mixture is then heated with excess of sodium hydroxide. The liberated ammonia gas is absorbed in an excess of standard solution of sulphuric acid. The amount of ammonia produced is determined by estimating the amount of sulphuric acid consumed in the reaction. It is done by estimating unreacted sulphuric acid left after the absorption of ammonia by titrating it with standard alkali solution. The difference between the initial amount of acid taken and that left



digestion (heating in Kjeldahl's flask) Kjeldahl's distillation

Fig.12.16 *Kjeldahl method. Nitrogen-containing compound is treated with concentrated H_2SO_4 to get ammonium sulphate which liberates ammonia on treating with NaOH; ammonia is absorbed in known volume of standard acid.*

after the reaction gives the amount of acid reacted with ammonia.

$$\text{Organic compound} + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$
$$\xrightarrow{2\text{NaOH}} Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

Let the mass of organic compound taken = m g
Volume of H_2SO_4 of molarity, M,
taken = V mL

Volume of NaOH of molarity, M, used for titration of excess of $H_2SO_4 = V_1$ mL

V_1mL of NaOH of molarity M

= V_1 /2 mL of H_2SO_4 of molarity M

Volume of H_2SO_4 of molarity M unused = $(V - V_1/2)$ mL

$(V- V_1/2)$ mL of H_2SO_4 of molarity M

= $2(V-V_1/2)$ mL of NH_3 solution of molarity M.

1000 mL of 1 M NH_3 solution contains 17g NH_3 or 14 g of N

$2(V-V_1/2)$ mL of NH_3 solution of molarity M contains:

$$\frac{14 \times M \times 2(V - V_1/2)}{1000} \text{ g N}$$

$$\text{Percentage of N} = \frac{14 \times M \times 2(V\text{-}V_1/2)}{1000} \times \frac{100}{m}$$

$$= \frac{1.4 \times M \times 2(V\text{-}V_1/2)}{m}$$

Kjeldahl method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulphate under these conditions.

Problem 12.22

During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 mL of 1 M H_2SO_4. Find out the percentage of nitrogen in the compound.

Solution

1 M of 10 mL H_2SO_4=1M of 20 mL NH_3
1000 mL of 1M ammonia contains 14 g nitrogen
20 mL of 1M ammonia contains

$$\frac{14 \times 20}{1000} \text{ g nitrogen}$$

$$\text{Percentage of nitrogen} = \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0\%$$

12.10.3 Halogens

Carius method: A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as Carius tube, (Fig.12.17) in a furnace. Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed.

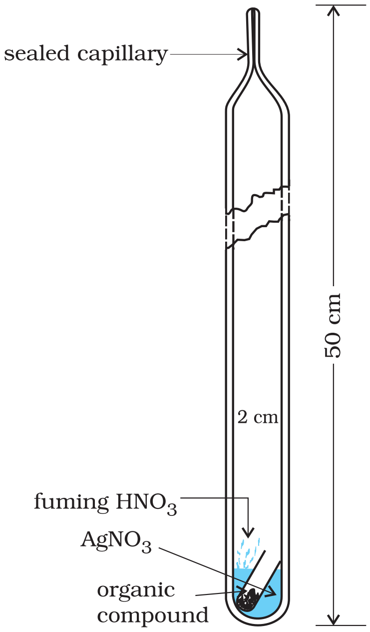


Fig. 12.17 *Carius method. Halogen containing organic compound is heated with fuming nitric acid in the presence of silver nitrate.*

Let the mass of organic

compound taken = m g

Mass of AgX formed = m_1 g

1 mol of AgX contains 1 mol of X

Mass of halogen in m_1g of AgX

$$= \frac{\text{atomic mass of X} \times m_1 \text{g}}{\text{molecular mass of AgX}}$$

Percentage of halogen

$$= \frac{\text{atomic mass of X} \times m_1 \times 100}{\text{molecular mass of AgX} \times m}$$

Problem 12.23

In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 g of AgBr. Find out the percentage of bromine in the compound.

Solution

Molar mass of AgBr = 108 + 80

= 188 g mol^{-1}

188 g AgBr contains 80 g bromine

$$0.12 \text{ g AgBr contains } \frac{80 \times 0.12}{188} \text{ g bromine}$$

$$\text{Percentage of bromine} = \frac{80 \times 0.12 \times 100}{188 \times 0.15}$$

= 34.04%

12.10.4 Sulphur

A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid. Sulphur present in the compound is oxidised to sulphuric acid. It is precipitated as barium sulphate by adding excess of barium chloride solution in water. The precipitate is filtered, washed, dried and weighed. The percentage of sulphur can be calculated from the mass of barium sulphate.

Let the mass of organic

compound taken = m g

and the mass of barium

sulphate formed = m_1g

1 mol of $BaSO_4$ = 233 g $BaSO_4$ = 32 g sulphur

$$m_1 \text{ g } BaSO_4 \text{ contains } \frac{32 \times m_1}{233} \text{ g sulphur}$$

$$\text{Percentage of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m}$$

Problem 12.24

In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound?

Solution

Molecular mass of $BaSO_4$ = 137+32+64
= 233 g

233 g $BaSO_4$ contains 32 g sulphur

0.4813 g $BaSO_4$ contains $\frac{32 \times 0.4813}{233}$ g sulphur

$$\text{Percentage of sulphur} = \frac{32 \times 0.4813 \times 100}{233 \times 0.157} = 42.10\%$$

12.10.5 Phosphorus

A known mass of an organic compound is heated with fuming nitric acid whereupon phosphorus present in the compound is oxidised to phosphoric acid. It is precipitated as ammonium phosphomolybdate, $(NH_4)_3PO_4.12MoO_3$, by adding ammonia and ammonium molybdate. Alternatively, phosphoric acid may be precipitated as $MgNH_4PO_4$ by adding magnesia mixture which on ignition yields $Mg_2P_2O_7$.

Let the mass of organic compound taken = m g and mass of ammonium phospho molydate = m_1g

Molar mass of $(NH_4)_3PO_4.12MoO_3$ = 1877g

$$\text{Percentage of phosphorus} = \frac{31 \times m_1 \times 100}{1877 \times m}\%$$

If phosphorus is estimated as $Mg_2P_2O_7$,

$$\text{Percentage of phosphorus} = \frac{62 \times m_1 \times 100}{222 \times m}\%$$

where, 222 u is the molar mass of $Mg_2P_2O_7$, *m*, the mass of organic compound taken, m_1, the mass of $Mg_2P_2O_7$ formed and 62, the mass of two phosphorus atoms present in the compound $Mg_2P_2O_7$.

12.10.6 Oxygen

The percentage of oxygen in an organic compound is usually found by difference between the total percentage composition (100) and the sum of the percentages of all other elements. However, oxygen can also be estimated directly as follows:

A definite mass of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide. This mixture is passed through warm iodine pentoxide (I_2O_5) when carbon monoxide is oxidised to carbon dioxide producing iodine.

$$\text{Compound} \xrightarrow{\text{heat}} O_2 + \text{other gaseous products}$$

$$2C + O_2 \xrightarrow{1373\,K} 2CO] \times 5 \qquad (A)$$

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2] \times 2 \qquad (B)$$

On making the amount of CO produced in equation (A) equal to the amount of CO used in equation (B) by multiplying the equations (A) and (B) by 5 and 2 respectively; we find that each mole of oxygen liberated from the compound will produce two moles of carbondioxide.

Thus 88 g carbon dioxide is obtained if 32 g oxygen is liberated.

Let the mass of organic compound taken be *m* g

Mass of carbon dioxide produced be m_1 g

$\therefore$ m_1 g carbon dioxide is obtained from $\frac{32 \times m_1}{88}$ g O_2

$$\therefore \text{Percentage of oxygen} = \frac{32 \times m_1 \times 100}{88 \times m}\%$$

The percentage of oxygen can be derived from the amount of iodine produced also.

Presently, the estimation of elements in an organic compound is carried out by using microquantities of substances and automatic experimental techniques. The elements, carbon, hydrogen and nitrogen present in a compound are determined by an apparatus known as CHN *elemental analyser*. The analyser requires only a very small amount of the substance (1-3 mg) and displays the values on a screen within a short time. A detailed discussion of such methods is beyond the scope of this book.

SUMMARY

In this unit, we have learnt some basic concepts in structure and reactivity of organic compounds, which are formed due to covalent bonding. The nature of the covalent bonding in organic compounds can be described in terms of **orbitals hybridisation** concept, according to which carbon can have sp^3, sp^2 and sp hybridised orbitals. The sp^3, sp^2 and sp hybridised carbons are found in compounds like methane, ethene and ethyne respectively. The tetrahedral shape of methane, planar shape of ethene and linear shape of ethyne can be understood on the basis of this concept. A sp^3 hybrid orbital can overlap with 1*s* orbital of hydrogen to give a carbon - hydrogen (C–H) single bond (sigma, σ bond). Overlap of a sp^2 orbital of one carbon with sp^2 orbital of another results in the formation of a carbon–carbon σ bond. The unhybridised *p* orbitals on two adjacent carbons can undergo lateral (side-by-side) overlap to give a pi (π) bond. Organic compounds can be represented by various structural formulas. The three dimensional representation of organic compounds on paper can be drawn by **wedge** and **dash** formula.

Organic compounds can be classified on the basis of their structure or the functional groups they contain. A **functional group** is an atom or group of atoms bonded together in a unique fashion and which determines the physical and chemical properties of the compounds. The naming of the organic compounds is carried out by following a set of rules laid down by the International Union of Pure and Applied Chemistry (**IUPAC**). In IUPAC nomenclature, the names are correlated with the structure in such a way that the reader can deduce the structure from the name.

Organic reaction mechanism concepts are based on the structure of the substrate molecule, fission of a covalent bond, the attacking reagents, the electron displacement effects and the conditions of the reaction. These organic reactions involve breaking and making of covalent bonds. A covalent bond may be cleaved in **heterolytic** or **homolytic** fashion. A heterolytic cleavage yields **carbocations** or **carbanions**, while a homolytic cleavage gives **free radicals** as reactive intermediate. Reactions proceeding through heterolytic cleavage involve the complimentary pairs of reactive species. These are electron pair donor known as **nucleophile** and an electron pair acceptor known as **electrophile**. The **inductive**, **resonance**, **electromeric** and **hyperconjugation effects** may help in the polarisation of a bond making certain carbon atom or other atom positions as places of low or high electron densities.

Organic reactions can be broadly classified into following types; **substitution, addition, elimination** and **rearrangement** reactions.

Purification, qualitative and quantitative analysis of organic compounds are carried out for determining their structures. The methods of purification namely : sublimation, distillation and differential extraction are based on the difference in one or more physical properties. **Chromatography** is a useful technique of separation, identification and purification of compounds. It is classified into two categories : adsorption and partition chromatography. Adsorption chromatography is based on differential adsorption of various components of a mixture on an adsorbent. Partition chromatography involves continuous partitioning of the components of a mixture between stationary and mobile phases. After getting the compound in a pure form, its qualitative analysis is carried out for detection of elements present in it. Nitrogen, sulphur, halogens and phosphorus are detected by **Lassaigne's test**. Carbon and hydrogen are estimated by determining the amounts of carbon dioxide and water produced. Nitrogen is estimated by **Dumas** or **Kjeldahl's** method and halogens by **Carius** method. Sulphur and phosphorus are estimated by oxidising them to sulphuric and phosphoric acids respectively. The percentage of oxygen is usually determined by difference between the total percentage (100) and the sum of percentages of all other elements present.

EXERCISES

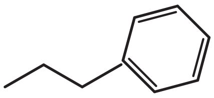
12.1 What are hybridisation states of each carbon atom in the following compounds ?
$CH_2=C=O$, $CH_3CH=CH_2$, $(CH_3)_2CO$, $CH_2=CHCN$, C_6H_6

12.2 Indicate the σ and π bonds in the following molecules :
C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2=C=CH_2$, CH_3NO_2, $HCONHCH_3$

12.3 Write bond line formulas for : Isopropyl alcohol, 2,3-Dimethylbutanal, Heptan-4-one.

12.4 Give the IUPAC names of the following compounds :

(a)



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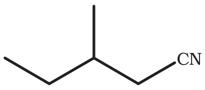

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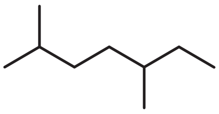

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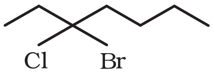
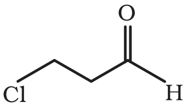


(e)



(f) Cl_2CHCH_2OH

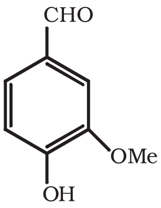
12.5 Which of the following represents the correct IUPAC name for the compounds concerned ? (a) 2,2-Dimethylpentane or 2-Dimethylpentane (b) 2,4,7-Trimethyloctane or 2,5,7-Trimethyloctane (c) 2-Chloro-4-methylpentane or 4-Chloro-2-methylpentane (d) But-3-yn-1-ol or But-4-ol-1-yne.

12.6 Draw formulas for the first five members of each homologous series beginning with the following compounds. (a) H–COOH (b) CH_3COCH_3 (c) $H–CH=CH_2$

12.7 Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for :
(a) 2,2,4-Trimethylpentane
(b) 2-Hydroxy-1,2,3-propanetricarboxylic acid
(c) Hexanedial

12.8 Identify the functional groups in the following compounds

(a)



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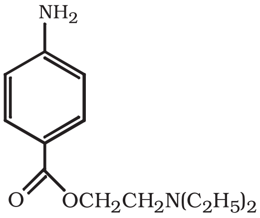

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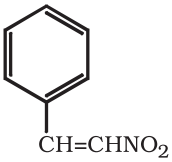


12.9 Which of the two: $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable and why ?

12.10 Explain why alkyl groups act as electron donors when attached to a π system.

12.11 Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.
(a) C_6H_5OH (b) $C_6H_5NO_2$ (c) $CH_3CH=CHCHO$ (d) $C_6H_5–CHO$ (e) $C_6H_5-\overset{+}{C}H_2$
(f) $CH_3CH=CH\overset{+}{C}H_2$

12.12 What are electrophiles and nucleophiles ? Explain with examples.

12.13 Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles:
(a) $CH_3COOH+\mathbf{HO^-}\rightarrow CH_3COO^-+H_2O$

(b) $CH_3COCH_3 + \mathbf{\bar{C}N} \rightarrow (CH_3)_2\,C(CN)(OH)$

(c) $C_6H_6 + \mathbf{CH_3\overset{+}{C}O} \rightarrow C_6H_5COCH_3$

12.14 Classify the following reactions in one of the reaction type studied in this unit.

(a) $CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH + Br^-$

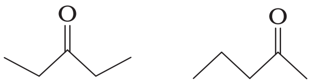
(b) $(CH_3)_2\,C = CH_2 + HCl \rightarrow (CH_3)_2\,ClC - CH_3$

(c) $CH_3CH_2Br + HO^- \rightarrow CH_2 = CH_2 + H_2O + Br^-$

(d) $(CH_3)_3\,C - CH_2OH + HBr \rightarrow (CH_3)_2\,CBrCH_2CH_2CH_3 + H_2O$

12.15 What is the relationship between the members of following pairs of structures ? Are they structural or geometrical isomers or resonance contributors ?

(a)



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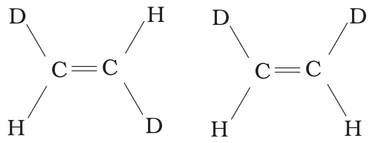
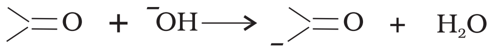


(c)

12.16 For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.

(a) $CH_3O - OCH_3 \rightarrow CH_3\dot{O} + \dot{O}CH_3$

(b)



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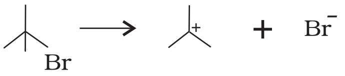

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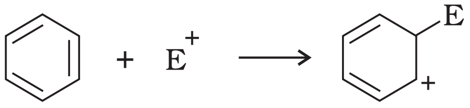


12.17 Explain the terms Inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

(b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

12.18 Give a brief description of the principles of the following techniques taking an example in each case.

(a) Crystallisation (b) Distillation (c) Chromatography

12.19 Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

12.20 What is the difference between distillation, distillation under reduced pressure and steam distillation ?

12.21 Discuss the chemistry of Lassaigne's test.

12.22 Differentiate between the principle of estimation of nitrogen in an organic compound by (i) Dumas method and (ii) Kjeldahl's method.

12.23 Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.

12.24 Explain the principle of paper chromatography.

12.25 Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

12.26 Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.

12.27 Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

12.28 Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation ?

12.29 Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

12.30 Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

12.31 Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

12.32 An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

12.33 A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5 M H_2SO_4. The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

12.34 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.

12.35 In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound.

12.36 In the organic compound $CH_2 = CH - CH_2 - CH_2 - C \equiv CH$, the pair of hydridised orbitals involved in the formation of: $C_2 - C_3$ bond is:

(a) $sp - sp^2$ (b) $sp - sp^3$ (c) $sp^2 - sp^3$ (d) $sp^3 - sp^3$

12.37 In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of:

(a) $Na_4[Fe(CN)_6]$ (b) $Fe_4[Fe(CN)_6]_3$ (c) $Fe_2[Fe(CN)_6]$ (d) $Fe_3[Fe(CN)_6]_4$

12.38 Which of the following carbocation is most stable ?

(a) $(CH_3)_3C.\overset{+}{C}H_2$ (b) $(CH_3)_3\overset{+}{C}$ (c) $CH_3CH_2\overset{+}{C}H_2$ (d) $CH_3\overset{+}{C}H\,CH_2CH_3$

12.39 The best and latest technique for isolation, purification and separation of organic compounds is:

(a) Crystallisation (b) Distillation (c) Sublimation (d) Chromatography

12.40 The reaction:

$CH_3CH_2I + KOH(aq) \rightarrow CH_3CH_2OH + KI$

is classified as :

(a) electrophilic substitution (b) nucleophilic substitution

(c) elimination (d) addition

UNIT 13

HYDROCARBONS

Objectives

After studying this unit, you will be able to

- name hydrocarbons according to IUPAC system of nomenclature;
- recognise and write structures of isomers of alkanes, alkenes, alkynes and aromatic hydrocarbons;
- learn about various methods of preparation of hydrocarbons;
- distinguish between alkanes, alkenes, alkynes and aromatic hydrocarbons on the basis of physical and chemical properties;
- draw and differentiate between various conformations of ethane;
- appreciate the role of hydrocarbons as sources of energy and for other industrial applications;
- predict the formation of the addition products of unsymmetrical alkenes and alkynes on the basis of electronic mechanism;
- comprehend the structure of benzene, explain aromaticity and understand mechanism of electrophilic substitution reactions of benzene;
- predict the directive influence of substituents in monosubstituted benzene ring;
- learn about carcinogenicity and toxicity.

> ***"Hydrocarbons are the important sources of energy."***

The term 'hydrocarbon' is self-explanatory which means compounds of carbon and hydrogen only. Hydrocarbons play a key role in our daily life. You must be familiar with the terms 'LPG' and 'CNG' used as fuels. LPG is the abbreviated form of liquified petroleum gas whereas CNG stands for compressed natural gas. Another term 'LNG' (liquified natural gas) is also in news these days. This is also a fuel and is obtained by liquifaction of natural gas. Petrol, diesel and kerosene oil are obtained by the fractional distillation of petroleum found under the earth's crust. Coal gas is obtained by the destructive distillation of coal. Natural gas is found in upper strata during drilling of oil wells. The gas after compression is known as compressed natural gas. LPG is used as a domestic fuel with the least pollution. Kerosene oil is also used as a domestic fuel but it causes some pollution. Automobiles need fuels like petrol, diesel and CNG. Petrol and CNG operated automobiles cause less pollution. All these fuels contain mixture of hydrocarbons, which are sources of energy. Hydrocarbons are also used for the manufacture of polymers like polythene, polypropene, polystyrene etc. Higher hydrocarbons are used as solvents for paints. They are also used as the starting materials for manufacture of many dyes and drugs. Thus, you can well understand the importance of hydrocarbons in your daily life. In this unit, you will learn more about hydrocarbons.

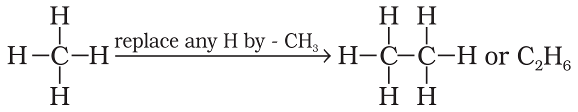
13.1 CLASSIFICATION

Hydrocarbons are of different types. Depending upon the types of carbon-carbon bonds present, they can be classified into three main categories – (i) saturated

(ii) unsaturated and (iii) aromatic hydrocarbons. Saturated hydrocarbons contain carbon-carbon and carbon-hydrogen single bonds. If different carbon atoms are joined together to form open chain of carbon atoms with single bonds, they are termed as alkanes as you have already studied in Unit 12. On the other hand, if carbon atoms form a closed chain or a ring, they are termed as cycloalkanes. Unsaturated hydrocarbons contain carbon-carbon multiple bonds – double bonds, triple bonds or both. Aromatic hydrocarbons are a special type of cyclic compounds. You can construct a large number of models of such molecules of both types (open chain and close chain) keeping in mind that carbon is tetravalent and hydrogen is monovalent. For making models of alkanes, you can use toothpicks for bonds and plasticine balls for atoms. For alkenes, alkynes and aromatic hydrocarbons, spring models can be constructed.

13.2 ALKANES

As already mentioned, alkanes are saturated open chain hydrocarbons containing carbon - carbon single bonds. Methane (CH_4) is the first member of this family. Methane is a gas found in coal mines and marshy places. If you replace one hydrogen atom of methane by carbon and join the required number of hydrogens to satisfy the tetravalence of the other carbon atom, what do you get? You get C_2H_6. This hydrocarbon with molecular formula C_2H_6 is known as ethane. Thus you can consider C_2H_6 as derived from CH_4 by replacing one hydrogen atom by -CH_3 group. Go on constructing alkanes by doing this theoretical exercise i.e., replacing hydrogen atom by –CH_3 group. The next molecules will be C_3H_8, C_4H_{10} …



$$H-\underset{H}{\overset{H}{C}}-H \xrightarrow{\text{replace any H by - }CH_3} H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H \text{ or } C_2H_6$$

These hydrocarbons are inert under normal conditions as they do not react with acids, bases and other reagents. Hence, they were earlier known as paraffins (*latin : parum,* little; *affinis,* affinity). Can you think of the general formula for alkane family or **homologous series**? If we examine the formula of different alkanes we find that the general formula for alkanes is C_nH_{2n+2}. It represents any particular homologue when *n* is given appropriate value. Can you recall the structure of methane? According to VSEPR theory (Unit 4), methane has a tetrahedral structure (Fig. 13.1), in which carbon atom lies at the centre and the four hydrogen atoms lie at the four corners of a regular tetrahedron. All H-C-H bond angles are of 109.5°.

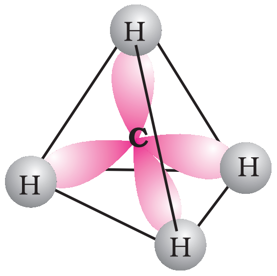


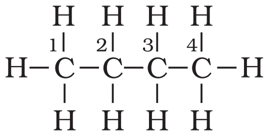
Fig. 13.1 *Structure of methane*

In alkanes, tetrahedra are joined together in which C-C and C-H bond lengths are 154 pm and 112 pm respectively (Unit 12). You have already read that C–C and C–H σ bonds are formed by head-on overlapping of sp^3 hybrid orbitals of carbon and 1*s* orbitals of hydrogen atoms.

13.2.1 Nomenclature and Isomerism

You have already read about nomenclature of different classes of organic compounds in Unit 12. Nomenclature and isomerism in alkanes can further be understood with the help of a few more examples. Common names are given in parenthesis. First three alkanes – methane, ethane and propane have only one structure but higher alkanes can have more than one structure. Let us write structures for C_4H_{10}. Four carbon atoms of C_4H_{10} can be joined either in a continuous chain or with a branched chain in the following two ways :

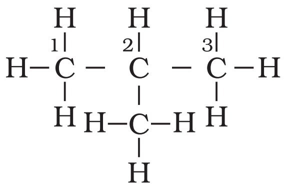
I



$$H-\underset{H}{\overset{H}{\overset{1}{C}}}-\underset{H}{\overset{H}{\overset{2}{C}}}-\underset{H}{\overset{H}{\overset{3}{C}}}-\underset{H}{\overset{H}{\overset{4}{C}}}-H$$

Butane (*n*- butane), (b.p. 273 K)

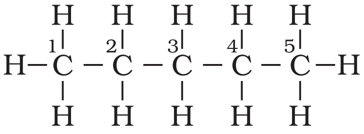
II



2-Methylpropane (isobutane)
(b.p.261 K)

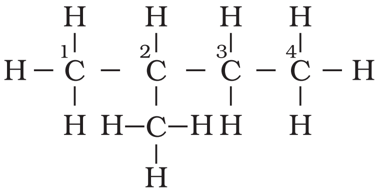
In how many ways, you can join five carbon atoms and twelve hydrogen atoms of C_5H_{12}? They can be arranged in three ways as shown in structures III–V

III



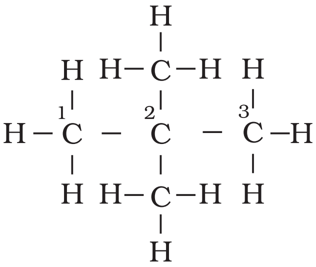
Pentane (*n*-pentane)
(b.p. 309 K)

IV



2-Methylbutane (isopentane)
(b.p. 301 K)

V



2,2-Dimethylpropane (neopentane)
(b.p. 282.5 K)

Structures I and II possess same molecular formula but differ in their boiling points and other properties. Similarly structures III, IV and V possess the same molecular formula but have different properties. Structures I and II are isomers of butane, whereas structures III, IV and V are isomers of pentane. Since difference in properties is due to difference in their structures, they are known as **structural isomers**. It is also clear that structures I and III have continuous chain of carbon atoms but structures II, IV and V have a branched chain. Such structural isomers which differ in chain of carbon atoms are known as **chain isomers**. Thus, you have seen that C_4H_{10} and C_5H_{12} have two and three chain isomers respectively.

Problem 13.1

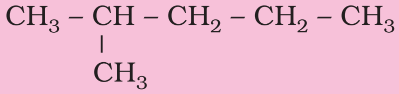
Write structures of different chain isomers of alkanes corresponding to the molecular formula C_6H_{14}. Also write their IUPAC names.

Solution

(i) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

n-Hexane

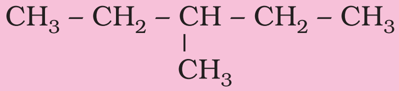
(ii)



$$CH_3-\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_2-CH_3$$

2-Methylpentane

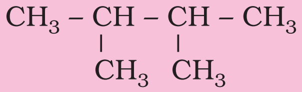
(iii)



$$CH_3-CH_2-\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_3$$

3-Methylpentane

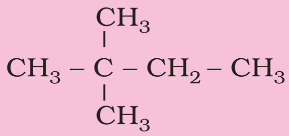
(iv)



$$CH_3-\underset{\overset{|}{CH_3}}{CH}-\underset{\overset{|}{CH_3}}{CH}-CH_3$$

2,3-Dimethylbutane

(v)



$$CH_3-\overset{\underset{|}{CH_3}}{\underset{\overset{|}{CH_3}}{C}}-CH_2-CH_3$$

2,2 - Dimethylbutane

Based upon the number of carbon atoms attached to a carbon atom, the carbon atom is termed as primary (1°), secondary (2°), tertiary (3°) or quaternary (4°). Carbon atom attached to no other carbon atom as in methane or to only one carbon atom as in ethane is called primary carbon atom. Terminal carbon atoms are always primary. Carbon atom attached to two carbon atoms is known as secondary. Tertiary carbon is attached to three carbon atoms and neo or quaternary carbon is attached to four carbon atoms. Can you identify 1°, 2°, 3° and 4° carbon atoms in structures I to V ? If you go on constructing structures for higher alkanes, you will be getting still larger number of isomers. C_6H_{14} has got five isomers and C_7H_{16} has nine. As many as 75 isomers are possible for $C_{10}H_{22}$.

In structures II, IV and V, you observed that $-CH_3$ group is attached to carbon atom numbered as 2. You will come across groups like $-CH_3$, $-C_2H_5$, $-C_3H_7$ etc. attached to carbon atoms in alkanes or other classes of compounds. These groups or substituents are known as alkyl groups as they are derived from alkanes by removal of one hydrogen atom. General formula for alkyl groups is C_nH_{2n+1} (Unit 12).

Let us recall the general rules for nomenclature already discussed in Unit 12. Nomenclature of substituted alkanes can further be understood by considering the following problem:

Problem 13.2

Write structures of different isomeric alkyl groups corresponding to the molecular formula C_5H_{11}. Write IUPAC names of alcohols obtained by attachment of –OH groups at different carbons of the chain.

Solution

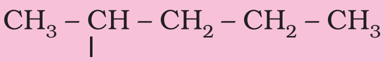
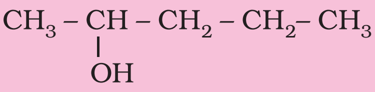
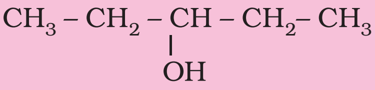
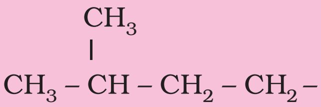
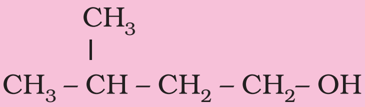
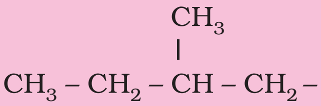
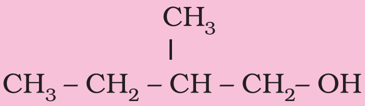
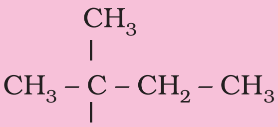
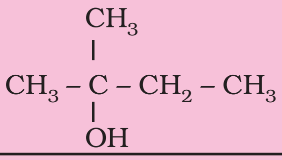
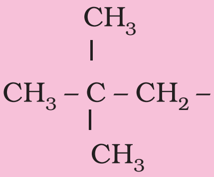
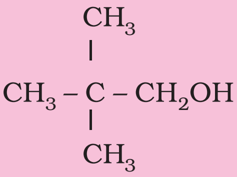
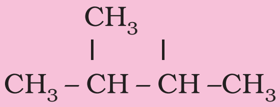
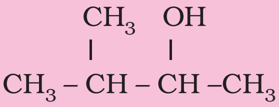
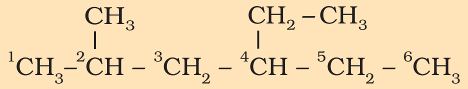
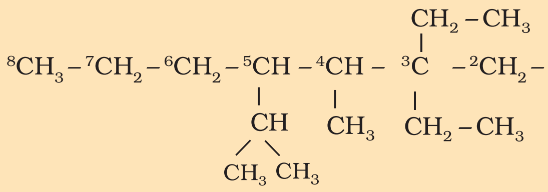
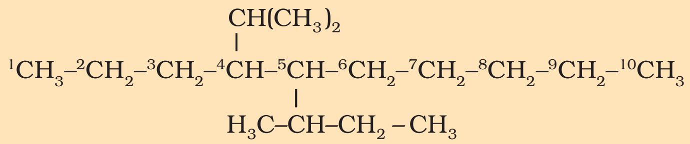
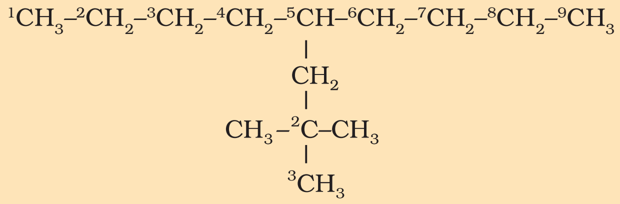
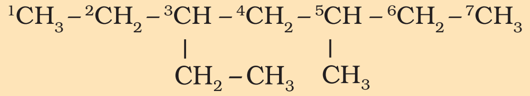
Structures of – C_5H_{11} group	Corresponding alcohols	Name of alcohol
(i) $CH_3-CH_2-CH_2-CH_2-CH_2-$	$CH_3-CH_2-CH_2-CH_2-CH_2-OH$	Pentan-1-ol
(ii)  $CH_3-\underset{\vert}{CH}-CH_2-CH_2-CH_3$	 $CH_3-\underset{\underset{OH}{\vert}}{CH}-CH_2-CH_2-CH_3$	Pentan-2-ol
(iii)  $CH_3-CH_2-\underset{\vert}{CH}-CH_2-CH_3$	 $CH_3-CH_2-\underset{\underset{OH}{\vert}}{CH}-CH_2-CH_3$	Pentan-3-ol
(iv)  $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-CH_2-$	 $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-CH_2-OH$	3-Methyl-butan-1-ol
(v)  $CH_3-CH_2-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-$	 $CH_3-CH_2-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-OH$	2-Methyl-butan-1-ol
(vi)  $CH_3-\underset{\vert}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-CH_3$	 $CH_3-\underset{\underset{OH}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-CH_3$	2-Methyl-butan-2-ol
(vii)  $CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-$	 $CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2OH$	2,2- Dimethyl-propan-1-ol
(viii)  $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-\overset{\vert}{CH}-CH_3$	 $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-\overset{\overset{OH}{\vert}}{CH}-CH_3$	3-Methyl-butan-2-ol

Table 13.1 Nomenclature of a Few Organic Compounds

Structure and IUPAC Name	Remarks
(a)  ${}^{1}CH_3-\overset{CH_3}{{}^{2}CH}-{}^{3}CH_2-\overset{CH_2-CH_3}{{}^{4}CH}-{}^{5}CH_2-{}^{6}CH_3$ (4 – Ethyl – 2 – methylhexane)	Lowest sum and alphabetical arrangement
(b)  (3,3-Diethyl-5-isopropyl-4-methyloctane)	Lowest sum and alphabetical arrangement
(c)  5-*sec*– Butyl-4-isopropyldecane	*sec* is not considered while arranging alphabetically; isopropyl is taken as one word
(d)  5-(2,2– Dimethylpropyl)nonane	Further numbering to the substituents of the side chain
(e)  ${}^{1}CH_3-{}^{2}CH_2-\underset{CH_2-CH_3}{{}^{3}CH}-{}^{4}CH_2-\underset{CH_3}{{}^{5}CH}-{}^{6}CH_2-{}^{7}CH_3$ 3–Ethyl–5–methylheptane	Alphabetical priority order

Problem 13.3

Write IUPAC names of the following compounds :

(i) $(CH_3)_3\,C\,CH_2C(CH_3)_3$

(ii) $(CH_3)_2\,C(C_2H_5)_2$

(iii) tetra – *tert*-butylmethane

Solution

(i) 2, 2, 4, 4-Tetramethylpentane

(ii) 3, 3-Dimethylpentane

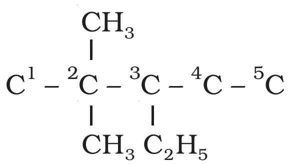
(iii) 3,3-Di-*tert*-butyl -2, 2, 4, 4 - tetramethylpentane

If it is important to write the correct IUPAC name for a given structure, it is equally important to write the correct structure from the given IUPAC name. To do this, first of all, the longest chain of carbon atoms corresponding to the parent alkane is written. Then after numbering it, the substituents are attached to the correct carbon atoms and finally valence of each carbon atom is satisfied by putting the correct number of hydrogen atoms. This can be clarified by writing the structure of 3-ethyl-2, 2–dimethylpentane in the following steps :

i) Draw the chain of five carbon atoms: $C-C-C-C-C$

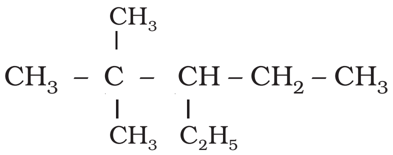
ii) Give number to carbon atoms: $C^1-C^2-C^3-C^4-C^5$

iii) Attach ethyl group at carbon 3 and two methyl groups at carbon 2



$$C^1-{}^2\underset{CH_3}{\overset{CH_3}{C}}-{}^3\underset{C_2H_5}{C}-{}^4C-{}^5C$$

iv) Satisfy the valence of each carbon atom by putting requisite number of hydrogen atoms :



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{C_2H_5}{CH}-CH_2-CH_3$$

Thus we arrive at the correct structure. If you have understood writing of structure from the given name, attempt the following problems.

Problem 13.4

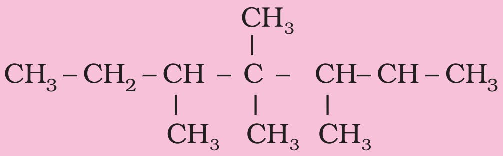
Write structural formulas of the following compounds :

(i) 3, 4, 4, 5–Tetramethylheptane

(ii) 2,5-Dimethyhexane

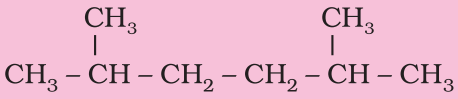
Solution

(i)



$$CH_3-CH_2-\underset{CH_3}{CH}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{CH}-CH-CH_3$$

(ii)



$$CH_3-\overset{CH_3}{CH}-CH_2-CH_2-\overset{CH_3}{CH}-CH_3$$

Problem 13.5

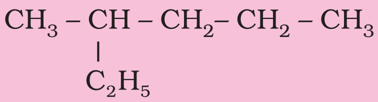
Write structures for each of the following compounds. Why are the given names incorrect? Write correct IUPAC names.

(i) 2-Ethylpentane

(ii) 5-Ethyl – 3-methylheptane

Solution

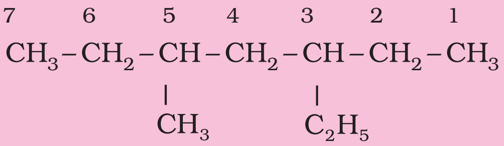
(i)



$$CH_3-\underset{C_2H_5}{CH}-CH_2-CH_2-CH_3$$

Longest chain is of six carbon atoms and not that of five. Hence, correct name is 3-Methylhexane.

(ii)



$$\overset{7}{CH_3}-\overset{6}{CH_2}-\underset{CH_3}{\overset{5}{CH}}-\overset{4}{CH_2}-\underset{C_2H_5}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

Numbering is to be started from the end which gives lower number to ethyl group. Hence, correct name is 3-ethyl-5-methylheptane.

13.2.2 Preparation

Petroleum and natural gas are the main sources of alkanes. However, alkanes can be prepared by following methods :

1. From unsaturated hydrocarbons

Dihydrogen gas adds to alkenes and alkynes in the presence of finely divided catalysts like platinum, palladium or nickel to form alkanes. This process is called **hydrogenation**. These metals adsorb dihydrogen gas on their surfaces and activate the hydrogen – hydrogen bond. Platinum and palladium catalyse the reaction at room temperature but relatively higher temperature and pressure are required with nickel catalysts.

$$\underset{\text{Ethene}}{CH_2=CH_2}+H_2\xrightarrow{Pt/Pd/Ni}\underset{\text{Ethane}}{CH_3-CH_3} \qquad (13.1)$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2}+H_2\xrightarrow{Pt/Pd/Ni}\underset{\text{Propane}}{CH_3-CH_2-CH_3} \qquad (13.2)$$

$$\underset{\text{Propyne}}{CH_3-C\equiv C-H}+2H_2\xrightarrow{Pt/Pd/Ni}\underset{\text{Propane}}{CH_3-CH_2-CH_3} \qquad (13.3)$$

2. From alkyl halides

i) Alkyl halides (except fluorides) on reduction with zinc and dilute hydrochloric acid give alkanes.

$$\underset{\text{Chloromethane}}{CH_3-Cl}+H_2\xrightarrow{Zn,\ H^+}\underset{\text{Methane}}{CH_4}+HCl \qquad (13.4)$$

$$\underset{\text{Chloroethane}}{C_2H_5-Cl} + H_2 \xrightarrow{Zn,\,H^+} \underset{\text{Ethane}}{C_2H_6} + HCl \qquad (13.5)$$

$$\underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl} + H_2 \xrightarrow{Zn,H^+} \underset{\text{Propane}}{CH_3CH_2CH_3} + HCl \qquad (13.6)$$

ii) Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as **Wurtz reaction** and is used for the preparation of higher alkanes containing even number of carbon atoms.

$$\underset{\text{Bromomethane}}{CH_3Br}+2Na+BrCH_3 \xrightarrow{\text{dry ether}} \underset{\text{Ethane}}{CH_3-CH_3}+2NaBr \qquad (13.7)$$

$$\underset{\text{Bromoethane}}{C_2H_5Br}+2Na+BrC_2H_5 \xrightarrow{\text{dry ether}} \underset{\text{n-Butane}}{C_2H_5-C_2H_5} \qquad (13.8)$$

What will happen if two different alkyl halides are taken?

3. *From carboxylic acids*

i) Sodium salts of carboxylic acids on heating with soda lime (mixture of sodium hydroxide and calcium oxide) give alkanes containing one carbon atom less than the carboxylic acid. This process of elimination of carbon dioxide from a carboxylic acid is known as **decarboxylation**.

$$\underset{\text{Sodium ethanoate}}{CH_3COO^-Na^+}+NaOH \xrightarrow[\Delta]{CaO} CH_4+Na_2CO_3$$

Problem 13.6

Sodium salt of which acid will be needed for the preparation of propane ? Write chemical equation for the reaction.

Solution

Butanoic acid,

$$CH_3CH_2CH_2COO^-Na^+ + NaOH \xrightarrow{CaO} CH_3CH_2CH_3+Na_2CO_3$$

ii) ***Kolbe's electrolytic method*** An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode.

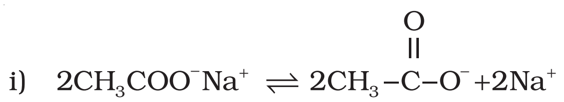
$$\underset{\text{Sodium acetate}}{2CH_3COO^-Na^+} + 2H_2O$$

$$\Big\downarrow \text{Electrolysis}$$

$$CH_3-CH_3+2CO_2+H_2+2NaOH \qquad (13.9)$$

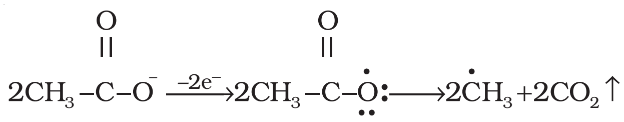
The reaction is supposed to follow the following path :

i)



$$2CH_3COO^-Na^+ \rightleftharpoons 2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + 2Na^+$$

ii) **At anode:**



$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- \xrightarrow{-2e^-} 2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{\underset{\cdot\cdot}{O}}\!: \longrightarrow 2\dot{C}H_3+2CO_2\uparrow$$

Acetate ion — Acetate free radical — Methyl free radical

iii) $H_3\dot{C} + \dot{C}H_3 \longrightarrow H_3C-CH_3\uparrow$

iv) **At cathode :**

$H_2O+e^- \rightarrow {}^-OH+\dot{H}$

$2\dot{H} \rightarrow H_2\uparrow$

Methane cannot be prepared by this method. Why?

13.2.3 Properties

Physical properties

Alkanes are almost non-polar molecules because of the covalent nature of C-C and C-H bonds and due to very little difference of electronegativity between carbon and hydrogen atoms. They possess weak van der Waals forces. Due to the weak forces, the first four members, C_1 to C_4 are gases, C_5 to C_{17} are liquids and those containing 18 carbon atoms or more are solids at 298 K. They are colourless and odourless. What do you think about solubility of alkanes in water based upon non-polar nature of alkanes? Petrol is a mixture of hydrocarbons and is used as a fuel for automobiles. Petrol and lower fractions of petroleum are also used for dry cleaning of clothes to remove grease stains. On the basis of this observation, what do you think about the nature of the greasy substance? You are correct if you say that grease (mixture of higher alkanes) is non-polar and, hence, hydrophobic in nature. It is generally observed that in relation to solubility of substances in solvents, polar substances are soluble in polar solvents, whereas the non-polar ones in non-polar solvents *i.e., like dissolves like*.

Boiling point (b.p.) of different alkanes are given in Table 13.2 from which it is clear that there is a steady increase in boiling point with increase in molecular mass. This is due to the fact that the intermolecular van der Waals forces increase with increase of the molecular size or the surface area of the molecule.

You can make an interesting observation by having a look on the boiling points of three isomeric pentanes viz., (pentane, 2-methylbutane and 2,2-dimethylpropane). It is observed (Table 13.2) that pentane having a continuous chain of five carbon atoms has the highest boiling point (309.1K) whereas 2,2 – dimethylpropane boils at 282.5K. With increase in number of branched chains, the molecule attains the shape of a sphere. This results in smaller area of contact and therefore weak intermolecular forces between spherical molecules, which are overcome at relatively lower temperatures.

Chemical properties

As already mentioned, alkanes are generally inert towards acids, bases, oxidising and reducing agents. However, they undergo the following reactions under certain conditions.

1. Substitution reactions

One or more hydrogen atoms of alkanes can be replaced by halogens, nitro group and sulphonic acid group. **Halogenation** takes place either at higher temperature (573-773 K) or in the presence of diffused sunlight or ultraviolet light. Lower alkanes do not undergo nitration and sulphonation reactions. These reactions in which hydrogen atoms of alkanes are substituted are known as *substitution reactions*. As an example, chlorination of methane is given below:

Halogenation

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{Chloromethane}}{CH_3Cl} + HCl \qquad (13.10)$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl \qquad (13.11)$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\text{Trichloromethane}}{CHCl_3} + HCl \qquad (13.12)$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{Tetrachloromethane}}{CCl_4} + HCl \qquad (13.13)$$

Table 13.2 Variation of Melting Point and Boiling Point in Alkanes

Molecular formula	Name	Molecular mass/u	b.p./(K)	m.p./(K)
CH_4	Methane	16	111.0	90.5
C_2H_6	Ethane	30	184.4	101.0
C_3H_8	Propane	44	230.9	85.3
C_4H_{10}	Butane	58	272.4	134.6
C_4H_{10}	2-Methylpropane	58	261.0	114.7
C_5H_{12}	Pentane	72	309.1	143.3
C_5H_{12}	2-Methylbutane	72	300.9	113.1
C_5H_{12}	2,2-Dimethylpropane	72	282.5	256.4
C_6H_{14}	Hexane	86	341.9	178.5
C_7H_{16}	Heptane	100	371.4	182.4
C_8H_{18}	Octane	114	398.7	216.2
C_9H_{20}	Nonane	128	423.8	222.0
$C_{10}H_{22}$	Decane	142	447.1	243.3
$C_{20}H_{42}$	Eicosane	282	615.0	236.2

$$CH_3\text{-}CH_3 + Cl_2 \xrightarrow{h\nu} CH_3-CH_2Cl + HCl$$

Chloroethane (13.14)

It is found that the rate of reaction of alkanes with halogens is $F_2 > Cl_2 > Br_2 > I_2$. Rate of replacement of hydrogens of alkanes is : 3° > 2° > 1°. Fluorination is too violent to be controlled. Iodination is very slow and a reversible reaction. It can be carried out in the presence of oxidizing agents like HIO_3 or HNO_3.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI \qquad (13.15)$$

$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O \qquad (13.16)$$

Halogenation is supposed to proceed via free radical chain mechanism involving three steps namely initiation, propagation and termination as given below:

Mechanism

(i) *Initiation* : The reaction is initiated by homolysis of chlorine molecule in the presence of light or heat. The Cl–Cl bond is weaker than the C–C and C–H bond and hence, is easiest to break.

$$Cl-Cl \xrightarrow[\text{homolysis}]{h\nu} \overset{\bullet}{C}l + \overset{\bullet}{C}l$$

Chlorine free radicals

(ii) *Propagation* : Chlorine free radical attacks the methane molecule and takes the reaction in the forward direction by breaking the C-H bond to generate methyl free radical with the formation of H-Cl.

(a) $$CH_4 + \overset{\bullet}{C}l \xrightarrow{h\nu} \overset{\bullet}{C}H_3 + H-Cl$$

The methyl radical thus obtained attacks the second molecule of chlorine to form CH_3-Cl with the liberation of another chlorine free radical by homolysis of chlorine molecule.

(b) $$\overset{\bullet}{C}H_3 + Cl-Cl \xrightarrow{h\nu} CH_3-Cl + \overset{\bullet}{C}l$$

Chlorine free radical

The chlorine and methyl free radicals generated above repeat steps (a) and (b) respectively and thereby setup a chain of reactions. The propagation steps (a) and (b) are those which directly give principal products, but many other propagation steps are possible and may occur. Two such steps given below explain how more highly haloginated products are formed.

$$CH_3Cl + \overset{\bullet}{C}l \rightarrow \overset{\bullet}{C}H_2Cl + HCl$$

$$\overset{\bullet}{C}H_2Cl + Cl-Cl \rightarrow CH_2Cl_2 + \overset{\bullet}{C}l$$

(iii) *Termination:* The reaction stops after some time due to consumption of reactants and / or due to the following side reactions :

The possible chain terminating steps are :

(a) $$\overset{\bullet}{C}l + \overset{\bullet}{C}l \rightarrow Cl-Cl$$

(b) $$H_3\overset{\bullet}{C} + \overset{\bullet}{C}H_3 \rightarrow H_3C-CH_3$$

(c) $$H_3\overset{\bullet}{C} + \overset{\bullet}{C}l \rightarrow H_3C-Cl$$

Though in (c), $CH_3 - Cl$, the one of the products is formed but free radicals are consumed and the chain is terminated. The above mechanism helps us to understand the reason for the formation of ethane as a byproduct during chlorination of methane.

2. Combustion

Alkanes on heating in the presence of air or dioxygen are completely oxidized to carbon dioxide and water with the evolution of large amount of heat.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \quad \Delta_cH^{\ominus} = -890\ \text{kJ mol}^{-1} \qquad (13.17)$$

$$C_4H_{10}(g) + 13/2\ O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l); \quad \Delta_cH^{\ominus} = -2875.84\ \text{kJ mol}^{-1} \qquad (13.18)$$

The general combustion equation for any alkane is :

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)\,H_2O \qquad (13.19)$$

Due to the evolution of large amount of heat during combustion, alkanes are used as fuels.

During incomplete combustion of alkanes with insufficient amount of air or dioxygen, carbon black is formed which is used in the manufacture of ink, printer ink, black pigments and as filters.

$$CH_4(g)+O_2(g)\xrightarrow[\text{combustion}]{\text{Incomplete}}C(s)+2H_2O(l) \qquad (13.20)$$

3. Controlled oxidation

Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalysts give a variety of oxidation products.

(i) $2CH_4+O_2\xrightarrow{\text{Cu/523K/100atm}}\underset{\text{Methanol}}{2CH_3OH}$ (13.21)

(ii) $CH_4 + O_2\xrightarrow[\Delta]{Mo_2O_3}\underset{\text{Methanal}}{HCHO} + H_2O$ (13.22)

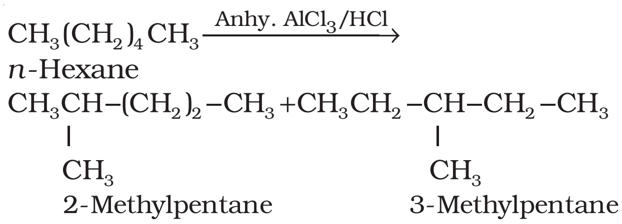
(iii) $2CH_3CH_3+3O_2\xrightarrow[\Delta]{(CH_3COO)_2Mn}\underset{\text{Ethanoic acid}}{2CH_3COOH} + 2H_2O$ (13.23)

(iv) Ordinarily alkanes resist oxidation but alkanes having tertiary H atom can be oxidized to corresponding alcohols by potassium permanganate.

$$\underset{\text{2-Methylpropane}}{(CH_3)_3CH}\xrightarrow[\text{Oxidation}]{KMnO_4}\underset{\text{2-Methylpropan-2-ol}}{(CH_3)_3COH} \qquad (13.24)$$

4. Isomerisation

n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes. Major products are given below. Some minor products are also possible which you can think over. Minor products are generally not reported in organic reactions.

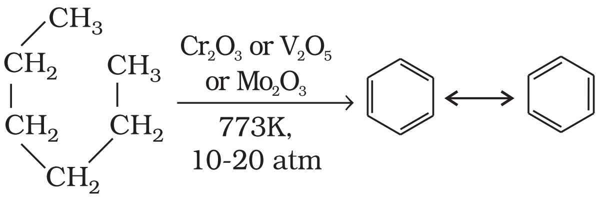


$$\underset{n\text{-Hexane}}{CH_3(CH_2)_4CH_3}\xrightarrow{\text{Anhy. }AlCl_3/HCl}\underset{\text{2-Methylpentane}}{CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2)_2-CH_3}+\underset{\text{3-Methylpentane}}{CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3}$$

(13.25)

5. Aromatization

n-Alkanes having six or more carbon atoms on heating to 773K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina get **dehydrogenated** and cyclised to benzene and its homologues. This reaction is known as *aromatization* or *reforming*.



(13.26)

Toluene (C_7H_8) is methyl derivative of benzene. Which alkane do you suggest for preparation of toluene ?

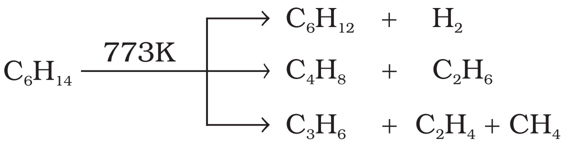
6. Reaction with steam

Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen. This method is used for industrial preparation of dihydrogen gas

$$CH_4 + H_2O\xrightarrow[\Delta]{Ni}CO + 3H_2 \qquad (13.27)$$

7. Pyrolysis

Higher alkanes on heating to higher temperature decompose into lower alkanes, alkenes etc. Such a decomposition reaction into smaller fragments by the application of heat is called *pyrolysis* or *cracking*.



(13.28)

Pyrolysis of alkanes is believed to be a free radical reaction. Preparation of oil gas or petrol gas from kerosene oil or petrol involves the principle of pyrolysis. For example, dodecane, a constituent of kerosene oil on heating to 973K in the presence of platinum, palladium or nickel gives a mixture of heptane and pentene.

$$\underset{\text{Dodecane}}{C_{12}H_{26}}\xrightarrow[973K]{Pt/Pd/Ni}\underset{\text{Heptane}}{C_7H_{16}}+\underset{\text{Pentene}}{C_5H_{10}}+\text{other products} \qquad (13.29)$$

13.2.4 Conformations

Alkanes contain carbon-carbon sigma (σ) bonds. Electron distribution of the sigma molecular orbital is symmetrical around the internuclear axis of the C–C bond which is not disturbed due to rotation about its axis. This permits free rotation about C–C single bond. This rotation results into different spatial arrangements of atoms in space which can change into one another. Such spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called **conformations** or **conformers** or **rotamers**. Alkanes can thus have infinite number of conformations by rotation around C-C single bonds. However, it may be remembered that rotation around a C-C single bond is not completely free. It is hindered by a small energy barrier of 1-20 kJ mol^{-1} due to weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called **torsional strain**.

Conformations of ethane : Ethane molecule (C_2H_6) contains a carbon – carbon single bond with each carbon atom attached to three hydrogen atoms. Considering the ball and stick model of ethane, keep one carbon atom stationary and rotate the other carbon atom around the C-C axis. This rotation results into infinite number of spatial arrangements of hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms attached to the other carbon atom. These are called **conformational isomers** (conformers). Thus there are infinite number of conformations of ethane. However, there are two extreme cases. One such conformation in which hydrogen atoms attached to two carbons are as closed together as possible is called **eclipsed** conformation and the other in which hydrogens are as far apart as possible is known as the **staggered** conformation. Any other intermediate conformation is called a **skew** conformation.It may be remembered that in all the conformations, the bond angles and the bond lengths remain the same. Eclipsed and the staggered conformations can be represented by **Sawhorse** and **Newman projections**.

1. Sawhorse projections

In this projection, the molecule is viewed along the molecular axis. It is then projected on paper by drawing the central C–C bond as a somewhat longer straight line. Upper end of the line is slightly tilted towards right or left hand side. The front carbon is shown at the lower end of the line, whereas the rear carbon is shown at the upper end. Each carbon has three lines attached to it corresponding to three hydrogen atoms. The lines are inclined at an angle of 120° to each other. Sawhorse projections of eclipsed and staggered conformations of ethane are depicted in Fig. 13.2.

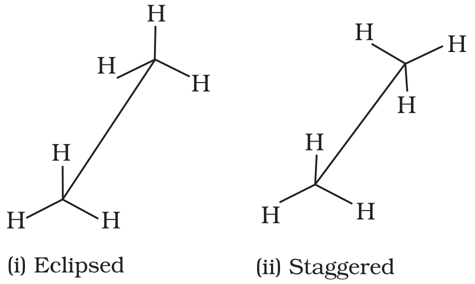


Fig. 13.2 *Sawhorse projections of ethane*

2. Newman projections

In this projection, the molecule is viewed at the C–C bond head on. The carbon atom nearer to the eye is represented by a point. Three hydrogen atoms attached to the front carbon atom are shown by three lines drawn at an angle of 120° to each other. The rear carbon atom (the carbon atom away from the eye) is represented by a circle and the three hydrogen atoms are shown attached to it by the shorter lines drawn at an angle of 120° to each other. The Newman's projections are depicted in Fig. 13.3.

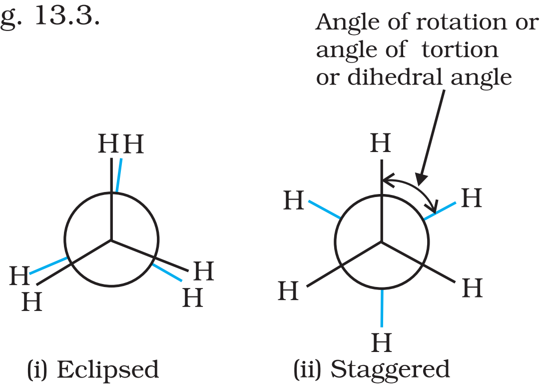


Fig. 13.3 *Newman's projections of ethane*

Relative stability of conformations: As mentioned earlier, in staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive forces, minimum energy and maximum stability of the molecule. On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon – hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions. To check the increased repulsive forces, molecule will have to possess more energy and thus has lesser stability. As already mentioned, the repulsive interaction between the electron clouds, which affects stability of a conformation, is called **torsional strain**. Magnitude of torsional strain depends upon the angle of rotation about C–C bond. This angle is also called **dihedral angle** or **torsional angle**. Of all the conformations of ethane, the *staggered form has the least torsional strain and the eclipsed form, the maximum torsional strain*. Therefore, staggered conformation is more stable than the eclipsed conformation. Hence, molecule largely remains in staggered conformation or we can say that it is preferred conformation. Thus it may be inferred that rotation around C–C bond in ethane is not completely free. The energy difference between the two extreme forms is of the order of 12.5 kJ mol^{-1}, which is very small. Even at ordinary temperatures, the ethane molecule gains thermal or kinetic energy sufficient enough to overcome this energy barrier of 12.5 kJ mol^{-1} through intermolecular collisions. Thus, it can be said that rotation about carbon-carbon single bond in ethane is almost free for all practical purposes. It has not been possible to separate and isolate different conformational isomers of ethane.

13.3 ALKENES

Alkenes are unsaturated hydrocarbons containing at least one double bond. What should be the general formula of alkenes? If there is one double bond between two carbon atoms in alkenes, they must possess two hydrogen atoms less than alkanes. Hence, general formula for alkenes is C_nH_{2n}. Alkenes are also known as olefins (oil forming) since the first member, ethylene or ethene (C_2H_4) was found to form an oily liquid on reaction with chlorine.

13.3.1 Structure of Double Bond

Carbon-carbon double bond in alkenes consists of one strong sigma (σ) bond (bond enthalpy about 397 kJ mol^{-1}) due to head-on overlapping of sp^2 hybridised orbitals and one weak pi (π) bond (bond enthalpy about 284 kJ mol^{-1}) obtained by lateral or sideways overlapping of the two 2*p* orbitals of the two carbon atoms. The double bond is shorter in bond length (134 pm) than the C–C single bond (154 pm). You have already read that the pi (π) bond is a weaker bond due to poor sideways overlapping between the two 2*p* orbitals. Thus, the presence of the pi (π) bond makes alkenes behave as sources of loosely held mobile electrons. Therefore, alkenes are easily attacked by reagents or compounds which are in search of electrons. Such reagents are called **electrophilic reagents**. The presence of weaker π-bond makes alkenes unstable molecules in comparison to alkanes and thus, alkenes can be changed into single bond compounds by combining with the electrophilic reagents. Strength of the double bond (bond enthalpy, 681 kJ mol^{-1}) is greater than that of a carbon-carbon single bond in ethane (bond enthalpy, 348 kJ mol^{-1}). Orbital diagrams of ethene molecule are shown in Figs. 13.4 and 13.5.

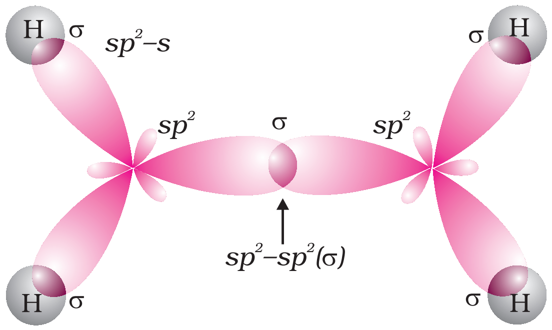
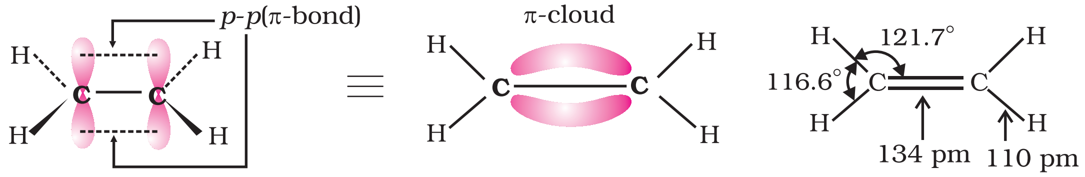


Fig. 13.4 *Orbital picture of ethene depicting σ bonds only*

13.3.2 Nomenclature

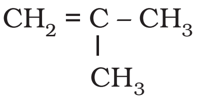
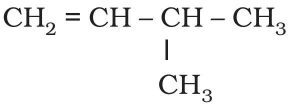
For nomenclature of alkenes in IUPAC system, the longest chain of carbon atoms containing the double bond is selected. Numbering of the chain is done from the end which is nearer to



(a) (b) (c)

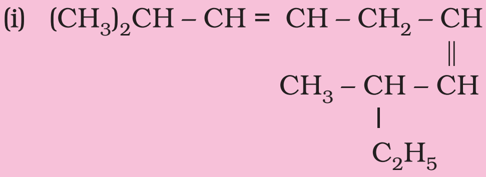
Fig. 13.5 *Orbital picture of ethene showing formation of (a) π-bond, (b) π-cloud and (c) bond angles and bond lengths*

the double bond. The suffix '*ene*' replaces '*ane*' of alkanes. It may be remembered that first member of alkene series is: CH_2 (replacing n by 1 in C_nH_{2n}) known as methene but has a very short life. As already mentioned, first stable member of alkene series is C_2H_4 known as ethylene (common) or ethene (IUPAC). IUPAC names of a few members of alkenes are given below :

Structure	**IUPAC name**
$CH_3-CH=CH_2$	Propene
$CH_3-CH_2-CH=CH_2$	But – 1 - ene
$CH_3-CH=CH–CH_3$	But-2-ene
$CH_2=CH-CH=CH_2$	Buta – 1,3 - diene
 $CH_2=C(CH_3)-CH_3$	2-Methylprop-1-ene
 $CH_2=CH-CH(CH_3)-CH_3$	3-Methylbut-1-ene

Problem 13.7

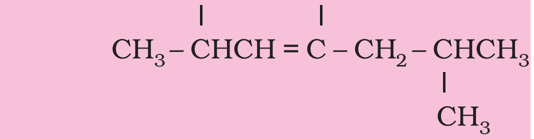
Write IUPAC names of the following compounds:

(i) 

$(CH_3)_2CH-CH=CH-CH_2-CH=CH-CH(C_2H_5)-CH_3$

(ii) 

(iii) $CH_2=C(CH_2CH_2CH_3)_2$

(iv) 

$CH_3-CH(CH_2CH_2CH_2CH_3)-CH=C(CH_2CH_3)-CH_2-CH(CH_3)-CH_3$

Solution

(i) 2,8-Dimethyl-3, 6-decadiene;

(ii) 1,3,5,7 Octatetraene;

(iii) 2-*n*-Propylpent-1-ene;

(iv) 4-Ethyl-2,6-dimethyl-dec-4-ene;

Problem 13.8

Calculate number of sigma (σ) and pi (π) bonds in the above structures (i-iv).

Solution

σ bonds : 33, π bonds : 2

σ bonds : 17, π bonds : 4

σ bonds : 23, π bond : 1

σ bonds : 41, π bond : 1

13.3.3 Isomerism

Alkenes show both structural isomerism and geometrical isomerism.

Structural isomerism : As in alkanes, ethene (C_2H_4) and propene (C_3H_6) can have only one structure but alkenes higher than propene have different structures. Alkenes possessing C_4H_8 as molecular formula can be written in the following three ways:

I. $\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_3$

But-1-ene

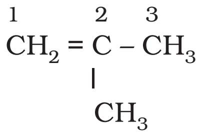
(C_4H_8)

II. $\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_3$

But-2-ene

(C_4H_8)

III.



$$\overset{1}{C}H_2 = \overset{2}{C}(CH_3) - \overset{3}{C}H_3$$

2-Methyprop-1-ene

(C_4H_8)

Structures I and III, and II and III are the examples of **chain isomerism** whereas structures I and II are **position isomers**.

Problem 13.9

Write structures and IUPAC names of different structural isomers of alkenes corresponding to C_5H_{10}.

Solution

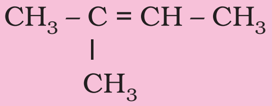
(a) $CH_2 = CH - CH_2 - CH_2 - CH_3$

Pent-1-ene

(b) $CH_3 - CH{=}CH - CH_2 - CH_3$

Pent-2-ene

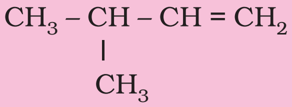
(c)



$$CH_3 - C(CH_3) = CH - CH_3$$

2-Methylbut-2-ene

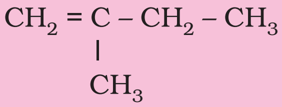
(d)



$$CH_3 - CH(CH_3) - CH = CH_2$$

3-Methylbut-1-ene

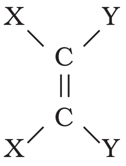
(e)



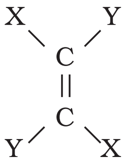
$$CH_2 = C(CH_3) - CH_2 - CH_3$$

2-Methylbut-1-ene

Geometrical isomerism: Doubly bonded carbon atoms have to satisfy the remaining two valences by joining with two atoms or groups. If the two atoms or groups attached to each carbon atom are different, they can be represented by YX C = C XY like structure. YX C = C XY can be represented in space in the following two ways :

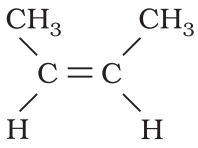


(a)

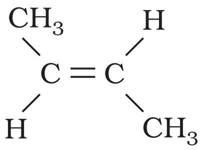


(b)

In (a), the two identical atoms *i.e.*, both the X or both the Y lie on the same side of the double bond but in (b) the two X or two Y lie across the double bond or on the opposite sides of the double bond. This results in different geometry of (a) and (b) i.e. disposition of atoms or groups in space in the two arrangements is different. Therefore, they are **stereoisomers**. They would have the same geometry if atoms or groups around C=C bond can be rotated but rotation around C=C bond is not free. It is restricted. For understanding this concept, take two pieces of strong cardboards and join them with the help of two nails. Hold one cardboard in your one hand and try to rotate the other. Can you really rotate the other cardboard ? The answer is no. The rotation is restricted. This illustrates that the restricted rotation of atoms or groups around the doubly bonded carbon atoms gives rise to different geometries of such compounds. The stereoisomers of this type are called **geometrical isomers**. The isomer of the type (a), in which two identical atoms or groups lie on the same side of the double bond is called ***cis* isomer** and the other isomer of the type (b), in which identical atoms or groups lie on the opposite sides of the double bond is called ***trans* isomer** . Thus *cis* and *trans* isomers have the same structure but have different configuration (arrangement of atoms or groups in space). Due to different arrangement of atoms or groups in space, these isomers differ in their properties like melting point, boiling point, dipole moment, solubility etc. Geometrical or *cis*-*trans* isomers of but-2-ene are represented below :

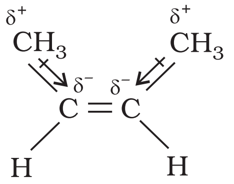


cis-But-2-ene
(b.p. 277 K)

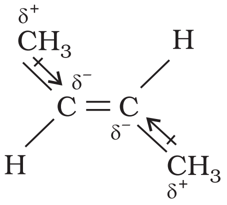


trans-But-2-ene
(b.p. 274 K)

Cis form of alkene is found to be more polar than the *trans* form. For example, dipole moment of *cis*-but-2-ene is 0.33 Debye, whereas, dipole moment of the *trans* form is almost zero or it can be said that *trans*-but-2-ene is non-polar. This can be understood by drawing geometries of the two forms as given below from which it is clear that in the *trans*-but-2-ene, the two methyl groups are in opposite directions, Threfore, dipole moments of C-CH_3 bonds cancel, thus making the *trans* form non-polar.



cis-But-2-ene
(μ = 0.33D)



trans-But-2-ene
(μ = 0)

In the case of solids, it is observed that the *trans* isomer has higher melting point than the *cis* form.

Geometrical or *cis-trans* isomerism is also shown by alkenes of the types XYC = CXZ and XYC = CZW

Problem 13.10

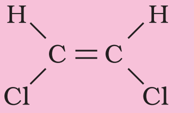
Draw *cis* and *trans* isomers of the following compounds. Also write their IUPAC names :

(i) CHCl = CHCl

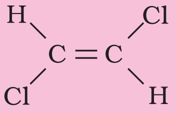
(ii) $C_2H_5CCH_3 = CCH_3C_2H_5$

Solution

(i)

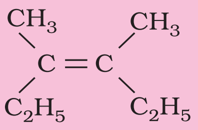


cis-1, 2-Dichloroethene

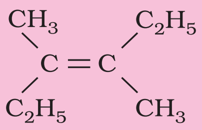


trans-1, 2-Dichloroethene

(ii)



cis-3, 4-Dimethylhex-3-ene



trans-3, 4-Dimethylhex -3-ene

Problem 13.11

Which of the following compounds will show *cis-trans* isomerism?

(i) $(CH_3)_2C = CH - C_2H_5$

(ii) $CH_2 = CBr_2$

(iii) $C_6H_5CH = CH - CH_3$

(iv) $CH_3CH = CCl\ CH_3$

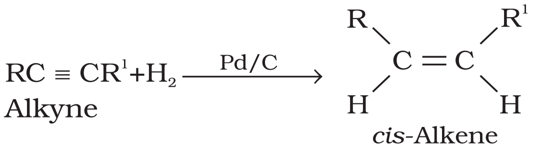
Solution

(iii) and (iv). In structures (i) and (ii), two identical groups are attached to one of the doubly bonded carbon atom.

13.3.4 Preparation

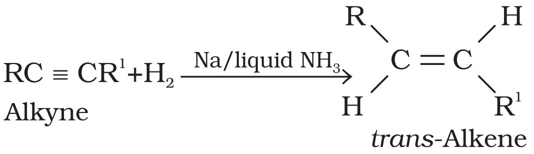
1. ***From alkynes:*** Alkynes on partial reduction with calculated amount of dihydrogen in the presence of *palladised* charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as *Lindlar's catalyst*. Alkenes thus obtained are having *cis* geometry. However, alkynes on reduction with sodium in liquid ammonia form *trans* alkenes.

i)



(13.30)

ii)



(13.31)

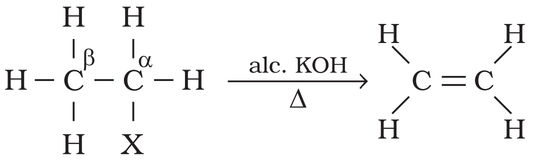
iii) $\underset{\text{Ethyne}}{CH{\equiv}CH+H_2} \xrightarrow{Pd/C} \underset{\text{Ethene}}{CH_2{=}CH_2}$ (13.32)

iv) $\underset{\text{Propyne}}{CH_3{-}C{\equiv}CH+H_2} \xrightarrow{Pd/C} \underset{\text{Propene}}{CH_3{-}CH{=}CH_2}$ (13.33)

Will propene thus obtained show geometrical isomerism? Think for the reason in support of your answer.

2. ***From alkyl halides***: Alkyl halides (R-X) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol,

say, ethanol) eliminate one molecule of halogen acid to form alkenes. This reaction is known as **dehydrohalogenation** i.e., removal of halogen acid. This is example of **β-elimination reaction**, since hydrogen atom is eliminated from the β carbon atom (carbon atom next to the carbon to which halogen is attached).



$$H-\overset{H}{\underset{H}{C_\beta}}-\overset{H}{\underset{X}{C_\alpha}}-H \xrightarrow[\Delta]{\text{alc. KOH}} H_2C=CH_2$$

(X = Cl, Br, I)

(13.34)

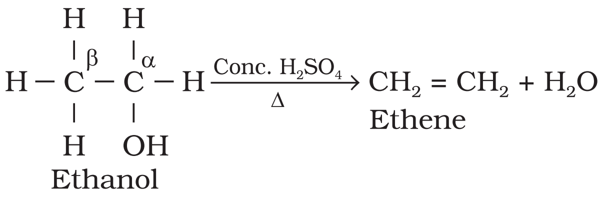
Nature of halogen atom and the alkyl group determine rate of the reaction. It is observed that for halogens, the rate is: iodine > bromine > chlorine, while for alkyl groups it is : tert > secondary > primary.

3. ***From vicinal dihalides:*** Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as *vicinal dihalides*. Vicinal dihalides on treatment with zinc metal lose a molecule of ZnX_2 to form an alkene. This reaction is known as **dehalogenation**.

$$CH_2Br-CH_2Br+Zn \longrightarrow CH_2=CH_2+ZnBr_2 \quad (13.35)$$

$$CH_3CHBr-CH_2Br+Zn \longrightarrow CH_3CH=CH_2 +ZnBr_2 \quad (13.36)$$

4. ***From alcohols by acidic dehydration:*** You have read during nomenclature of different homologous series in Unit 12 that alcohols are the hydroxy derivatives of alkanes. They are represented by R–OH where, R is C_nH_{2n+1}. Alcohols on heating with concentrated sulphuric acid form alkenes with the elimination of one water molecule. Since a water molecule is eliminated from the alcohol molecule in the presence of an acid, this reaction is known as **acidic dehydration of alcohols**. This reaction is also the example of β-elimination reaction since –OH group takes out one hydrogen atom from the β-carbon atom.



$$H-\overset{H}{\underset{H}{C_\beta}}-\overset{H}{\underset{OH}{C_\alpha}}-H \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CH_2=CH_2+H_2O$$

(13.37)

13.3.5 Properties

Physical properties

Alkenes as a class resemble alkanes in physical properties, except in types of isomerism and difference in polar nature. The first three members are gases, the next fourteen are liquids and the higher ones are solids. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents like benzene, petroleum ether. They show a regular increase in boiling point with increase in size *i.e.*, every – CH_2 group added increases boiling point by 20–30 K. Like alkanes, straight chain alkenes have higher boiling point than isomeric branched chain compounds.

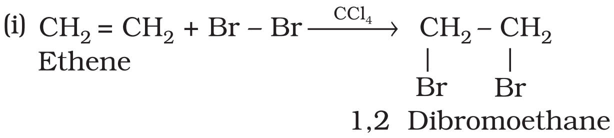
Chemical properties

Alkenes are the rich source of loosely held pi (π) electrons, due to which they show addition reactions in which the electrophiles add on to the carbon-carbon double bond to form the addition products. Some reagents also add by free radical mechanism. There are cases when under special conditions, alkenes also undergo free radical substitution reactions. Oxidation and ozonolysis reactions are also quite prominent in alkenes. A brief description of different reactions of alkenes is given below:

1. ***Addition of dihydrogen:*** Alkenes add up one molecule of dihydrogen gas in the presence of finely divided nickel, palladium or platinum to form alkanes (Section 13.2.2)

2. ***Addition of halogens :*** Halogens like bromine or chlorine add up to alkene to form vicinal dihalides. However, iodine does not show addition reaction under

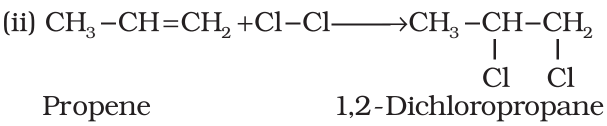
normal conditions. The reddish orange colour of bromine solution in carbon tetrachloride is discharged when bromine adds up to an unsaturation site. This reaction is used as a test for unsaturation. Addition of halogens to alkenes is an example of electrophilic addition reaction involving cyclic halonium ion formation which you will study in higher classes.



$$\text{(i)}\ CH_2=CH_2 + Br-Br \xrightarrow{CCl_4} \underset{Br}{CH_2}-\underset{Br}{CH_2}$$

Ethene 1,2 Dibromoethane

(13.38)



$$\text{(ii)}\ CH_3-CH=CH_2 + Cl-Cl \longrightarrow CH_3-\underset{Cl}{CH}-\underset{Cl}{CH_2}$$

Propene 1,2-Dichloropropane

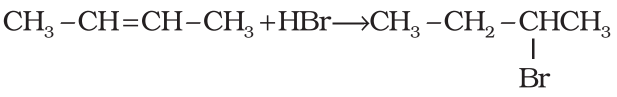
(13.39)

3. ***Addition of hydrogen halides:*** Hydrogen halides (HCl, HBr,HI) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is HI > HBr > HCl. Like addition of halogens to alkenes, addition of hydrogen halides is also an example of electrophilic addition reaction. Let us illustrate this by taking addition of HBr to symmetrical and unsymmetrical alkenes

Addition reaction of HBr to symmetrical alkenes

Addition reactions of HBr to symmetrical alkenes (similar groups attached to double bond) take place by electrophilic addition mechanism.

$$CH_2=CH_2 + H-Br \longrightarrow CH_3-CH_2-Br \qquad (13.40)$$

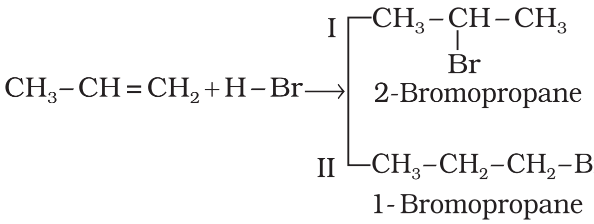


$$CH_3-CH=CH-CH_3 + HBr \longrightarrow CH_3-CH_2-\underset{Br}{CH}CH_3$$

(13.41)

Addition reaction of HBr to unsymmetrical alkenes (Markovnikov Rule)

How will H – Br add to propene ? The two possible products are I and II.



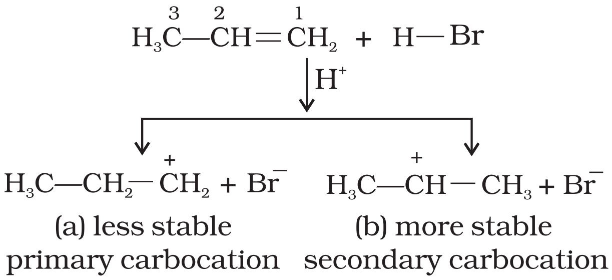
$$CH_3-CH=CH_2 + H-Br \longrightarrow \begin{cases} \text{I}\quad CH_3-\underset{Br}{CH}-CH_3 \quad \text{2-Bromopropane} \\ \text{II}\quad CH_3-CH_2-CH_2-Br \quad \text{1-Bromopropane} \end{cases}$$

(13.42)

Markovnikov, a Russian chemist made a generalisation in 1869 after studying such reactions in detail. These generalisations led Markovnikov to frame a rule called **Markovnikov rule.** The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. Thus according to this rule, product I *i.e.,* 2-bromopropane is expected. In actual practice, this is the principal product of the reaction. This generalisation of Markovnikov rule can be better understood in terms of mechanism of the reaction.

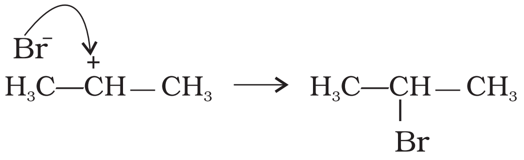
Mechanism

Hydrogen bromide provides an electrophile, H^+, which attacks the double bond to form carbocation as shown below :



(i) The secondary carbocation (b) is more stable than the primary carbocation (a), therefore, the former predominates because it is formed at a faster rate.

(ii) The carbocation (b) is attacked by Br^- ion to form the product as follows :

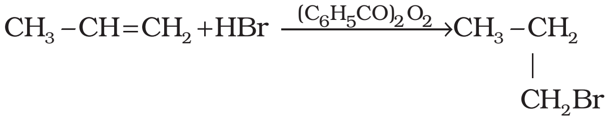


$$Br^- \quad H_3C-\overset{+}{C}H-CH_3 \longrightarrow H_3C-\underset{Br}{CH}-CH_3$$

2-Bromopropane (major product)

Anti Markovnikov addition or peroxide effect or Kharash effect

In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule. This happens only with HBr but not with HCl and HI. This addition reaction was observed by M.S. Kharash and F.R. Mayo in 1933 at the University of Chicago. This reaction is known as *peroxide* or *Kharash* effect or addition reaction anti to Markovnikov rule.

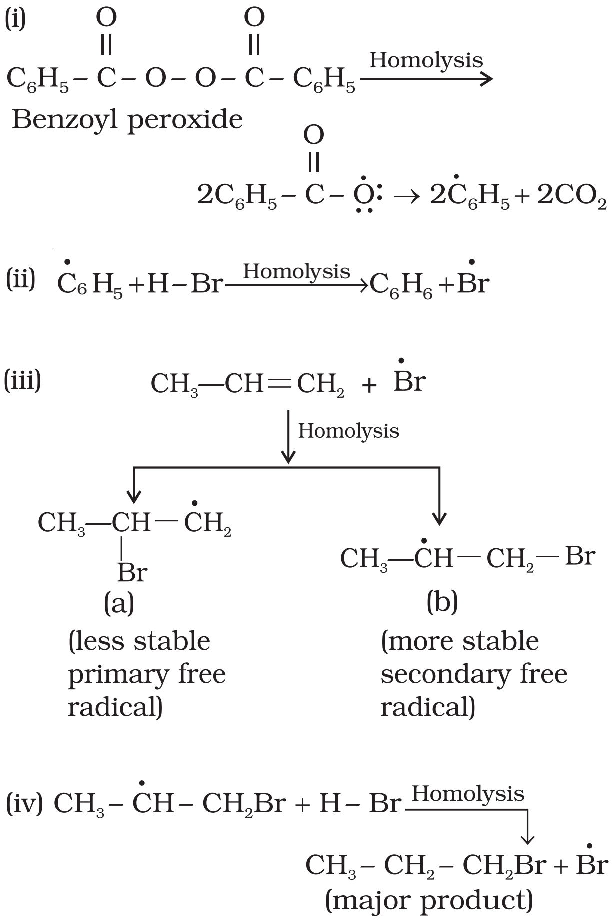


$$CH_3-CH=CH_2+HBr\xrightarrow{(C_6H_5CO)_2O_2}CH_3-\underset{\displaystyle CH_2Br}{\underset{|}{CH_2}}$$

1-Bromopropane

(13.43)

Mechanism : Peroxide effect proceeds via free radical chain mechanism as given below:



(i) $$C_6H_5-\overset{\overset{\displaystyle O}{||}}{C}-O-O-\overset{\overset{\displaystyle O}{||}}{C}-C_6H_5\xrightarrow{\text{Homolysis}}$$

Benzoyl peroxide

$$2C_6H_5-\overset{\overset{\displaystyle O}{||}}{C}-\underset{\cdot\cdot}{\dot{O}}: \rightarrow 2\dot{C}_6H_5+2CO_2$$

(ii) $$\dot{C}_6H_5+H-Br\xrightarrow{\text{Homolysis}}C_6H_6+\dot{Br}$$

(iii) $$CH_3-CH=CH_2+\dot{Br}\xrightarrow{\text{Homolysis}}$$

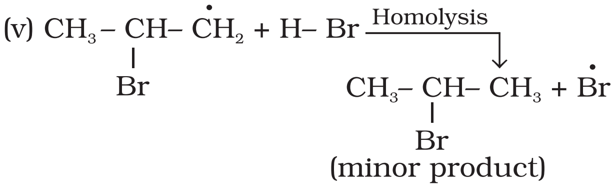
$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\dot{C}H_2 \qquad CH_3-\dot{C}H-CH_2-Br$$

(a) (less stable primary free radical)

(b) (more stable secondary free radical)

(iv) $$CH_3-\dot{C}H-CH_2Br+H-Br\xrightarrow{\text{Homolysis}}CH_3-CH_2-CH_2Br+\dot{Br}$$

(major product)



(v) $$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\dot{C}H_2+H-Br\xrightarrow{\text{Homolysis}}CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3+\dot{Br}$$

(minor product)

The secondary free radical obtained in the above mechanism (step iii) is more stable than the primary. This explains the formation of 1-bromopropane as the major product. It may be noted that the peroxide effect is not observed in addition of HCl and HI. This may be due to the fact that the H–Cl bond being stronger (430.5 kJ mol^{-1}) than H–Br bond (363.7 kJ mol^{-1}), is not cleaved by the free radical, whereas the H–I bond is weaker (296.8 kJ mol^{-1}) and iodine free radicals combine to form iodine molecules instead of adding to the double bond.

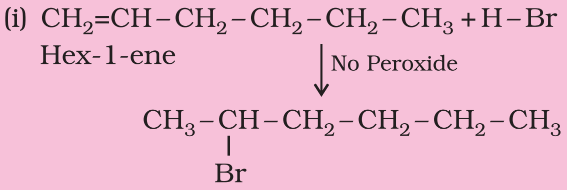
Problem 13.12

Write IUPAC names of the products obtained by addition reactions of HBr to hex-1-ene

(i) in the absence of peroxide and

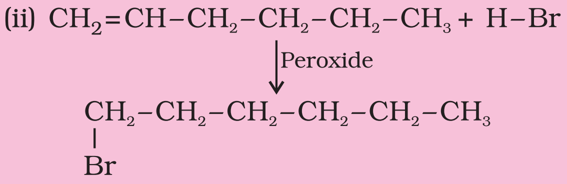
(ii) in the presence of peroxide.

Solution



(i) $$\underset{\text{Hex-1-ene}}{CH_2=CH-CH_2-CH_2-CH_2-CH_3}+H-Br\xrightarrow{\text{No Peroxide}}CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-CH_2-CH_2-CH_3$$

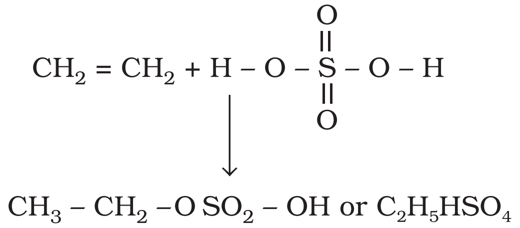
2-Bromohexane



(ii) $$CH_2=CH-CH_2-CH_2-CH_2-CH_3+H-Br\xrightarrow{\text{Peroxide}}\underset{\displaystyle Br}{\underset{|}{CH_2}}-CH_2-CH_2-CH_2-CH_2-CH_3$$

1-Bromohexane

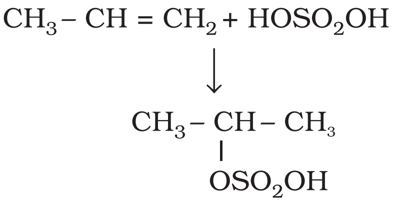
4. ***Addition of sulphuric acid*** : Cold concentrated sulphuric acid adds to alkenes in accordance with Markovnikov rule to form alkyl hydrogen sulphate by the electrophilic addition reaction.



$$CH_2=CH_2+H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-H \longrightarrow CH_3-CH_2-OSO_2-OH \text{ or } C_2H_5HSO_4$$

Ethyl hydrogen sulphate

(13.44)

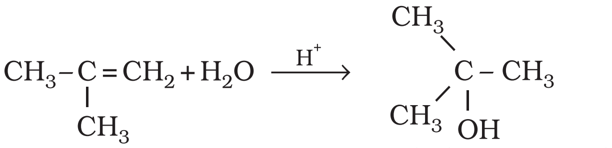


$$CH_3-CH=CH_2+HOSO_2OH \longrightarrow CH_3-\underset{\underset{OSO_2OH}{|}}{CH}-CH_3$$

Propyl hydrogen sulphate

(13.45)

5. ***Addition of water :*** In the presence of a few drops of concentrated sulphuric acid alkenes react with water to form alcohols, in accordance with the Markovnikov rule.

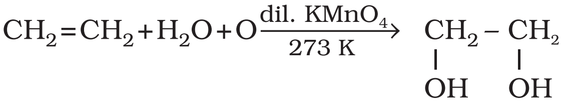


$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2+H_2O \xrightarrow{H^+} (CH_3)_2\underset{\underset{OH}{|}}{C}-CH_3$$

2-Methylpropene 2-Methylpropan-2-ol

(13.46)

6. ***Oxidation:*** Alkenes on reaction with cold, dilute, aqueous solution of potassium permanganate (Baeyer's reagent) produce vicinal glycols. Decolorisation of $KMnO_4$ solution is used as a test for unsaturation.



$$CH_2=CH_2+H_2O+O \xrightarrow[273\text{ K}]{\text{dil. }KMnO_4} \underset{\underset{OH}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH_2}$$

Ethane-1, 2-diol
(Glycol)

(13.47)

$$CH_3-CH=CH_2+H_2O+O \xrightarrow[273\text{ K}]{\text{dil. }KMnO_4} CH_3CH(OH)CH_2OH$$

Propane-1, 2-diol

(13.48)

b) Acidic potassium permanganate or acidic potassium dichromate oxidises alkenes to ketones and/or acids depending upon the nature of the alkene and the experimental conditions

$$(CH_3)_2C=CH_2 \xrightarrow{KMnO_4/H^+} (CH_3)_2C=O + CO_2+H_2O$$

2-Methlypropene Propan-2-one

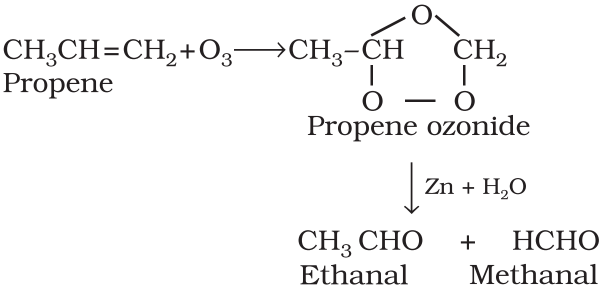
(13.49)

$$CH_3-CH=CH-CH_3 \xrightarrow{KMnO_4/H^+} 2CH_3COOH$$

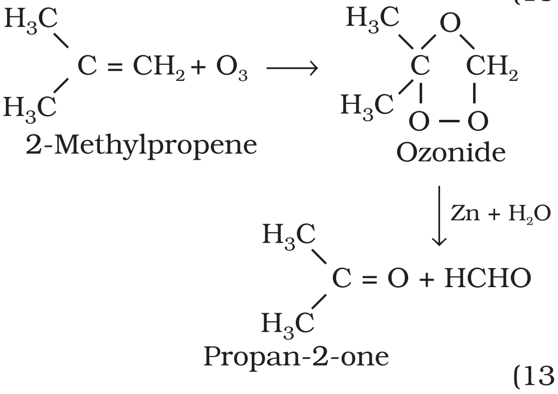
But-2-ene Ethanoic acid

(13.50)

7. ***Ozonolysis*** **:** Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by Zn-H_2O to smaller molecules. This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.



(13.51)



(13.52)

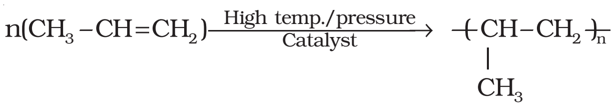
8. ***Polymerisation:*** You are familiar with polythene bags and polythene sheets. Polythene is obtained by the combination of large number of ethene molecules at high temperature, high pressure and in the presence of a catalyst. The large molecules thus obtained are called polymers. This reaction is known as **polymerisation.** The simple compounds from which polymers

are made are called **monomers**. Other alkenes also undergo polymerisation.

$$n(CH_2{=}CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} -\!\!(CH_2-CH_2)\!\!-_n$$

Polythene

(13.53)



$$n(CH_3-CH{=}CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} -\!\!(\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2)\!\!-_n$$

Polypropene

(13.54)

Polymers are used for the manufacture of plastic bags, squeeze bottles, refrigerator dishes, toys, pipes, radio and T.V. cabinets etc. Polypropene is used for the manufacture of milk crates, plastic buckets and other moulded articles. Though these materials have now become common, excessive use of polythene and polypropylene is a matter of great concern for all of us.

13.4 ALKYNES

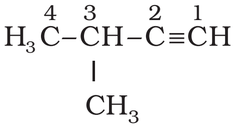
Like alkenes, alkynes are also unsaturated hydrocarbons. They contain at least one triple bond between two carbon atoms. The number of hydrogen atoms is still less in alkynes as compared to alkenes or alkanes. Their general formula is C_nH_{2n-2}.

The first stable member of alkyne series is ethyne which is popularly known as acetylene. Acetylene is used for arc welding purposes in the form of oxyacetylene flame obtained by mixing acetylene with oxygen gas. Alkynes are starting materials for a large number of organic compounds. Hence, it is interesting to study this class of organic compounds.

13.4.1 Nomenclature and Isomerism

In common system, alkynes are named as derivatives of acetylene. In IUPAC system, they are named as derivatives of the corresponding alkanes replacing '*ane*' by the suffix '*yne*'. The position of the triple bond is indicated by the first triply bonded carbon. Common and IUPAC names of a few members of alkyne series are given in Table 13.2.

You have already learnt that ethyne and propyne have got only one structure but there are two possible structures for butyne – (i) but-1-yne and (ii) but-2-yne. Since these two compounds differ in their structures due to the position of the triple bond, they are known as **position isomers**. In how many ways, you can construct the structure for the next homologue i.e., the next alkyne with molecular formula C_5H_8? Let us try to arrange five carbon atoms with a continuous chain and with a side chain. Following are the possible structures :

	Structure	IUPAC name
I.	$H\overset{1}{C}\equiv\overset{2}{C}-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_3$	Pent–1-yne
II.	$H_3\overset{1}{C}-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{C}H_2-\overset{5}{C}H_3$	Pent–2-yne
III.	 $H_3\overset{4}{C}-\underset{\underset{\displaystyle CH_3}{\vert}}{\overset{3}{C}H}-\overset{2}{C}\equiv\overset{1}{C}H$	3-Methylbut–1-yne

Structures I and II are position isomers and structures I and III or II and III are chain isomers.

Problem 13.13

Write structures of different isomers corresponding to the 5th member of alkyne series. Also write IUPAC names of all the isomers. What type of isomerism is exhibited by different pairs of isomers?

Solution

5th member of alkyne has the molecular formula C_6H_{10}. The possible isomers are:

Table 13.2 Common and IUPAC Names of Alkynes (C_nH_{2n-2})

Value of n	Formula	Structure	Common name	IUPAC name
2	C_2H_2	$H-C\equiv CH$	Acetylene	Ethyne
3	C_3H_4	$CH_3-C\equiv CH$	Methylacetylene	Propyne
4	C_4H_6	$CH_3CH_2-C\equiv CH$	Ethylacetylene	But-1-yne
4	C_4H_6	$CH_3-C\equiv C-CH_3$	Dimethylacetylene	But-2-yne

(a) $HC \equiv C - CH_2 - CH_2 - CH_2 - CH_3$

Hex-1-yne

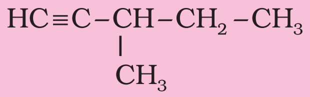
(b) $CH_3 - C \equiv C - CH_2 - CH_2 - CH_3$

Hex-2-yne

(c) $CH_3 - CH_2 - C \equiv C - CH_2 - CH_3$

Hex-3-yne

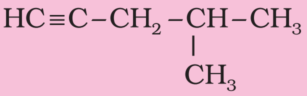
(d)



$$HC\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

3-Methylpent-1-yne

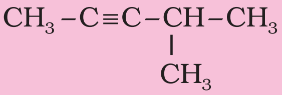
(e)



$$HC\equiv C-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

4-Methylpent-1-yne

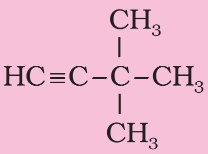
(f)



$$CH_3-C\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

4-Methylpent-2-yne

(g)



$$HC\equiv C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

3,3-Dimethylbut-1-yne

Position and chain isomerism shown by different pairs.

13.4.2 Structure of Triple Bond

Ethyne is the simplest molecule of alkyne series. Structure of ethyne is shown in Fig. 13.6.

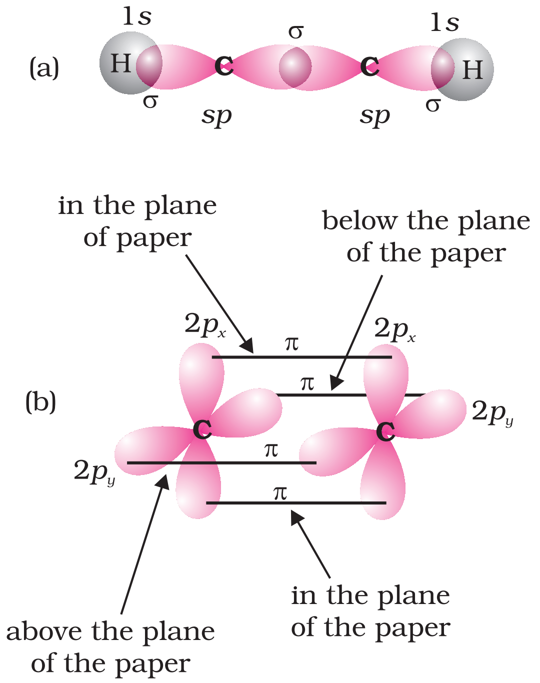


Fig. 13.6 *Orbital picture of ethyne showing (a) sigma overlaps (b) pi overlaps.*

Each carbon atom of ethyne has two *sp* hybridised orbitals. Carbon-carbon sigma (σ) bond is obtained by the head-on overlapping of the two *sp* hybridised orbitals of the two carbon atoms. The remaining *sp* hybridised orbital of each carbon atom undergoes overlapping along the internuclear axis with the 1*s* orbital of each of the two hydrogen atoms forming two C-H sigma bonds. H-C-C bond angle is of 180°. Each carbon has two unhybridised *p* orbitals which are perpendicular to each other as well as to the plane of the C-C sigma bond. The 2*p* orbitals of one carbon atom are parallel to the 2*p* orbitals of the other carbon atom, which undergo lateral or sideways overlapping to form two pi (π) bonds between two carbon atoms. Thus ethyne molecule consists of one C–C σ bond, two C–H σ bonds and two C–C π bonds. The strength of C≡C bond (bond enthalpy 823 kJ mol^{-1}) is more than those of C=C bond (bond enthalpy 681 kJ mol^{-1}) and C–C bond (bond enthalpy 348 kJ mol^{-1}). The C≡C bond length is shorter (120 pm) than those of C=C (133 pm) and C–C (154 pm). Electron cloud between two carbon atoms is cylindrically symmetrical about the internuclear axis. Thus, ethyne is a linear molecule.

13.4.3 Preparation

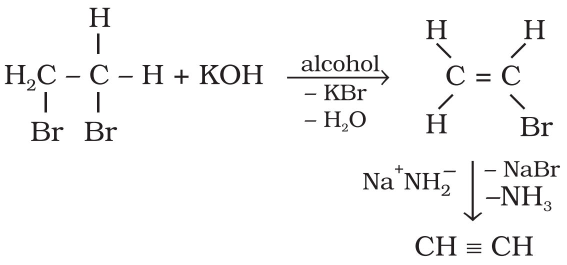
1. *From calcium carbide:* On industrial scale, ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared by heating quick lime with coke. Quick lime can be obtained by heating limestone as shown in the following reactions:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \qquad (13.55)$$

$$CaO + 3C \longrightarrow \underset{\text{Calcium carbide}}{CaC_2} + CO \qquad (13.56)$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2 \qquad (13.57)$$

2. ***From vicinal dihalides :*** Vicinal dihalides on treatment with alcoholic *potassium hydroxide* undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide gives alkyne.



13.4.4 Properties

Physical properties

Physical properties of alkynes follow the same trend of alkenes and alkanes. First three members are gases, the next eight are liquids and the higher ones are solids. All alkynes are colourless. Ethyene has characteristic odour. Other members are odourless. Alkynes are weakly polar in nature. They are lighter than water and immiscible with water but soluble in organic solvents like ethers, carbon tetrachloride and benzene. Their melting point, boiling point and density increase with increase in molar mass.

Chemical properties

Alkynes show acidic nature, addition reactions and polymerisation reactions as follows :

A. Acidic character of alkyne: Sodium metal and sodamide ($NaNH_2$) are strong bases. They react with ethyne to form sodium acetylide with the liberation of dihydrogen gas. These reactions have not been observed in case of ethene and ethane thus indicating that ethyne is acidic in nature in comparison to ethene and ethane. Why is it so ? Has it something to do with their structures and the hybridisation ? You have read that hydrogen atoms in ethyne are attached to the *sp* hybridised carbon atoms whereas they are attached to sp^2 hybridised carbon atoms in ethene and sp^3 hybridised carbons in ethane. Due to the maximum percentage of *s* character (50%), the *sp* hybridised orbitals of carbon atoms in ethyne molecules have highest electronegativity; hence, these attract the shared electron pair of the C-H bond of ethyne to a greater extent than that of the sp^2 hybridised orbitals of carbon in ethene and the sp^3 hybridised orbital of carbon in ethane. Thus in ethyne, hydrogen atoms can be liberated as protons more easily as compared to ethene and ethane. Hence, hydrogen atoms of ethyne attached to triply bonded carbon atom are acidic in nature. You may note that the hydrogen atoms attached to the triply bonded carbons are acidic but not all the hydrogen atoms of alkynes.

$$HC \equiv CH + Na \rightarrow \underset{\text{Monosodium ethynide}}{HC \equiv C^-Na^+} + \tfrac{1}{2}H_2 \qquad (13.59)$$

$$HC \equiv C^-Na^+ + Na \rightarrow \underset{\text{Disodium ethynide}}{Na^+C^- \equiv C^-Na^+} + \tfrac{1}{2}H_2 \qquad (13.60)$$

$$\begin{gathered} CH_3-C\equiv C-H \quad + \quad Na^+NH_2^- \\ \downarrow \\ \underset{\text{Sodium propynide}}{CH_3-C\equiv C^-Na^+} \quad + \quad NH_3 \end{gathered} \qquad (13.61)$$

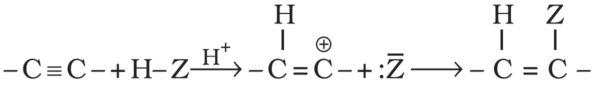
These reactions are not shown by alkenes and alkanes, hence used for distinction between alkynes, alkenes and alkanes. What about the above reactions with but-1-yne and but-2-yne ? Alkanes, alkenes and alkynes follow the following trend in their acidic behaviour :

i) $HC{\equiv}CH > H_2C{=}CH_2 > CH_3{-}CH_3$

ii) $HC{\equiv}CH > CH_3-C{\equiv}CH >> CH_3-C{\equiv}C-CH_3$

B. *Addition reactions*: Alkynes contain a triple bond, so they add up, two molecules of dihydrogen, halogen, hydrogen halides etc.

Formation of the addition product takes place according to the following steps.



$$-C\equiv C- + H-Z \xrightarrow{H^+} -\overset{H}{\underset{}{C}}=\overset{\oplus}{C}- + :\bar{Z} \longrightarrow -\overset{H}{C}=\overset{Z}{C}-$$

Vinylic cation

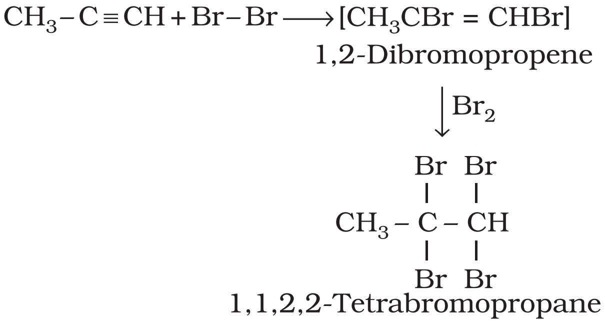
The addition product formed depends upon stability of vinylic cation. Addition in unsymmetrical alkynes takes place according to Markovnikov rule. Majority of the reactions of alkynes are the examples of electrophilic addition reactions. A few addition reactions are given below:

(i) *Addition of dihydrogen*

$$HC\equiv CH + H_2 \xrightarrow{Pt/Pd/Ni} [H_2C=CH_2] \xrightarrow{H_2} CH_3-CH_3 \qquad (13.62)$$

$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propene}}{[CH_3-CH=CH_2]} \xrightarrow{H_2} \underset{\text{Propane}}{CH_3-CH_2-CH_3} \qquad (13.63)$$

(ii) Addition of halogens

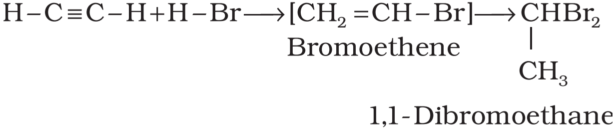


$$CH_3-C\equiv CH + Br-Br \longrightarrow \underset{\text{1,2-Dibromopropene}}{[CH_3CBr=CHBr]} \xrightarrow{Br_2} \underset{\text{1,1,2,2-Tetrabromopropane}}{CH_3-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{CH}}} \qquad (13.64)$$

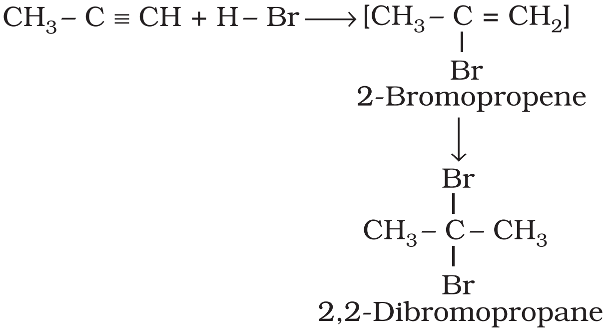
Reddish orange colour of the solution of bromine in carbon tetrachloride is decolourised. This is used as a test for unsaturation.

(iii) Addition of hydrogen halides

Two molecules of hydrogen halides (HCl, HBr, HI) add to alkynes to form *gem* dihalides (in which two halogens are attached to the same carbon atom)



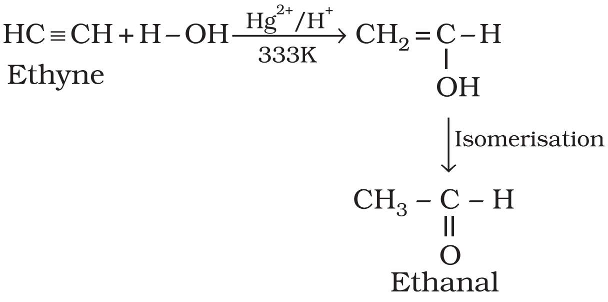
$$H-C\equiv C-H + H-Br \longrightarrow \underset{\text{Bromoethene}}{[CH_2=CH-Br]} \longrightarrow \underset{\text{1,1-Dibromoethane}}{\underset{CH_3}{CHBr_2}} \qquad (13.65)$$



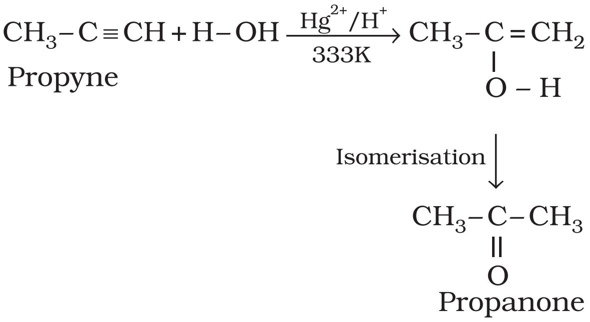
$$CH_3-C\equiv CH + H-Br \longrightarrow \underset{\text{2-Bromopropene}}{[CH_3-\underset{Br}{C}=CH_2]} \longrightarrow \underset{\text{2,2-Dibromopropane}}{CH_3-\overset{Br}{\underset{Br}{C}}-CH_3} \qquad (13.66)$$

(iv) Addition of water

Like alkanes and alkenes, alkynes are also immiscible and do not react with water. However, one molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333 K to form carbonyl compounds.



$$\underset{\text{Ethyne}}{HC\equiv CH} + H-OH \xrightarrow[333K]{Hg^{2+}/H^+} CH_2=\underset{OH}{C}-H \xrightarrow{\text{Isomerisation}} \underset{\text{Ethanal}}{CH_3-\underset{O}{\overset{}{C}}-H} \qquad (13.67)$$



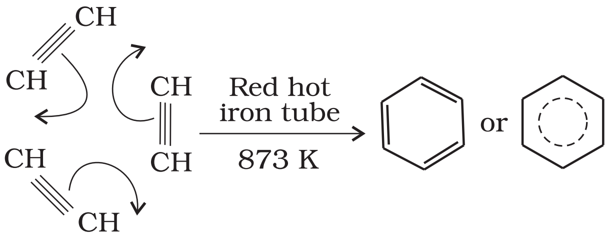
$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + H-OH \xrightarrow[333K]{Hg^{2+}/H^+} CH_3-\underset{O-H}{C}=CH_2 \xrightarrow{\text{Isomerisation}} \underset{\text{Propanone}}{CH_3-\underset{O}{C}-CH_3} \qquad (13.68)$$

(v) Polymerisation

(a) *Linear polymerisation*: Under suitable conditions, linear polymerisation of ethyne takes place to produce polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of $(CH = CH - CH = CH)$ and can be represented as $-\!\left(CH = CH - CH = CH\right)_{n}\!-$ Under special conditions, this polymer conducts electricity.

Thin film of polyacetylene can be used as electrodes in batteries. These films are good conductors, lighter and cheaper than the metal conductors.

(b) ***Cyclic polymerisation:*** Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene, which is the starting molecule for the preparation of derivatives of benzene, dyes, drugs and large number of other organic compounds. This is the best route for entering from aliphatic to aromatic compounds as discussed below:

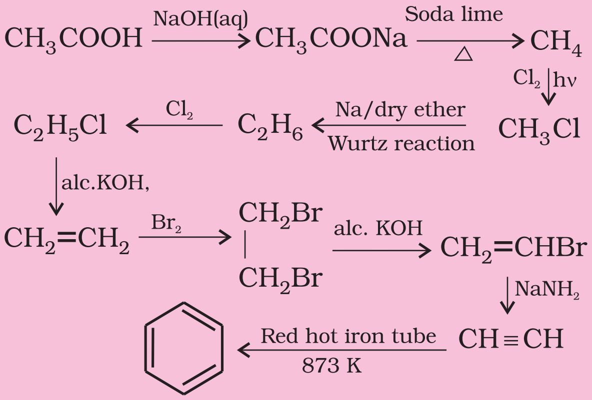


(13.69)

Problem 13.14

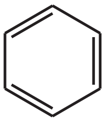
How will you convert ethanoic acid into benzene?

Solution

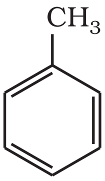


13.5 AROMATIC HYDROCARBON

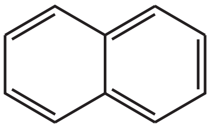
These hydrocarbons are also known as '**arenes**'. Since most of them possess pleasant odour (*Greek; aroma meaning pleasant smelling*), the class of compounds was named as '*aromatic compounds*'. Most of such compounds were found to contain benzene ring. Benzene ring is highly unsaturated but in a majority of reactions of aromatic compounds, the unsaturation of benzene ring is retained. However, there are examples of aromatic hydrocarbons which do not contain a benzene ring but instead contain other highly unsaturated ring. Aromatic compounds containing benzene ring are known as **benzenoids** and those not containing a benzene ring are known as **non-benzenoids**. Some examples of arenes are given below:



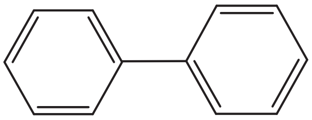
Benzene



Toluene



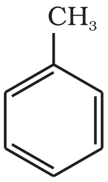
Naphthalene



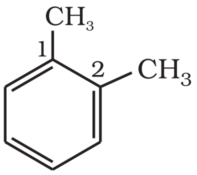
Biphenyl

13.5.1 Nomenclature and Isomerism

The nomenclature and isomerism of aromatic hydrocarbons has already been discussed in Unit 12. All six hydrogen atoms in benzene are equivalent; so it forms one and only one type of monosubstituted product. When two hydrogen atoms in benzene are replaced by two similar or different monovalent atoms or groups, three different position isomers are possible. The 1, 2 or 1, 6 is known as the *ortho* (*o*–), the 1, 3 or 1, 5 *as meta* (*m*–) and the 1, 4 as *para* (*p*–) disubstituted compounds. A few examples of derivatives of benzene are given below:



Methylbenzene
(Toluene)



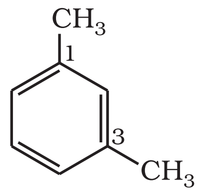
1,2-Dimethylbenzene
(*o*-Xylene)

Friedrich August Kekulé,a German chemist was born in 1829 at Darmsdt in Germany. He became Professor in 1856 and Fellow of Royal Society in 1875. He made major contribution to structural organic chemistry by proposing in 1858 that carbon atoms can join to one another to form chains and later in 1865,he found an answer to the challenging problem of benzene structure by suggesting that these chains can close to form rings. He gave the dynamic structural formula to benzene which forms the basis for its modern electronic structure. He described the discovery of benzene structure later as:

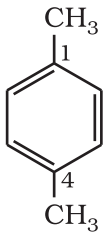
"I was sitting writing at my textbook,but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire, and dozed. Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of this kind, could now distinguish larger structures of manifold conformations; long rows,sometimes more closely fitted together; all twisting and turning in snake like motion. But look! What was that? One of the snakes had seized hold of it's own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I woke;.... I spent the rest of the night working out the consequences of the hypothesis. Let us learn to dream, gentlemen, and then perhaps we shall learn the truth but let us beware of making our dreams public before they have been approved by the waking mind."(1890).

One hundred years later, on the occasion of Kekulé's centenary celebrations a group of compounds having polybenzenoid structures have been named as Kekulenes.

FRIEDRICH AUGUST KEKULÉ (7th September 1829–13th July 1896)



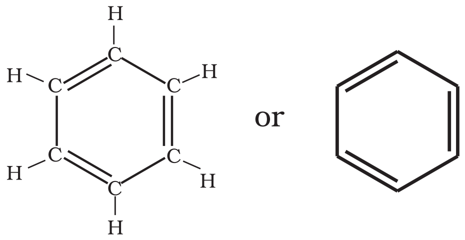
1,3 Dimethylbenzene
(*m*-Xylene)



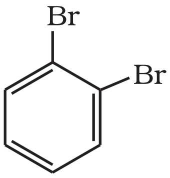
1,4-Dimethylbenzene
(*p*-Xylene)

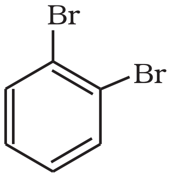
13.5.2 Structure of Benzene

Benzene was isolated by Michael Faraday in 1825. The molecular formula of benzene, C_6H_6, indicates a high degree of unsaturation. This molecular formula did not account for its relationship to corresponding alkanes, alkenes and alkynes which you have studied in earlier sections of this unit. What do you think about its possible structure? Due to its unique properties and unusual stability, it took several years to assign its structure. Benzene was found to be a stable molecule and found to form a triozonide which indicates the presence of three double bonds. Benzene was further found to produce one and only one monosubstituted derivative which indicated that all the six carbon and six hydrogen atoms of benzene are identical. On the basis of this observation August Kekulé in 1865 proposed the following structure for benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom.

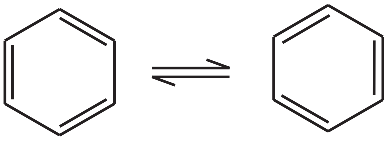


The Kekulé structure indicates the possibility of two isomeric 1, 2-dibromobenzenes. In one of the isomers, the bromine atoms are attached to the doubly bonded carbon atoms whereas in the other, they are attached to the singly bonded carbons.





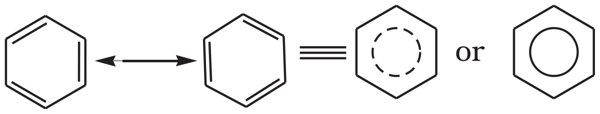
However, benzene was found to form only one ortho disubstituted product. This problem was overcome by Kekulé by suggesting the concept of oscillating nature of double bonds in benzene as given below.



Even with this modification, Kekulé structure of benzene fails to explain unusual stability and preference to substitution reactions than addition reactions, which could later on be explained by resonance.

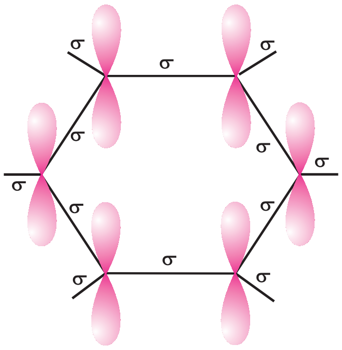
Resonance and stability of benzene

According to Valence Bond Theory, the concept of oscillating double bonds in benzene is now explained by resonance. Benzene is a hybrid of various resonating structures. The two structures, A and B given by Kekulé are the main contributing structures. The hybrid structure is represented by inserting a circle or a dotted circle in the hexagon as shown in (C). The circle represents the six electrons which are delocalised between the six carbon atoms of the benzene ring.



(A) (B) (C)

The orbital overlapping gives us better picture about the structure of benzene. All the six carbon atoms in benzene are sp^2 hybridized. Two sp^2 hybrid orbitals of each carbon atom overlap with sp^2 hybrid orbitals of adjacent carbon atoms to form six C—C sigma bonds which are in the hexagonal plane. The remaining sp^2 hybrid orbital of each carbon atom overlaps with *s* orbital of a hydrogen atom to form six C—H sigma bonds. Each carbon atom is now left with one unhybridised *p* orbital perpendicular to the plane of the ring as shown below:



The unhybridised *p* orbital of carbon atoms are close enough to form a π bond by lateral overlap. There are two equal possibilities of forming three π bonds by overlap of *p* orbitals of C_1 –C_2, $C_3 - C_4$, $C_5 - C_6$ or $C_2 - C_3$, $C_4 - C_5$, $C_6 - C_1$ respectively as shown in the following figures.

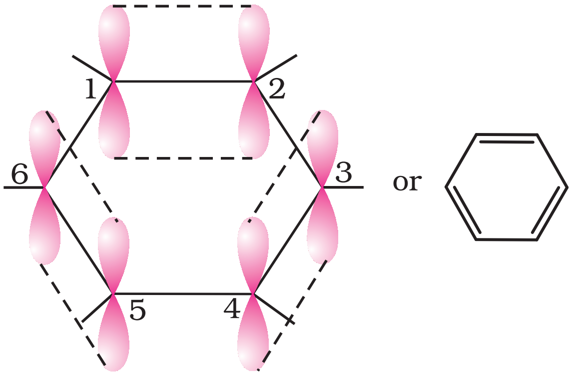


Fig. 13.7 (a)

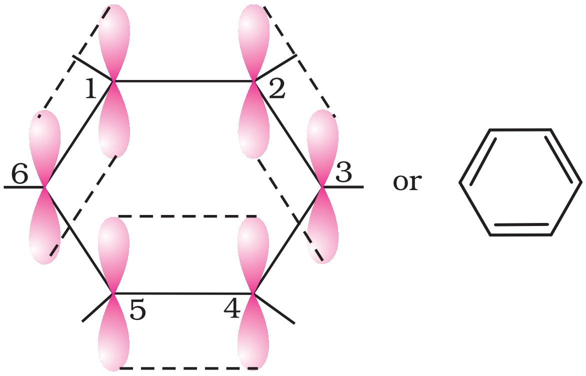


Fig. 13.7 (b)

Structures shown in Fig. 13.7(a) and (b) correspond to two Kekulé's structure with localised π bonds. The internuclear distance between all the carbon atoms in the ring has been determined by the X-ray diffraction to be the same; there is equal probability for the *p* orbital of each carbon atom to overlap with the *p* orbitals of adjacent carbon atoms [Fig. 13.7 (c)]. This can be represented in the form of two doughtnuts (rings) of electron clouds [Fig. 13.7 (d)], one above and one below the plane of the hexagonal ring as shown below:

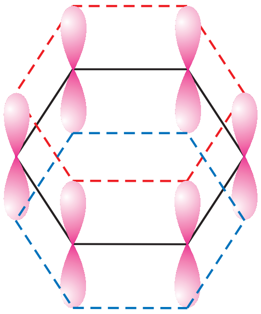
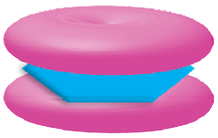


Fig. 13.7 (c)

or



(electron cloud)

Fig. 13.7 (d)

The six π electrons are thus delocalised and can move freely about the six carbon nuclei, instead of any two as shown in Fig. 13.6 (a) or (b). The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localised between two carbon atoms. Therefore, presence of delocalised π electrons in benzene makes it more stable than the hypothetical cyclohexatriene.

X-Ray diffraction data reveals that benzene is a planar molecule. Had any one of the above structures of benzene (A or B) been correct, two types of C—C bond lengths were expected. However, X-ray data indicates that all the six C—C bond lengths are of the same order (139 pm) which is intermediate between C— C single bond (154 pm) and C—C double bond (133 pm). Thus the absence of pure double bond in benzene accounts for the reluctance of benzene to show addition reactions under normal conditions, thus explaining the unusual behaviour of benzene.

13.5.3 Aromaticity

Benzene was considered as parent 'aromatic' compound. Now, the name is applied to all the ring systems whether or not having benzene ring, possessing following characteristics.

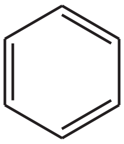
(i) Planarity

(ii) Complete delocalisation of the π electrons in the ring

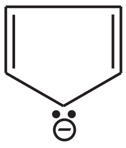
(iii) Presence of $(4n + 2)$ π electrons in the ring where n is an integer ($n = 0, 1, 2, \ldots$).

This is often referred to as **Hückel Rule**.

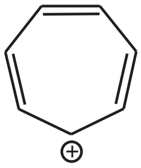
Some examples of aromatic compounds are given below:



Benzene

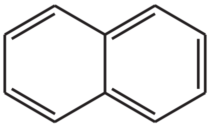


Cyclopentadienyl anion

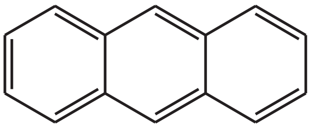


Cycloheptatrienyl cation

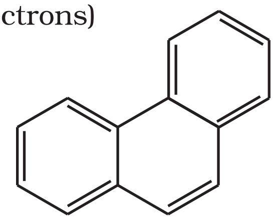
(n=1, 6π electrons)



Naphthalene
(n = 2, 10 π electrons)



Anthracene



Phenanthrene

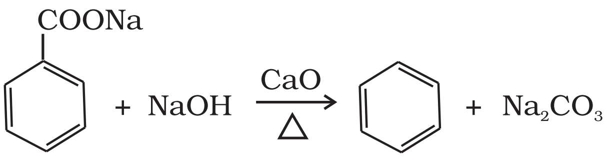
(n =3, 14 π electrons)

13.5.4 Preparation of Benzene

Benzene is commercially isolated from coal tar. However, it may be prepared in the laboratory by the following methods.

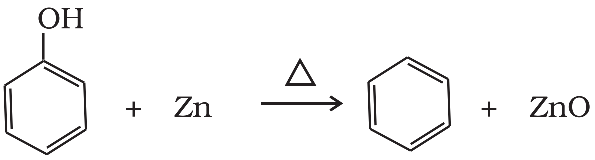
(i) ***Cyclic polymerisation of ethyne:*** (Section 13.4.4)

(ii) ***Decarboxylation of aromatic acids:*** Sodium salt of benzoic acid on heating with sodalime gives benzene.



(13.70)

(iii) ***Reduction of phenol:*** Phenol is reduced to benzene by passing its vapours over heated zinc dust



(13.71)

13.5.5 Properties

Physical properties

Aromatic hydrocarbons are non- polar molecules and are usually colourless liquids or solids with a characteristic aroma. You are also familiar with naphthalene balls which are used in toilets and for preservation of clothes because of unique smell of the compound and the moth repellent property. Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solvents. They burn with sooty flame.

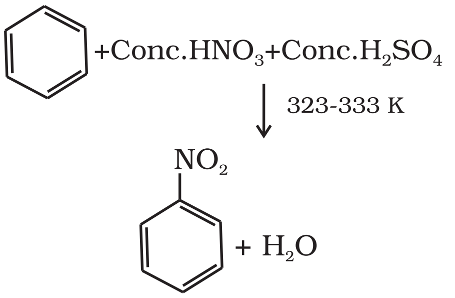
Chemical properties

Arenes are characterised by electrophilic substitution reactions. However, under special conditions they can also undergo addition and oxidation reactions.

Electrophilic substitution reactions

The common electrophilic substitution reactions of arenes are nitration, halogenation, sulphonation, Friedel Craft's alkylation and acylation reactions in which attacking reagent is an electrophile (E^+)

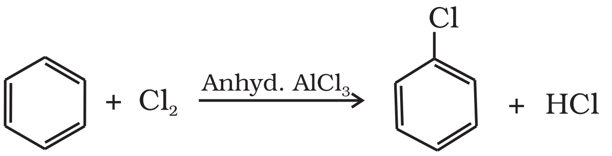
(i) ***Nitration:*** A nitro group is introduced into benzene ring when benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture).



(13.72)

Nitrobenzene

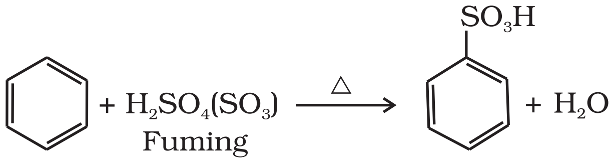
(ii) ***Halogenation:*** Arenes react with halogens in the presence of a Lewis acid like anhydrous $FeCl_3$, $FeBr_3$ or $AlCl_3$ to yield haloarenes.



Chlorobenzene

(13.73)

(iii) ***Sulphonation:*** The replacement of a hydrogen atom by a sulphonic acid group in a ring is called sulphonation. It is carried out by heating benzene with fuming sulphuric acid (oleum).

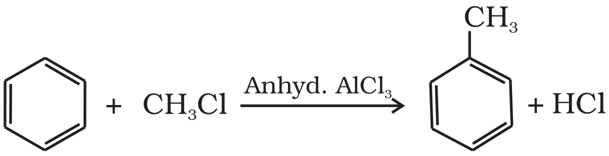


Fuming sulphuric acid

Benzene sulphonic acid

(13.74)

(iv) ***Friedel-Crafts alkylation reaction:*** When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenene is formed.



Toluene

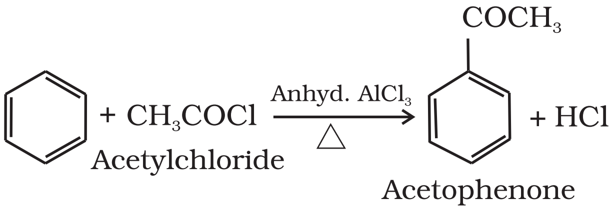
(13.75)

Ethylbenzene

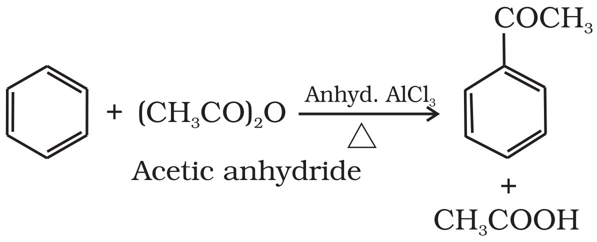
(13.76)

Why do we get isopropyl benzene on treating benzene with 1-chloropropane instead of *n*-propyl benzene?

(v) ***Friedel-Crafts acylation reaction:*** The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids ($AlCl_3$) yields acyl benzene.

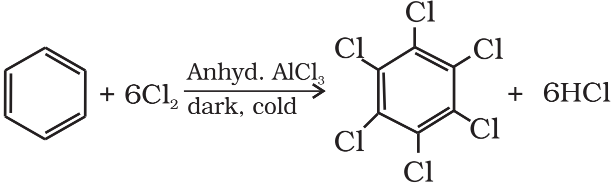


(13.77)



(13.78)

If excess of electrophilic reagent is used, further substitution reaction may take place in which other hydrogen atoms of benzene ring may also be successively replaced by the electrophile. For example, benzene on treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ can be chlorinated to hexachlorobenzene (C_6Cl_6)



Hexachlorobenzene (C_6Cl_6)

(13.79)

Mechanism of electrophilic substitution reactions:

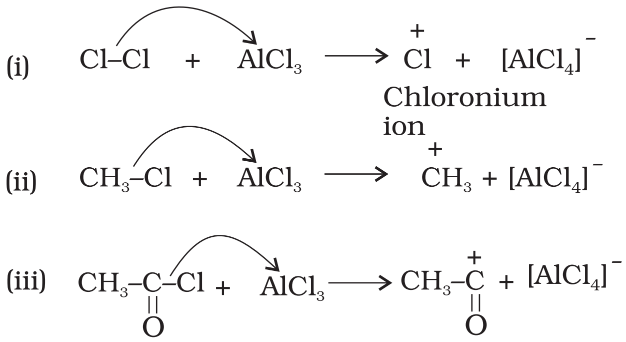
According to experimental evidences, S_E (S = substitution; E = electrophilic) reactions are supposed to proceed via the following three steps:

(a) Generation of the eletrophile

(b) Formation of carbocation intermediate

(c) Removal of proton from the carbocation intermediate

(a) ***Generation of electrophile*** $E^{\oplus}$: During chlorination, alkylation and acylation of benzene, anhydrous $AlCl_3$, being a Lewis acid helps in generation of the elctrophile $Cl^{\oplus}$, $R^{\oplus}$, $R\overset{\oplus}{C}O$ (acylium ion) respectively by combining with the attacking reagent.



$$\text{(i)}\quad Cl\text{–}Cl + AlCl_3 \longrightarrow \overset{+}{Cl} + [AlCl_4]^-$$

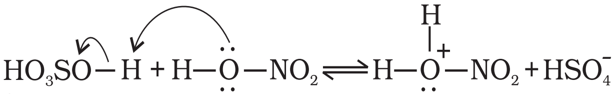
Chloronium ion

$$\text{(ii)}\quad CH_3\text{–}Cl + AlCl_3 \longrightarrow \overset{+}{C}H_3 + [AlCl_4]^-$$

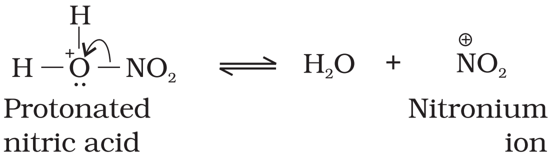
$$\text{(iii)}\quad CH_3\text{–}\underset{\underset{O}{\|}}{C}\text{–}Cl + AlCl_3 \longrightarrow CH_3\text{–}\underset{\underset{O}{\|}}{\overset{+}{C}} + [AlCl_4]^-$$

In the case of nitration, the electrophile, nitronium ion, $\overset{+}{N}O_2$ is produced by transfer of a proton (from sulphuric acid) to nitric acid in the following manner:

Step I

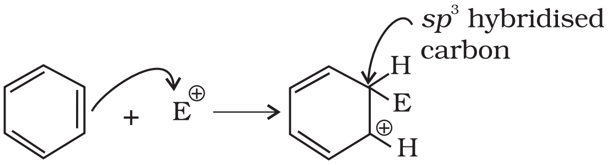


Step II



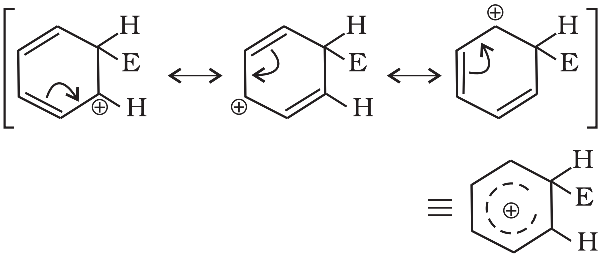
It is interesting to note that in the process of generation of nitronium ion, sulphuric acid serves as an acid and nitric acid as a base. Thus, it is a simple acid-base equilibrium.

(b) ***Formation of Carbocation (arenium ion):*** Attack of electrophile results in the formation of σ-complex or arenium ion in which one of the carbon is sp^3 hybridised.



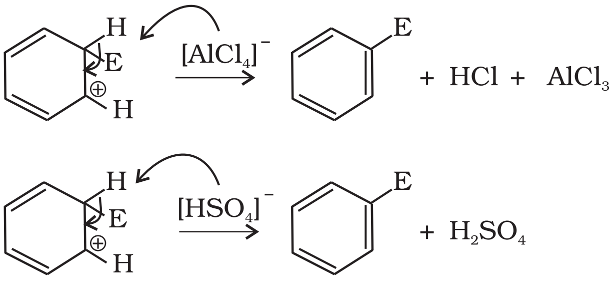
sigma complex (arenium ion)

The arenium ion gets stabilised by resonance:



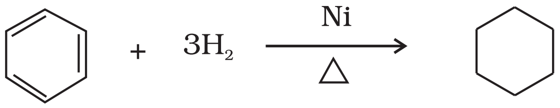
Sigma complex or arenium ion loses its aromatic character because delocalisation of electrons stops at sp^3 hybridised carbon.

(c) ***Removal of proton:*** To restore the aromatic character, σ-complex releases proton from sp^3 hybridised carbon on attack by $[AlCl_4]^-$ (in case of halogenation, alkylation and acylation) and $[HSO_4]^-$ (in case of nitration).



Addition reactions

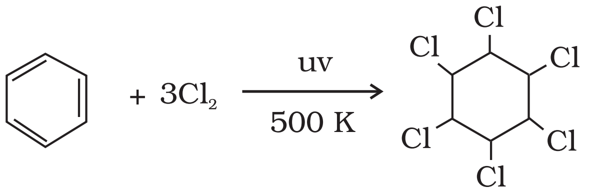
Under vigorous conditions, *i.e.*, at high temperature and/ or pressure in the presence of nickel catalyst, hydrogenation of benzene gives cyclohexane.



Cyclohexane

(13.80)

Under ultra-violet light, three chlorine molecules add to benzene to produce benzene hexachloride, $C_6H_6Cl_6$ which is also called gammaxane.



Benzene hexachloride,
(BHC)

(13.81)

Combustion: When heated in air, benzene burns with sooty flame producing CO_2 and H_2O

$$C_6H_6 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O \qquad (13.82)$$

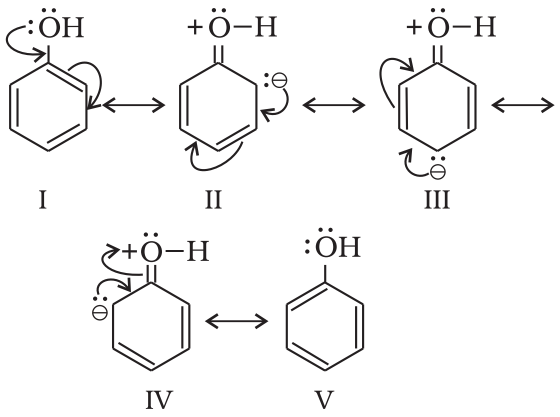
General combustion reaction for any hydrocarbon may be given by the following chemical equation:

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow x\,CO_2 + \frac{y}{2}\,H_2O \qquad (13.83)$$

13.5.6 Directive influence of a functional group in monosubstituted benzene

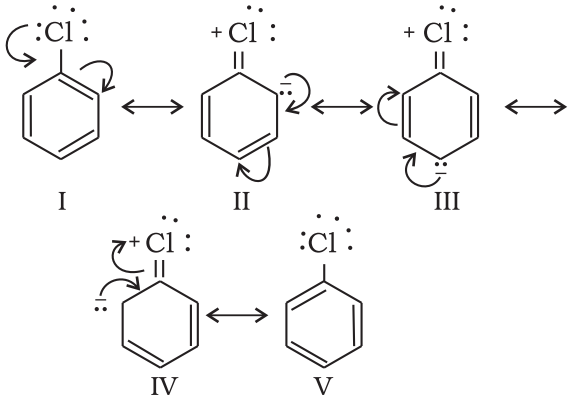
When monosubstituted benzene is subjected to further substitution, three possible disubstituted products are not formed in equal amounts. Two types of behaviour are observed. Either *ortho and para* products or *meta* product is predominantly formed. It has also been observed that this behaviour depends on the nature of the substituent already present in the benzene ring and not on the nature of the entering group. This is known as directive influence of substituents. Reasons for *ortho*/ *para or meta* directive nature of groups are discussed below:

Ortho and para directing groups: The groups which direct the incoming group to *ortho* and *para* positions are called *ortho* and *para* directing groups. As an example, let us discuss the directive influence of phenolic (–OH) group. Phenol is resonance hybrid of following structures:



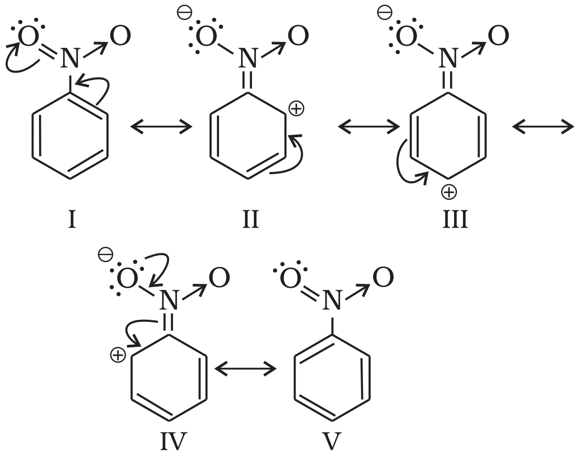
It is clear from the above resonating structures that the electron density is more on *o*– and *p*– positions. Hence, the substitution takes place mainly at these positions. However, it may be noted that –I effect of – OH group also operates due to which the electron density on *ortho* and *para* positions of the benzene ring is slightly reduced. But the overall electron density increases at these positions of the ring due to resonance. Therefore, –OH group **activates** the benzene ring for the attack by an electrophile. Other examples of **activating** groups are $-NH_2$, $-NHR$, $-NHCOCH_3$, $-OCH_3$, $-CH_3$, $-C_2H_5$, etc.

In the case of aryl halides, halogens are moderately **deactivating**. Because of their strong – I effect, overall electron density on benzene ring decreases. It makes further substitution difficult. However, due to resonance the electron density on *o–* and *p–* positions is greater than that at the *m*-position. Hence, they are also *o–* and *p–* directing groups. Resonance structures of chlorobenzene are given below:



***Meta* directing group:** The groups which direct the incoming group to *meta* position are called *meta* directing groups. Some examples of *meta* directing groups are $-NO_2$, $-CN$, $-CHO$, $-COR$, $-COOH$, $-COOR$, $-SO_3H$, etc.

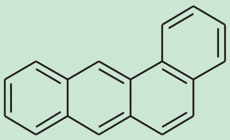
Let us take the example of nitro group. Nitro group reduces the electron density in the benzene ring due to its strong–I effect. Nitrobenzene is a resonance hybrid of the following structures.



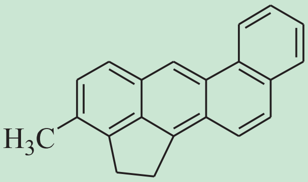
In this case, the overall electron density on benzene ring decreases making further substitution difficult, therefore these groups are also called '**deactivating groups**'. The electron density on *o–* and *p–* position is comparatively less than that at *meta* position. Hence, the electrophile attacks on comparatively electron rich *meta* position resulting in *meta* substitution.

13.6 CARCINOGENICITY AND TOXICITY

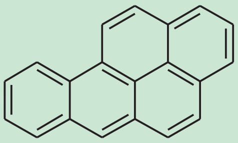
Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property. Such polynuclear hydrocarbons are formed on incomplete combustion of organic materials like tobacco, coal and petroleum. They enter into human body and undergo various biochemical reactions and finally damage DNA and cause cancer. Some of the carcinogenic hydrocarbons are given below (see box).



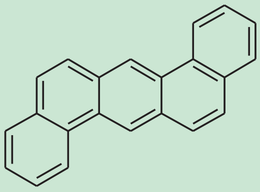
1,2-Benzanthracene



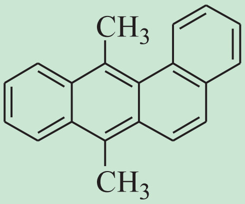
3-Methylcholanthrene



1,2-Benzpyrene



1,2,5,6-Dibenzanthracene



9,10-Dimethyl-1,2-benzanthracene

SUMMARY

Hydrocarbons are the compounds of carbon and hydrogen only. Hydrocarbons are mainly obtained from coal and petroleum, which are the major **sources of energy**. **Petrochemicals** are the prominent starting materials used for the manufacture of a large number of commercially important products. LPG (liquefied petroleum gas) and CNG (compressed natural gas), the main sources of energy for domestic fuels and the automobile industry, are obtained from petroleum. Hydrocarbons are classified as **open chain saturated** (alkanes) and **unsaturated** (alkenes and alkynes), **cyclic** (alicyclic) and **aromatic**, according to their structure.

The important reactions of alkanes are **free radical substitution**, **combustion**, **oxidation** and **aromatization**. Alkenes and alkynes undergo addition reactions, which are mainly **electrophilic additions**. Aromatic hydrocarbons, despite having unsaturation, undergo mainly **electrophilic substitution** reactions. These undergo addition reactions only under special conditions.

Alkanes show conformational isomerism due to free rotation along the C–C sigma bonds. Out of **staggered** and the **eclipsed** conformations of ethane, staggered conformation is more stable as hydrogen atoms are farthest apart. Alkenes exhibit **geometrical (*cis-trans*) isomerism** due to restricted rotation around the carbon–carbon double bond.

Benzene and **benzenoid** compounds show aromatic character. Aromaticity, the property of being aromatic is possessed by compounds having specific electronic structure characterised by Hückel $(4n+2)\pi$ electron rule. The nature of groups or substituents attached to benzene ring is responsible for activation or deactivation of the benzene ring towards further electrophilic substitution and also for orientation of the incoming group. Some of the polynuclear hydrocarbons having fused benzene ring system have carcinogenic property.

EXERCISES

13.1 How do you account for the formation of ethane during chlorination of methane ?

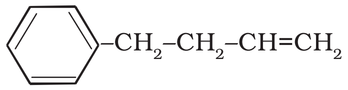
13.2 Write IUPAC names of the following compounds :

(a) $CH_3CH=C(CH_3)_2$

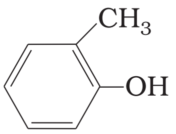
(b) $CH_2=CH-C\equiv C-CH_3$

(c)

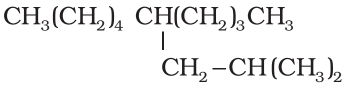
(d)



(e)

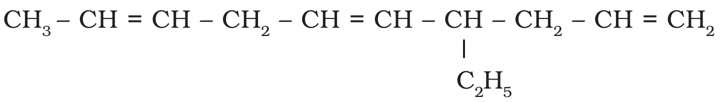


(f)



$CH_3(CH_2)_4\underset{CH_2-CH(CH_3)_2}{CH}(CH_2)_3CH_3$

(g)



$CH_3-CH=CH-CH_2-CH=CH-\underset{C_2H_5}{CH}-CH_2-CH=CH_2$

13.3 For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated :

(a) C_4H_8 (one double bond)

(b) C_5H_8 (one triple bond)

13.4 Write IUPAC names of the products obtained by the ozonolysis of the following compounds :

(i) Pent-2-ene

(ii) 3,4-Dimethylhept-3-ene

(iii) 2-Ethylbut-1-ene

(iv) 1-Phenylbut-1-ene

13.5 An alkene ‘A’ on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of ‘A’.

13.6 An alkene ‘A’ contains three C – C, eight C – H σ bonds and one C – C π bond. ‘A’ on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of ‘A’.

13.7 Propanal and pentan-3-one are the ozonolysis products of an alkene? What is the structural formula of the alkene?

13.8 Write chemical equations for combustion reaction of the following hydrocarbons:

(i)	Butane	(ii)	Pentene
(iii)	Hexyne	(iv)	Toluene

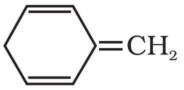
13.9 Draw the *cis* and *trans* structures of hex-2-ene. Which isomer will have higher b.p. and why?

13.10 Why is benzene extra ordinarily stable though it contains three double bonds?

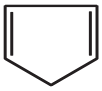
13.11 What are the necessary conditions for any system to be aromatic?

13.12 Explain why the following systems are not aromatic?

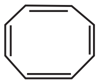
(i)



(ii)



(iii)



13.13 How will you convert benzene into

(i)	*p*-nitrobromobenzene	(ii)	*m*- nitrochlorobenzene
(iii)	*p* - nitrotoluene	(iv)	acetophenone?

13.14 In the alkane $H_3C-CH_2-C(CH_3)_2-CH_2-CH(CH_3)_2$, identify 1°,2°,3° carbon atoms and give the number of H atoms bonded to each one of these.

13.15 What effect does branching of an alkane chain has on its boiling point?

13.16 Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.

13.17 Write down the products of ozonolysis of 1,2-dimethylbenzene (*o*-xylene). How does the result support Kekulé structure for benzene?

13.18 Arrange benzene, *n*-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour.

13.19 Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

13.20 How would you convert the following compounds into benzene?

(i) Ethyne (ii) Ethene (iii) Hexane

13.21 Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

13.22 Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+

(a) Chlorobenzene, 2,4-dinitrochlorobenzene, *p*-nitrochlorobenzene

(b) Toluene, *p*-$H_3C-C_6H_4-NO_2$, *p*-$O_2N-C_6H_4-NO_2$.

13.23 Out of benzene, *m*–dinitrobenzene and toluene which will undergo nitration most easily and why?

13.24 Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.

13.25 Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.

UNIT 14

ENVIRONMENTAL CHEMISTRY

Objectives

After studying this unit, you will be able to

- understand the meaning of environmental chemistry;
- define atmospheric pollution, list reasons for global warming. green house effect and acid rain;
- identify causes for ozone layer depletion and its effects;
- give reasons for water pollution and know about international standards for drinking water;
- describe causes of soil pollution;
- suggest and adopt strategies for control of environmental pollution;
- appreciate the importance of green chemistry in day to day life.

> ***"The world has achieved brilliance without wisdom, power without conscience. Ours is a world of nuclear giants and ethical infants."***

You have already studied about environment in your earlier classes. Environmental studies deal with the sum of all social, economical, biological, physical and chemical interrelations with our surroundings. In this unit the focus will be on environmental chemistry. Environmental chemistry deals with the study of the origin, transport, reactions, effects and fates of chemical species in the environment. Let us discuss some important aspects of environmental chemistry.

14.1 ENVIRONMENTAL POLLUTION

Environmental pollution is the effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings. A substance, which causes pollution, is known as pollutant. Pollutants can be solid, liquid or gaseous substances present in greater concentration than in natural abundance and are produced due to human activities or due to natural happenings. Do you know, an average human being requires nearly 12-15 times more air than the food. So, even small amounts of pollutants in the air become significant compared to similar levels present in the food. Pollutants can be degradable, like discarded vegetables which rapidly break down by natural processes. On the other hand, pollutants which are slowly degradable, remain in the environment in an unchanged form for many decades. For example, substances such as dichlorodiphenyltrichloroethane (DDT), plastic materials, heavy metals, many chemicals, nuclear wastes etc., once released into the environment are difficult to remove. These pollutants cannot be degraded by natural processes and are harmful to living organisms. In the process of environmental pollution, pollutants originate from a source and get transported by air or water or are dumped into the soil by human beings.

14.2 ATMOSPHERIC POLLUTION

The atmosphere that surrounds the earth is not of the same thickness at all heights. There are concentric layers of air or regions and each layer has different density. The lowest region of atmosphere in which the human beings along with other organisms live is called **troposphere**. It extends up to the height of ~ 10 km from sea level. Above the troposphere, between 10 and 50 km above sea level lies **stratosphere**. Troposphere is a turbulent, dusty zone containing air, much water vapour and clouds. This is the region of strong air movement and cloud formation. The stratosphere, on the other hand, contains dinitrogen, dioxygen, ozone and little water vapour.

Atmospheric pollution is generally studied as tropospheric and stratospheric pollution. The presence of ozone in the stratosphere prevents about 99.5 per cent of the sun's harmful ultraviolet (UV) radiations from reaching the earth's surface and thereby protecting humans and other animals from its effect.

14.2.1 Tropospheric Pollution

Tropospheric pollution occurs due to the presence of undesirable solid or gaseous particles in the air. The following are the major gaseous and particulate pollutants present in the troposphere:

1. Gaseous air pollutants: These are oxides of sulphur, nitrogen and carbon, hydrogen sulphide, hydrocarbons, ozone and other oxidants.
2. Particulate pollutants: These are dust, mist, fumes, smoke, smog etc.

1. Gaseous air pollutants

(a) Oxides of Sulphur: Oxides of sulphur are produced when sulphur containing fossil fuel is burnt. The most common species, sulphur dioxide, is a gas that is poisonous to both animals and plants. It has been reported that even a low concentration of sulphur dioxide causes respiratory diseases e.g., asthma, bronchitis, emphysema in human beings. Sulphur dioxide causes irritation to the eyes, resulting in tears and redness. High concentration of SO_2 leads to stiffness of flower buds which eventually fall off from plants. Uncatalysed oxidation of sulphur dioxide is slow. However, the presence of particulate matter in polluted air catalyses the oxidation of sulphur dioxide to sulphur trioxide.

$$2SO_2\,(g) + O_2\,(g) \rightarrow 2SO_3(g)$$

The reaction can also be promoted by ozone and hydrogen peroxide.

$$SO_2\,(g) + O_3\,(g) \rightarrow SO_3(g) + O_2\,(g)$$

$$SO_2(g) + H_2O_2(l) \rightarrow H_2SO_4(aq)$$

(b) Oxides of Nitrogen: Dinitrogen and dioxygen are the main constituents of air. These gases do not react with each other at a normal temperature. At high altitudes when lightning strikes, they combine to form oxides of nitrogen. NO_2 is oxidised to nitrate ion, NO_3^- which is washed into soil, where it serves as a fertilizer. In an automobile engine, (at high temperature) when fossil fuel is burnt, dinitrogen and dioxygen combine to yield significant quantities of nitric oxide (NO) and nitrogen dioxide (NO_2) as given below:

$$N_2\,(g) + O_2\,(g) \xrightarrow{1483K} 2NO(g)$$

NO reacts instantly with oxygen to give NO_2

$$2NO\,(g) + O_2\,(g) \rightarrow 2NO_2\,(g)$$

Rate of production of NO_2 is faster when nitric oxide reacts with ozone in the stratosphere.

$$NO\,(g) + O_3\,(g) \rightarrow NO_2\,(g) + O_2\,(g)$$

The irritant red haze in the traffic and congested places is due to oxides of nitrogen. Higher concentrations of NO_2 damage the leaves of plants and retard the rate of photosynthesis. Nitrogen dioxide is a lung irritant that can lead to an acute respiratory disease in children. It is toxic to living tissues also. Nitrogen dioxide is also harmful to various textile fibres and metals.

(c) Hydrocarbons: Hydrocarbons are composed of hydrogen and carbon only and are formed by incomplete combustion of fuel used in automobiles. Hydrocarbons are carcinogenic, *i.e.*, they cause cancer. They harm plants by causing ageing, breakdown of tissues and shedding of leaves, flowers and twigs.

(d) Oxides of Carbon

(i) Carbon monoxide: Carbon monoxide (CO) is one of the most serious air pollutants. It is a colourless and odourless gas, highly poisonous to living beings because of its ability to block the delivery of oxygen to the organs and tissues. It is produced as a result of incomplete combustion of carbon. Carbon monoxide is mainly released into the air by automobile exhaust. Other sources, which produce CO, involve incomplete combustion of coal, firewood, petrol, etc. The number of vehicles has been increasing over the years all over the world. Many vehicles are poorly maintained and several have inadequate pollution control equipments resulting in the release of greater amount of carbon monoxide and other polluting gases. Do you know why carbon monoxide is poisonous? It binds to haemoglobin to form carboxyhaemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. In blood, when the concentration of carboxyhaemoglobin reaches about 3–4 per cent, the oxygen carrying capacity of blood is greatly reduced. This oxygen deficiency, results into headache, weak eyesight, nervousness and cardiovascular disorder. This is the reason why people are advised not to smoke. In pregnant women who have the habit of smoking the increased CO level in blood may induce premature birth, spontaneous abortions and deformed babies.

(ii) Carbon dioxide: Carbon dioxide (CO_2) is released into the atmosphere by respiration, burning of fossil fuels for energy, and by decomposition of limestone during the manufacture of cement. It is also emitted during volcanic eruptions. Carbon dioxide gas is confined to troposphere only. Normally it forms about 0.03 per cent by volume of the atmosphere. With the increased use of fossil fuels, a large amount of carbon dioxide gets released into the atmosphere. Excess of CO_2 in the air is removed by green plants and this maintains an appropriate level of CO_2 in the atmosphere. Green plants require CO_2 for photosynthesis and they, in turn, emit oxygen, thus maintaining the delicate balance. As you know, deforestation and burning of fossil fuel increases the CO_2 level and disturb the balance in the atmosphere. The increased amount of CO_2 in the air is mainly responsible for global warming.

Global Warming and Greenhouse Effect

About 75 % of the solar energy reaching the earth is absorbed by the earth's surface, which increases its temperature. The rest of the heat radiates back to the atmosphere. Some of the heat is trapped by gases such as carbon dioxide, methane, ozone, chlorofluorocarbon compounds (CFCs) and water vapour in the atmosphere. Thus, they add to the heating of the atmosphere. This causes global warming.

We all know that in cold places flowers, vegetables and fruits are grown in glass covered areas called greenhouse. Do you know that we humans also live in a greenhouse? Of course, we are not surrounded by glass but a blanket of air called the atmosphere, which has kept the temperature on earth constant for centuries. But it is now undergoing change, though slowly. Just as the glass in a greenhouse holds the sun's warmth inside, atmosphere traps the sun's heat near the earth's surface and keeps it warm. This is called *natural greenhouse effect* because it maintains the temperature and makes the earth perfect for life. In a greenhouse, solar radiations pass through the transparent glass and heat up the soil and the plants. The warm soil and plants emit infrared radiations. Since glass is opaque to infrared radiations (thermal region), it partly reflects and partly absorbs these radiations. This mechanism keeps the energy of the sun trapped in the greenhouse. Similarly, carbon dioxide molecules also trap heat as they are transparent to sunlight but not to the heat radiation. If the amount of carbon dioxide crosses the delicate proportion of 0.03 per cent, the natural greenhouse balance may get disturbed. Carbon dioxide is the major contributor to global warming.

Besides carbon dioxide, other greenhouse gases are methane, water vapour, nitrous oxide, CFCs and ozone. Methane is produced naturally when vegetation is burnt, digested or rotted in the absence of oxygen. Large amounts of methane are released in paddy fields, coal mines, from rotting garbage dumps and by fossil fuels. Chlorofluorocarbons (CFCs) are man-made industrial chemicals used in air conditioning etc. CFCs are also damaging the ozone layer (Section 14.2.2). Nitrous oxide occurs naturally in the environment. In recent years, their quantities have increased significantly due to the use of chemical fertilizers and the burning of fossil fuels. If these trends continue, the average global temperature will increase to a level which may lead to melting of polar ice caps and flooding of low lying areas all over the earth. Increase in the global temperature increases the incidence of infectious diseases like dengue, malaria, yellow fever, sleeping sickness etc.

Think it Over

What can we do to reduce the rate of global warming?

If burning of fossil fuels, cutting down forests and trees add to greenhouse gases in the atmosphere, we must find ways to use these just efficiently and judiciously. One of the simple things which we can do to reduce global warming is to minimise the use of automobiles. Depending upon the situation, one can use bicycle, public transport system, or go for carpool. We should plant more trees to increase the green cover. Avoid burning of dry leaves, wood etc. It is illegal to smoke in public places and work places, because it is harmful not only for the one who is smoking but also for others, and therefore, we should avoid it. Many people do not understand the greenhouse effect and the global warming. We can help them by sharing the information that we have.

Acid rain

We are aware that normally rain water has a pH of 5.6 due to the presence of H^+ ions formed by the reaction of rain water with carbon

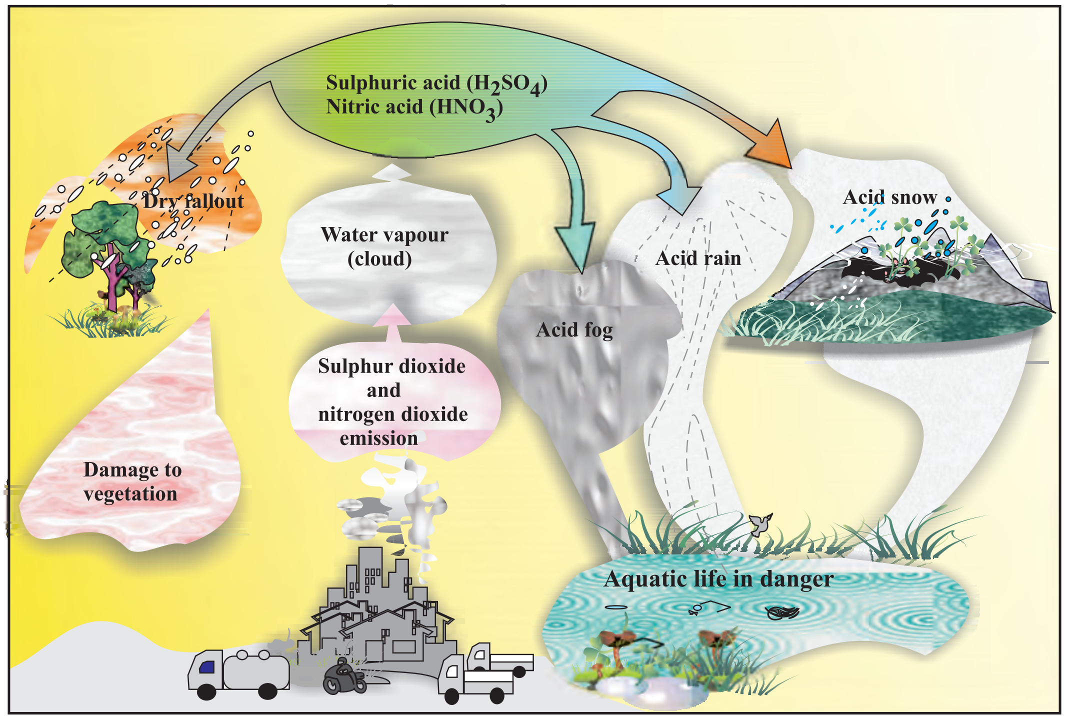


Fig. 14.1 *Acid deposition*

dioxide present in the atmosphere.

$$H_2O\,(l) + CO_2\,(g) \rightleftharpoons H_2CO_3\,(aq)$$

$$H_2CO_3\,(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

When the pH of the rain water drops below 5.6, it is called acid rain.

Acid rain refers to the ways in which acid from the atmosphere is deposited on the earth's surface. Oxides of nitrogen and sulphur which are acidic in nature can be blown by wind along with solid particles in the atmosphere and finally settle down either on the ground as dry deposition or in water, fog and snow as wet deposition. (Fig. 14.1)

Acid rain is a byproduct of a variety of human activities that emit the oxides of sulphur and nitrogen in the atmosphere. As mentioned earlier, burning of fossil fuels (which contain sulphur and nitrogenous matter) such as coal and oil in power stations and furnaces or petrol and diesel in motor engines produce sulphur dioxide and nitrogen oxides. SO_2 and NO_2 after oxidation and reaction with water are major contributors to acid rain, because polluted air usually contains particulate matter that catalyse the oxidation.

$$2SO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \rightarrow 2H_2SO_4\,(aq)$$

$$4NO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \rightarrow 4HNO_3\,(aq)$$

Ammonium salts are also formed and can be seen as an atmospheric haze (aerosol of fine particles). Aerosol particles of oxides or ammonium salts in rain drops result in wet-deposition. SO_2 is also absorbed directly on both solid and liquid ground surfaces and is thus deposited as dry-deposition.

Acid rain is harmful for agriculture, trees and plants as it dissolves and washes away nutrients needed for their growth. It causes respiratory ailments in human beings and animals. When acid rain falls and flows as ground water to reach rivers, lakes etc. it affects plants and animal life in aquatic ecosystem. It corrodes water pipes resulting in the leaching of heavy metals such as iron, lead and copper into the drinking water. Acid rain damages buildings and other structures made of stone or metal. The Taj Mahal in India has been affected by acid rain.

Activity 1

You can collect samples of water from nearby places and record their pH values. Discuss your results in the class. Let us discuss how we can help to reduce the formation of acid rain.

This can be done by reducing the emission of sulphur dioxide and nitrogen dioxide in the atmosphere. We should use less vehicles driven by fossil fuels; use less sulphur content fossil fuels for power plants and industries. We should use natural gas which is a better fuel than coal or use coal with less sulphur content. Catalytic converters must be used in cars to reduce the effect of exhaust fumes on the atmosphere. The main component of the converter is a ceramic honeycomb coated with precious metals — Pd, Pt and Rh. The exhaust gases containing unburnt fuel, CO and NO_x, when pass through the converter at 573 K, are converted into CO_2 and N_2. We can also reduce the acidity of the soil by adding powdered limestone to neutralise the acidity of the soil. Many people do not know of acid rain and its harmful effects. We can make them aware by passing on this information and save the Nature.

Taj Mahal and Acid Rain

The air around the city of Agra, where the Taj Mahal is located, contains fairly high levels of sulphur and nitrogen oxides. It is mainly due to a large number of industries and power plants around the area. Use of poor quality of coal, kerosene and firewood as fuel for domestic purposes add up to this problem. The resulting acid rain reacts with marble, $CaCO_3$ of Taj Mahal ($CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$) causing damage to this wonderful monument that has attracted people from around the world. As a result, the monument is being slowly disfigured and the marble is getting discoloured and lustreless. The Government of India announced an action plan in early 1995 to prevent the disfiguring of this historical monument. Mathura refinery has already taken suitable measures to check the emission of toxic gases.

This plan aims at clearing the air in the **'Taj Trapezium'**– an area that includes the towns of Agra, Firozabad, Mathura and Bharatpur. Under this plan more than 2000 polluting industries lying inside the trapezium would switch over to the use of natural gas or liquefied petroleum gas instead of coal or oil. A new natural gas pipeline would bring more than half a million cubic metres of natural gas a day to this area. People living in the city will also be encouraged to use liquefied petroleum gas in place of coal, kerosene or firewood. Vehicles plying on highways in the vicinity of Taj would be encouraged to use low sulphur content diesel.

2. Particulate Pollutants

Particulates pollutants are the minute solid particles or liquid droplets in air. These are present in vehicle emissions, smoke particles from fires, dust particles and ash from industries. Particulates in the atmosphere may be viable or non-viable. The viable particulates *e.g.*, bacteria, fungi, moulds, algae etc., are minute living organisms that are dispersed in the atmosphere. Human beings are allergic to some of the fungi found in air. They can also cause plant diseases.

Non-viable particulates may be classified according to their nature and size as follows:

(a) Smoke particulates consist of solid or mixture of solid and liquid particles formed during combustion of organic matter. Examples are cigarette smoke, smoke from burning of fossil fuel, garbage and dry leaves, oil smoke etc.

(b) Dust is composed of fine solid particles (over 1μm in diameter), produced during crushing, grinding and attribution of solid materials. Sand from sand blasting, saw dust from wood works, pulverized coal, cement and fly ash from factories, dust storms etc., are some typical examples of this type of particulate emission.

(c) Mists are produced by particles of spray liquids and by condensation of vapours in air. Examples are sulphuric acid mist and herbicides and insecticides that miss their targets and travel through air and form mists.

(d) Fumes are generally obtained by the condensation of vapours during sublimation, distillation, boiling and several other chemical reactions. Generally, organic solvents, metals and metallic oxides form fume particles.

The effect of particulate pollutants are largely dependent on the particle size. Air-borne particles such as dust, fumes, mist etc., are dangerous for human health. Particulate pollutants bigger than 5 microns are likely to lodge in the nasal passage, whereas particles of about 10 micron enter into lungs easily.

Lead used to be a major air pollutant emitted by vehicles. Leaded petrol used to be the primary source of air-borne lead emission in Indian cities. This problem has now been overcome by using unleaded petrol in most of the cities in India. Lead interferes with the development and maturation of red blood cells.

Smog

The word smog is derived from smoke and fog. This is the most common example of air pollution that occurs in many cities throughout the world. There are two types of smog:

(a) Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and sulphur dioxide. Chemically it is a reducing mixture and so it is also called as reducing smog.

(b) Photochemical smog occurs in warm, dry and sunny climate. The main components of the photochemical smog result from the action of sunlight on unsaturated hydrocarbons and nitrogen oxides produced by automobiles and factories. Photochemical smog has high concentration of oxidising agents and is, therefore, called as oxidising smog.

Formation of photochemical smog

When fossil fuels are burnt, a variety of pollutants are emitted into the earth's troposphere. Two of the pollutants that are emitted are hydrocarbons (unburnt fuels) and nitric oxide (NO). When these pollutants build up to sufficiently high levels, a chain reaction occurs from their interaction with sunlight in which NO is converted into nitrogen dioxide (NO_2). This NO_2 in turn absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atom (Fig. 14.2).

$$NO_2(g) \xrightarrow{h\nu} NO(g) + O(g) \qquad \text{(i)}$$

Oxygen atoms are very reactive and combine with the O_2 in air to produce ozone.

$$O(g) + O_2(g) \rightleftharpoons O_3(g) \qquad \text{(ii)}$$

The ozone formed in the above reaction (ii) reacts rapidly with the NO(g) formed in the reaction (i) to regenerate NO_2. NO_2 is a brown gas and at sufficiently high levels can contribute to haze.

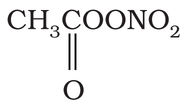
$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \qquad \text{(iii)}$$

Ozone is a toxic gas and both NO_2 and O_3 are strong oxidising agents and can react with the unburnt hydrocarbons in the polluted air to produce chemicals such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN).

$$3CH_4 + 2O_3 \rightarrow \underset{\text{Formaldehyde}}{3CH_2=O} + 3H_2O$$

$CH_2=CHCH=O$

Acrolein



$$CH_3\underset{\underset{O}{\parallel}}{C}OONO_2$$

Peroxyacetyl nitrate (PAN)

Effects of photochemical smog

The common components of photochemical smog are ozone, nitric oxide, acrolein, formaldehyde and peroxyacetyl nitrate (PAN). Photochemical smog causes serious health problems. Both ozone and PAN act as powerful eye irritants. Ozone and nitric oxide irritate the nose and throat and their high concentration causes headache, chest pain, dryness of the throat, cough and difficulty in breathing. Photochemical smog leads to cracking of rubber and extensive damage to plant life. It also causes corrosion of metals, stones, building materials, rubber and painted surfaces.

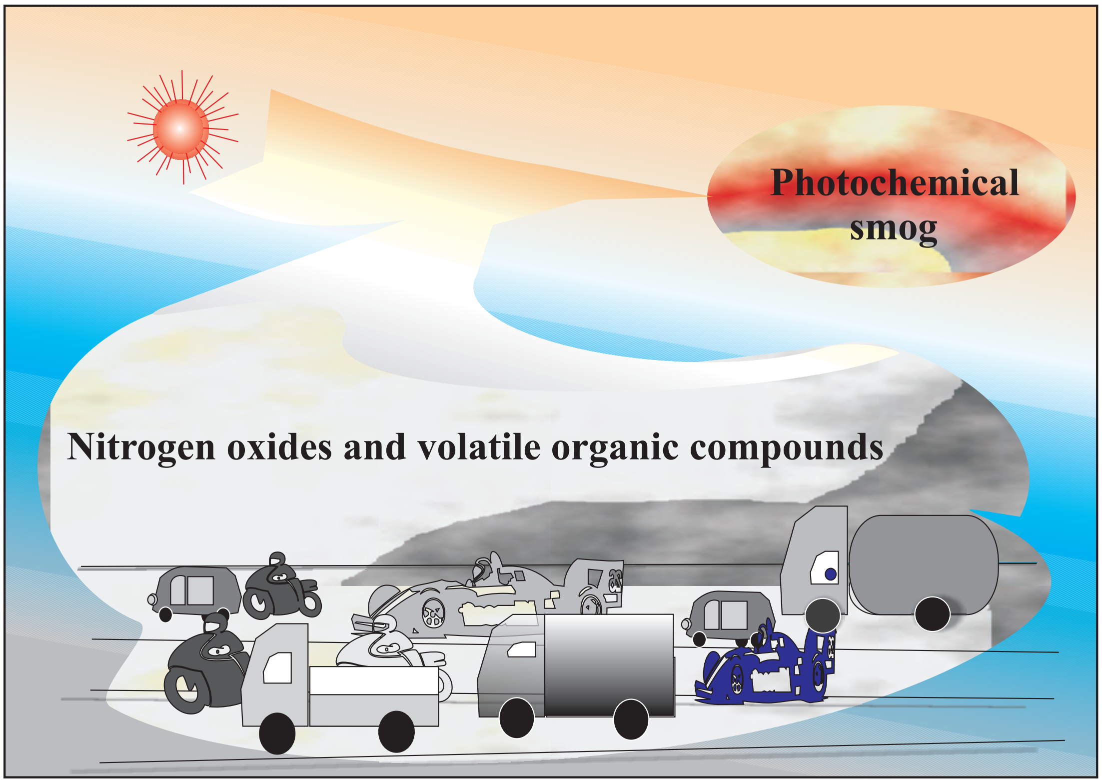


Fig. 14.2 *Photochemical smog occurs where sunlight acts on vehicle pollutants.*

How can photochemical smog be controlled ?

Many techniques are used to control or reduce the formation of photochemical smog. If we control the primary precursors of photochemical smog, such as NO_2 and hydrocarbons, the secondary precursors such as ozone and PAN, the photochemical smog will automatically be reduced. Usually catalytic converters are used in the automobiles, which prevent the release of nitrogen oxide and hydrocarbons to the atmosphere. Certain plants e.g., Pinus, Juniparus, Quercus, Pyrus and Vitis can metabolise nitrogen oxide and therefore, their plantation could help in this matter.

14.2.2 Stratospheric Pollution

Formation and Breakdown of Ozone

The upper stratosphere consists of considerable amount of ozone (O_3), which protects us from the harmful ultraviolet (UV) radiations (λ 255 nm) coming from the sun. These radiations cause skin cancer (melanoma) in humans. Therefore, it is important to maintain the ozone shield.

Ozone in the stratosphere is a product of UV radiations acting on dioxygen (O_2) molecules. The UV radiations split apart molecular oxygen into free oxygen (O) atoms. These oxygen atoms combine with the molecular oxygen to form ozone.

$$O_2\,(g) \xrightarrow{UV} O(g) + O(g)$$

$$O(g) + O_2\,(g) \xrightleftharpoons{UV} O_3\,(g)$$

Ozone is thermodynamically unstable and decomposes to molecular oxygen. Thus, a dynamic equilibrium exists between the production and decomposition of ozone molecules. In recent years, there have been reports of the depletion of this protective ozone layer because of the presence of certain chemicals in the stratosphere. The main reason of ozone layer depletion is believed to be the release of chlorofluorocarbon compounds (CFCs), also known as freons. These compounds are nonreactive, non flammable, non toxic organic molecules and therefore used in refrigerators, air conditioners, in the production of plastic foam and by the electronic industry for cleaning computer parts etc. Once CFCs are released in the atmosphere, they mix with the normal atmospheric gases and eventually reach the stratosphere. In stratosphere, they get broken down by powerful UV radiations, releasing chlorine free radical.

$$CF_2Cl_2\,(g) \xrightarrow{UV} \dot{C}l\,(g) + \dot{C}F_2Cl\,(g) \qquad \text{(i)}$$

The chlorine radical then react with stratospheric ozone to form chlorine monoxide radicals and molecular oxygen.

$$\dot{C}l\,(g) + O_3\,(g) \rightarrow Cl\dot{O}\,(g) + O_2\,(g) \qquad \text{(ii)}$$

Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals.

$$Cl\dot{O}\,(g) + O\,(g) \rightarrow \dot{C}l\,(g) + O_2\,(g) \qquad \text{(iii)}$$

The chlorine radicals are continuously regenerated and cause the breakdown of ozone. Thus, CFCs are transporting agents for continuously generating chlorine radicals into the stratosphere and damaging the ozone layer.

The Ozone Hole

In 1980s atmospheric scientists working in Antarctica reported about depletion of ozone layer commonly known as ozone hole over the South Pole. It was found that a unique set of conditions was responsible for the ozone hole. In summer season, nitrogen dioxide and methane react with chlorine monoxide (reaction iv) and chlorine atoms (reaction v) forming chlorine sinks, preventing much ozone depletion, whereas in winter, special type of clouds called polar stratospheric clouds are formed over Antarctica. These polar stratospheric clouds provide surface on which chlorine nitrate formed (reaction iv) gets hydrolysed to form hypochlorous acid (reaction (vi)). It also reacts with hydrogen chloride produced as per reaction (v) to give molecular chlorine.

$$Cl\dot{O}\,(g) + NO_2\,(g) \rightarrow ClONO_2(g) \qquad \text{(iv)}$$

$$\dot{C}l\,(g) + CH_4\,(g) \rightarrow \dot{C}H_3(g) + HCl(g) \qquad \text{(v)}$$

$$ClONO_2(g) + H_2O\,(g) \rightarrow HOCl\,(g) + HNO_3\,(g) \qquad \text{(vi)}$$

$$ClONO_2(g) + HCl\,(g) \rightarrow Cl_2\,(g) + HNO_3\,(g) \qquad \text{(vii)}$$

When sunlight returns to the Antarctica in the spring, the sun's warmth breaks up the clouds and HOCl and Cl_2 are photolysed by sunlight, as given in reactions (viii) and (ix).

$$HOCl\,(g) \xrightarrow{h\nu} \dot{O}H\,(g) + \dot{C}l(g) \qquad \text{(viii)}$$

$$Cl_2\,(g) \xrightarrow{h\nu} 2\,\dot{C}l\,(g) \qquad \text{(ix)}$$

The chlorine radicals thus formed, initiate the chain reaction for ozone depletion as described earlier.

Effects of Depletion of the Ozone Layer

With the depletion of ozone layer, more UV radiation filters into troposphere. UV radiations lead to ageing of skin, cataract, sunburn, skin cancer, killing of many phytoplanktons, damage to fish productivity etc. It has also been reported that plant proteins get easily affected by UV radiations which leads to the harmful mutation of cells. It also increases evaporation of surface water through the stomata of the leaves and decreases the moisture content of the soil. Increase in UV radiations damage paints and fibres, causing them to fade faster.

14.3 WATER POLLUTION

Water is essential for life. Without water there would be no life. We usually take water as granted for its purity, but we must ensure the quality of water. Pollution of water originates from human activities. Through different paths, pollution reaches surface or ground water. Easily identified source or place of pollution is called as point source. e.g., municipal and industrial discharge pipes where pollutants enter the water-source. Non point sources of pollution are those where a source of pollution cannot be easily identified, e.g., agricultural run off (from farm, animals and crop-lands), acid rain, storm-water drainage (from streets, parking lots and lawns), etc. Table 14.1 lists the major water pollutants and their sources.

14.3.1 Causes of Water Pollution

(i) Pathogens: The most serious water pollutants are the disease causing agents called pathogens. Pathogens include bacteria and other organisms that enter water from domestic sewage and animal excreta. Human excreta contain bacteria such as *Escherichia coli* and *Streptococcus faecalis* which cause gastrointestinal diseases.

(ii) Organic wastes: The other major water pollutant is organic matter such as leaves, grass, trash etc. They pollute water as a consequence of run off. Excessive phytoplankton growth within water is also a cause of water pollution. These wastes are biodegradable.

The large population of bacteria decomposes organic matter present in water. They consume oxygen dissolved in water. The amount of oxygen that water can hold in the solution is limited. In cold water, dissolved oxygen (DO) can reach a concentration up to 10 ppm (parts per million), whereas oxygen in air is about 200,000 ppm. That is why even a moderate amount of organic matter when decomposes in water can deplete the water of its dissolved oxygen. The concentration of

Table 14.1 Major Water Pollutants

Pollutant	Source
Micro-organisms	Domestic sewage
Organic wastes	Domestic sewage, animal excreta and waste, decaying animals and plants, discharge from food processing factories.
Plant nutrients	Chemcial fertilizers
Toxic heavy metals	Industries and chemical factories
Sediments	Erosion of soil by agriculture and strip mining
Pesticides	Chemicals used for killing insects, fungi and weeds
Radioactive substances	Mining of uranium containing minerals
Heat	Water used for cooling in industries

dissolved oxygen in water is very important for aquatic life . If the concentration of dissolved oxygen of water is below 6 ppm, the growth of fish gets inhibited. Oxygen reaches water either through atmosphere or from the process of photosynthesis carried out by many aquatic green plants during day light. However, during night, photosynthesis stops but the plants continue to respire, resulting in reduction of dissolved oxygen. The dissolved oxygen is also used by microorganisms to oxidise organic matter.

If too much of organic matter is added to water, all the available oxygen is used up. This causes oxygen dependent aquatic life to die. Thus, anaerobic bacteria (which do not require oxygen) begin to break down the organic waste and produce chemicals that have a foul smell and are harmful to human health. Aerobic (oxygen requiring) bacteria degrade these organic wastes and keep the water depleted in dissolved oxygen.

Thus, the amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called **Biochemical Oxygen Demand (BOD)**. The amount of BOD in the water is a measure of the amount of organic material in the water, in terms of how much oxygen will be required to break it down biologically. Clean water would have BOD value of less than 5 ppm whereas highly polluted water could have a BOD value of 17 ppm or more.

(iii) Chemical Pollutants: As we know that water is an excellent solvent, water soluble inorganic chemicals that include heavy metals such as cadmium, mercury, nickel etc constitute an important class of pollutants. All these metals are dangerous to humans because our body cannot excrete them. Over the time, it crosses the tolerance limit. These metals then can damage kidneys, central nervous system, liver etc. Acids (like sulphuric acid) from mine drainage and salts from many different sources including raw salt used to melt snow and ice in the colder climates (sodium and calcium chloride) are water soluble chemical pollutants.

The organic chemicals are another group of substances that are found in polluted water. Petroleum products pollute many sources of water e.g., major oil spills in oceans. Other organic substances with serious impacts are the pesticides that drift down from sprays or runoff from lands. Various industrial chemicals like polychlorinated biphenyls, (PCBs) which are used as cleansing solvent, detergents and fertilizers add to the list of water pollutants. PCBs are suspected to be carcinogenic. Nowadays most of the detergents available are biodegradable. However, their use can create other problems. The bacteria responsible for degrading biodegradable detergent feed on it and grow rapidly. While growing, they may use up all the oxygen dissolved in water. The lack of oxygen kills all other forms of aquatic life such as fish and plants. Fertilizers contain phosphates as additives. The addition of phosphates in water enhances algae growth. Such profuse growth of algae, covers the water surface and reduces the oxygen concentration in water. This leads to anaerobic conditions, commonly with accumulation of abnoxious decay and animal death. Thus, bloom-infested water inhibits the growth of other living organisms in the water body. This process in which nutrient enriched water bodies support a dense plant population, which kills animal life by depriving it of oxygen and results in subsequent loss of biodiversity is known as ***Eutrophication***.

14.3.2 International Standards for Drinking Water

The International Standards for drinking water are given below and they must be followed.

Fluoride: For drinking purposes, water should be tested for fluoride ion concentration. Its deficiency in drinking water is harmful to man and causes diseases such as tooth decay etc. Soluble fluoride is often added to drinking water to bring its concentration upto 1 ppm or 1 mg dm^{-3}. The F^- ions make the enamel on teeth much harder by converting hydroxyapatite, $[3(Ca_3(PO_4)_2.Ca(OH)_2]$, the enamel on the surface of the teeth, into much harder fluorapatite, $[3(Ca_3(PO_4)_2.CaF_2]$.

However, F$^-$ ion concentration above 2 ppm causes brown mottling of teeth. At the same time, excess fluoride (over 10 ppm) causes harmful effect to bones and teeth, as reported from some parts of Rajasthan.

Lead: Drinking water gets contaminated with lead when lead pipes are used for transportation of water. The prescribed upper limit concentration of lead in drinking water is about 50 ppb. Lead can damage kidney, liver, reproductive system etc.

Sulphate: Excessive sulphate (>500 ppm) in drinking water causes laxative effect, otherwise at moderate levels it is harmless.

Nitrate: The maximum limit of nitrate in drinking water is 50 ppm. Excess nitrate in drinking water can cause disease such as methemoglobinemia ('blue baby' syndrome).

Other metals: The maximum concentration of some common metals recommended in drinking water are given in Table 14.2.

Table 14.2 Maximum Prescribed Concentration of Some Metals in Drinking Water.

Metal	Maximum concentration (ppm or mg dm^{-3})
Fe	0.2
Mn	0.05
Al	0.2
Cu	3.0
Zn	5.0
Cd	0.005

Activity 2

You can visit local water sources and observe if the river/lake/tank/pond are unpolluted/slightly polluted/ moderately polluted or severely polluted by looking at water or by checking pH of water. Document the name of the river and the nearby urban or industrial site from where the pollution is generated. Inform about this to Pollution Control Board's office set up by Government to measure pollution levels. Ensure that appropriate action is taken. You can write to the press also. Do not dump waste into a household or industrial drain which can enter directly to any water body, such as, river, pond, stream or lake. Use compost instead of chemical fertilizers in gardens. Avoid the use of pesticides like DDT, malathion etc., at home and try to use dried neem leaves to help keep insects away. Add a few crystals of potassium permanganate ($KMnO_4$) or bleaching powder to the water tank of your house.

14.4 SOIL POLLUTION

India being an agriculture based economy gives high priority to agriculture, fisheries and livestock development. The surplus production is stored by governmental and non-governmental organisations for the lean season. The food loss during the storage also needs special attention. Have you ever seen the damages caused to the crops, food items by insects, rodents, weeds and crop diseases etc? How can we protect them? You are acquainted with some insecticides and pesticides for protection of our crops. However, these insecticides, pesticides and herbicides cause soil pollution. Hence, there is a need for their judicious use.

14.4.1 Pesticides

Prior to World War II, many naturally occurring chemicals such as nicotine (by planting tobacco plants in the crop field), were used as pest controlling substance for major crops in agricultural practices.

During World War II, DDT was found to be of great use in the control of malaria and other insect-borne diseases. Therefore, after the war, DDT was put to use in agriculture to control the damages caused by insects, rodents, weeds and various crop diseases. However, due to adverse effects, its use has been banned in India.

Pesticides are basically synthetic toxic chemicals with ecological repercussions. The repeated use of the same or similar pesticides give rise to pests that are resistant to that group of pesticides thus making the pesticides ineffective. Therefore, as insect resistance of DDT increased, other organic toxins such as Aldrin and Dieldrin were introduced in the market by pesticide industry. Most of the organic toxins are water insoluble and non-biodegradable. These high persistent toxins are, therefore, transferred from lower trophic level to higher trophic level through food chain (Fig. 14.3). Over the time, the concentration of toxins in higher animals reach a level which causes serious metabolic and physiological disorders.

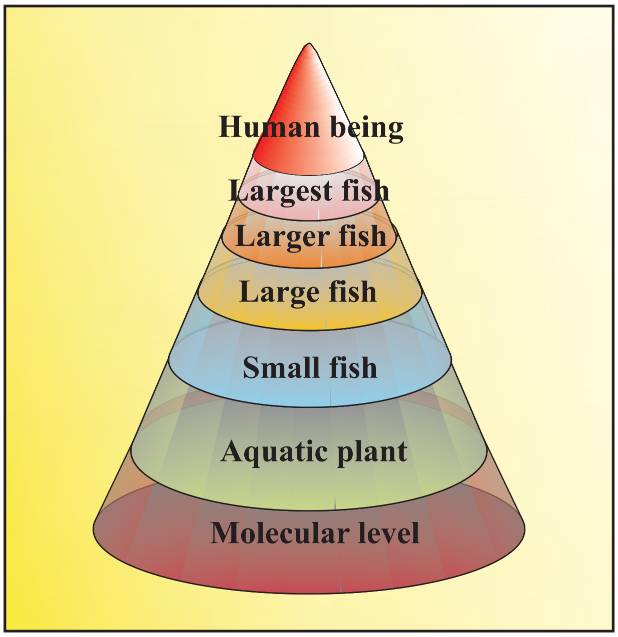


Fig. 14.3 *At each trophic level, the pollutant gets 10 times concentrated.*

In response to high persistence of chlorinated organic toxins, a new series of less persistent or more bio-degradable products called organo-phosphates and carbamates have been introduced in the market. But these chemicals are severe nerve toxins and hence more harmful to humans. As a result, there are reports of some pesticides related deaths of agricultural field workers. Insects have become resistant to these insecticides also. The insecticide industry is engaged in developing new groups of insecticides. But one has to think, is this the only solution to pest menace?

These days, the pesticide industry has shifted its attention to **herbicides** such as sodium chlorate ($NaClO_3$), sodium arsinite (Na_3AsO_3) and many others. During the first half of the last century, the shift from mechanical to chemical weed control had provided the industry with flourishing economic market. But one must remember that these are also not environment friendly.

Most herbicides are toxic to mammals but are not as persistent as organo-chlorides. These chemicals decompose in a few months. Like organo-chlorides, these too become concentrated in the food web. Some herbicides cause birth defects. Studies show that corn-fields sprayed with herbicides are more prone to insect attack and plant disease than fields that are weeded manually.

Pesticides and herbicides represent only a very small portion of widespread chemical pollution. A large number of other compounds that are used regularly in chemical and industrial processes for manufacturing activities are finally released in the atmosphere in one or other form.

14.5 INDUSTRIAL WASTE

Industrial solid wastes are also sorted out as biodegradable and non-degradable wastes. Biodegradable wastes are generated by cotton mills, food processing units, paper mills, and textile factories.

Non-biodegradable wastes are generated by thermal power plants which produce fly ash; integrated iron and steel plants which produce blast furnace slag and steel melting slag. Industries manufacturing aluminium, zinc and copper produce mud and tailings. Fertilizer industries produce gypsum. Hazardous wastes such as inflammables, composite explosives or highly reactive substances are produced by industries dealing in metals, chemicals, drugs, pharmaceuticals, dyes, pesticides, rubber goods etc.

The disposal of non-degradable industrial solid wastes, if not done by a proper and suitable method, may cause serious threat to the environment. New innovations have led to different uses of waste material. Nowadays, fly ash and slag from the steel industry are utilised by the cement industry. Large quantities of toxic wastes are usually destroyed by controlled incineration, whereas small quantities are burnt along with factory garbage in open bins. Moreover, solid wastes if not managed effectively, affect the components of the environment.

Do you know about waste recycling?

- Fuel obtained from plastic waste has high octane rating. It contains no lead and is known as "green fuel".
- Due to recent developments made in chemical and textile industries, clothes will be made from recycled plastic waste. These will be available soon in the global textile market.
- In India, our cities and towns face endless hours of power cut. We can also see piles of rotting garbage here and there. There is a good news that we can get rid from both these problems simultaneously. Technology has now been developed to produce electricity from the garbage. A pilot plant has been set up, where after removing ferrous metals, plastic, glass, paper etc. from garbage, it is mixed with water. It is then cultured with bacterial species for producing methane, commonly known as biogas. The remaining product is used as manure and biogas is used to produce electricity.

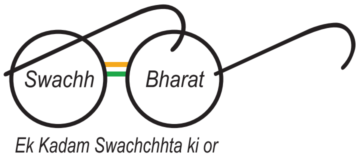
14.6 STRATEGIES TO CONTROL ENVIRONMENTAL POLLUTION

After studying air, water, soil and industrial waste pollution in this unit, by now you must have started feeling the need of controlling environmental pollution: How can you save your immediate environment? Think of the steps/activities, which you would like to undertake for controlling air, water, soil and industrial waste pollution in your neighbourhood. Here, an idea about the strategies for the management of waste is given.

14.6.1 Waste Management

Solid waste is not the only waste, which you see in your household garbage box. Besides household discards, there are medical, agricultural, industrial and mining wastes. The improper disposal of wastes is one of the major causes of environmental degradation. Therefore, the management of wastes is of utmost importance.

You must be aware of the '*Swachh Bharat Abhiyan*' or 'Clean India Mission' launched by the Government of India.



Two programmes are being implemented under the broad umbrella of the *Swachh Bharat Abhiyan*. These are *Swachh Bharat Mission–Urban* (SBM–U) and *Swachh Bharat Mission Gramin* (SBM–G). The SBM–U primarily aims at making Urban India free from open defecation and achieving 100% scientific management of solid waste in the country. The SBM–G targets to bring about an improvement in the general quality of life in rural areas by promoting cleanliness and hygiene, and eliminating open defecation. It is accelerating its efforts to achieve the goal of universal sanitation coverage by 2 October, 2019, which is the birth aniversary of Mahatma Gandhi. If you have participated in some event on *Swachh Bharat Mission*, write your experiences.

Collection and Disposal

Domestic wastes are collected in small bins, which are then transferred to community bins by private or municipal workers. From these community bins, these are collected and carried to the disposable site. At the site, garbage is sorted out and separated into biodegradable and non-biodegradable materials. Non-biodegradable materials such as plastic, glass, metal scraps etc. are sent for recycling. Biodegradable wastes are deposited in land fills and are converted into compost.

The waste if not collected in garbage bins, finds its way into the sewers. Some of it is eaten by cattle. Non-biodegradable wastes like polythene bag, metal scraps, etc. choke the sewers and cause inconvenience. Polythene bags, if swallowed by animals can cost their lives also.

As a normal practice, therefore, all domestic wastes should be properly collected and disposed. The poor management causes health problems leading to epidemics due to contamination of ground water. It is specially hazardous for those who are in direct contact with the waste such as rag pickers and workers involved in waste disposal, as they are the ones who handle waste materials mostly without protective device such as gloves or water proof boots and gas masks. What can you do for them?

14.7 GREEN CHEMISTRY

14.7.1 Introduction

It is well known fact that self-sufficiency in food has been achieved in India since late 20th century by using fertilizers and pesticides and exploring improved methods of farming, good quality seeds, irrigation etc. But over-exploitation of soil and excessive use of fertilizers and pesticides have resulted in the deterioration of soil, water and air.

The solution of this problem does not lie in stopping the process of development that has been set in; but to discover methods, which would help in the reduction of deterioration of the environment. *Green chemistry is a way of thinking and is about utilising the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment. Green chemistry is a production process that would bring about minimum pollution or deterioration to the environment. The byproducts generated during a process, if not used gainfully, add to the environmental pollution. Such processes are not only environmental unfriendly but also cost-ineffective. The waste generation and its disposal both are economically unsound. Utilisation of existing knowledge base for reducing the chemical*

Nobel goes to Green Chemists


Yves Chauvin


Robert H. Grubbs


Richard R. Schrock

Yves Chauvin, Institut Français du Pétrole, Rueil-Malmaison France, **Robert H. Grubbs** California Institute of Technology (Caltech), Pasadena, CA, USA and **Richard R. Schrock** Massachusetts Institute of Technology (MIT), Cambridge, MA, USA won the 2005 Nobel Prize in chemistry for work that reduces hazardous waste in creating new chemicals. The trio won the award for their development of the metathesis method in organic synthesis –a way to rearrange groups of atoms within molecules that the Royal Swedish Academy of Sciences likened to a dance in which couples change partners. The metathesis has tremendous commercial potential in the pharmaceuticals, biotechnology and food stuffs production industries. It is also used in the development of revolutionary environmentally-friendlier polymers.

This represents a great step forward for 'green chemistry', reducing potentially hazardous waste through smarter production. Metathesis is an example of how important application of basic science is for the benefit of man, society and the environment.

hazards along with the developmental activities is the foundation of green chemistry. Have you perceived the idea of green chemistry? It is well known that organic solvents such as benzene, toluene, carbon tetrachloride etc., are highly toxic. One should be careful while using them.

As you know, a chemical reaction involves reactants, attacking reagents and the medium in which the reaction takes place. Extent of any reaction depends upon physical parameters like temperature, pressure and use of catalyst. In a chemical reaction, if reactants are fully converted into useful environmental friendly products by using an environment friendly medium then there would be no chemical pollutants introduced in the environment.

During a synthesis, care must be taken to choose starting materials that can be converted into end products with yield approximately upto 100 per cent. This can be achieved by arriving at optimum conditions of synthesis. It may be worthwhile to carry out synthetic reactions in aqueous medium since water has high specific heat and low volatility. Water is cost effective, noninflammable and devoid of any carcinogenic effects.

14.7.2 Green Chemistry in day-to-day Life

(i) Dry Cleaning of Clothes

Tetra chlroroethene ($Cl_2C=CCl_2$) was earlier used as solvent for dry cleaning. The compound contaminates the ground water and is also a suspected carcinogen. The process using this compound is now being replaced by a process, where liquefied carbondioxide, with a suitable detergent is used. Replacement of halogenated solvent by liquid CO_2 will result in less harm to ground water.

These days hydrogen peroxide (H_2O_2) is used for the purpose of bleaching clothes in the process of laundary, which gives better results and makes use of lesser amount of water.

(ii) Bleaching of Paper

Chlorine gas was used earlier for bleaching paper. These days, hydrogen peroxide (H_2O_2) with suitable catalyst, which promotes the bleaching action of hydrogen peroxide, is used.

(iii) Synthesis of Chemicals

Ethanal (CH_3CHO) is now commercially prepared by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium with a yield of 90%.

$$CH_2 = CH_2 + O_2 \xrightarrow[\text{Pd(II)/Cu(II)(in water)}]{\text{Catalyst}} CH_3CHO\,(90\%)$$

(iv) 'Green Solution' to Clean Turbid Water

Powder of kernel of tamarind seeds has been found to be an effective material to make municipal and industrial waste water clean. It is non-toxic, biodegradable and cost-effective material. This powder is usually discarded as agricultural waste. The present practice is to use alum to treat such water. It has been found that alum increases toxic ions in treated water and can cause diseases.

Green chemistry, in a nutshell, is a cost effective approach which involves reduction in material, energy consumption and waste generation.

Think it Over

What is our responsibility as a human being to protect our environment?

Some concepts, if followed by an individual, contribute towards a better quality of our environment and human life. Always set up a compost tin in your garden or any other place in your home and use it to produce manure for your plants to reduce the use of fertilizers. Use a cloth bag and avoid asking for plastic carry bags when you buy groceries, vegetables or any other item. See that all newspapers, glass, aluminum and other items in your area are recycled. We might have to take little trouble to locate such dealers. We must realize that we do not have solutions for every problem but we can concentrate on issues, which we feel strongly about and can do some thing about. We should take care to put into practice whatever we preach. Always remember environment protection begins with us.

SUMMARY

Environmental chemistry plays a major role in environment. Chemical species present in the environment are either naturally occurring or generated by human activities. **Environmental pollution** is the effect of undesirable changes in the surrounding that have harmful effects on plants, animals and human beings. Pollutants exist in all the three states of matter. We have discussed only those pollutants, which are due to human activities, and can be controlled. Atmospheric pollution is generally studied as **tropospheric** and **stratospheric pollution**. Troposphere is the lowest region of the atmosphere (~10 km) in which man along with other organisms including plants exist. Whereas stratosphere extends above troposphere up to 50 km above sea level. Ozone layer is one of the important constituents of stratosphere. Tropospheric pollution is basically due to various oxides of sulphur, nitrogen, carbon, halogens and also due to particulate pollutants. The gaseous pollutants come down to the earth in the form of **acid rain**. 75% of the solar energy reaching earth is absorbed by the earth surface and rest is radiated back to the atmosphere. These gases mentioned above trap the heat which result into **global warming**. It is important to realise that these very gases are also responsible for the life on the earth as they trap the requisite amount of solar energy for the sustainance of life. The increase in the **greenhouse gases** is raising the temperature of the earth's atmosphere which, if not checked, may eventually result in melting of polar ice caps and consequently may submerge the costal land mass. Many human activities are producing chemicals, which are responsible for the **depletion of ozone layer** in the stratosphere, leading to the formation of **ozone hole**. Through the ozone hole, ultraviolet radiations can penetrate into the earth's atmosphere causing mutation of genes. Water is the elixir of life but the same water, if polluted by pathogens, organic wastes, toxic heavy metals, pesticides etc., will turn into poison. Therefore, one should take care to follow international standards to maintain purity levels of drinking water. Industrial wastes and excessive use of pesticides, result into pollution of land mass and water bodies. Judicious use of chemicals required for agricultural practices can lead to sustainable development. **Strategies for controlling environmental pollution** can be: (i) waste management *i.e.,* reduction of the waste and proper disposal, also recycling of materials and energy, (ii) adopting methods in day-to-day life, which results in the reduction of environmental pollution. The second method is a new branch of chemistry, which is in its infancy known as **green chemistry**. It utilizes the existing knowledge and practices so as to bring about reduction in the production of pollutants.

EXERCISES

14.1 Define environmental chemistry.
14.2 Explain tropospheric pollution in 100 words.
14.3 Carbon monoxide gas is more dangerous than carbon dioxide gas. Why?
14.4 List gases which are responsible for greenhouse effect.
14.5 Statues and monuments in India are affected by acid rain. How?
14.6 What is smog? How is classical smog different from photochemical smogs?

14.7 Write down the reactions involved during the formation of photochemical smog.

14.8 What are the harmful effects of photochemical smog and how can they be controlled?

14.9 What are the reactions involved for ozone layer depletion in the stratosphere?

14.10 What do you mean by ozone hole? What are its consequences?

14.11 What are the major causes of water pollution? Explain.

14.12 Have you ever observed any water pollution in your area? What measures would you suggest to control it?

14.13 What do you mean by Biochemical Oxygen Demand (BOD)?

14.14 Do you observe any soil pollution in your neighbourhood? What efforts will you make for controlling the soil pollution?

14.15 What are pesticides and herbicides? Explain giving examples.

14.16 What do you mean by green chemistry? How will it help decrease environmental pollution?

14.17 What would have happened if the greenhouse gases were totally missing in the earth's atmosphere? Discuss.

14.18 A large number of fish are suddenly found floating dead on a lake. There is no evidence of toxic dumping but you find an abundance of phytoplankton. Suggest a reason for the fish kill.

14.19 How can domestic waste be used as manure?

14.20 For your agricultural field or garden you have developed a compost producing pit. Discuss the process in the light of bad odour, flies and recycling of wastes for a good produce.

Answer to Some Selected Problems

UNIT 8

8.25 15 g

UNIT 12

12.32 Mass of carbon dioxide formed = 0.505 g

Mass of water formed = 0.0864 g

12.33 % fo nitrogen = 56

12.34 % of chlorine = 37.57

12.35 % of sulphur = 19.66

UNIT 13

13.1 Due to the side reaction in termination step by the combination of two $\dot{C}H_3$ free radicals.

13.2 (a) 2-Methyl-but-2-ene (b) Pent-1-ene-3-yne

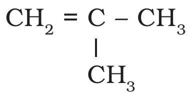
(c) Buta-1, 3-diene (d) 4-Phenylbut-1-ene

(e) 2-Methylphenol (f) 5-(2-Methylpropyl)-decane

(g) 4-Ethyldeca –1,5,8- triene

13.3 (a) (i) $CH_2 = CH - CH_2 - CH_3$ But-1-ene

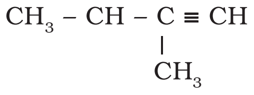
(ii) $CH_3 - CH_2 = CH - CH_3$ But-2-ene

(iii) 

$CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH_3$ 2-Methylpropene

(b) (i) $HC \equiv C - CH_2 - CH_2 - CH_3$ Pent-1-yne

(ii) $CH_3 - C \equiv C - CH_2 - CH_3$ Pent-2-yne

(iii) 

$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - C \equiv CH$ 3-Methylbut-1-yne

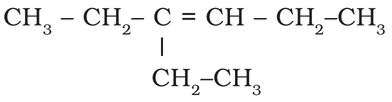
13.4 (i) Ethanal and propanal (ii) Butan-2-one and pentan-2-one

(iii) Methanal and pentan-3-one (iv) Propanal and benzaldehyde

13.5 3-Ethylpent-2-ene

13.6 But-2-ene

13.7 4-Ethylhex-3-ene



$CH_3 - CH_2 - \underset{\displaystyle CH_2 - CH_3}{\underset{|}{C}} = CH - CH_2 - CH_3$

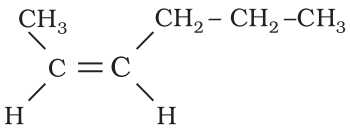
13.8 (a) $C_4H_{10}(g)+13/2\,O_2(g) \xrightarrow{\Delta} 4CO_2(g)+5H_2O(g)$

(b) $C_5H_{10}(g)+15/2\,O_2(g) \xrightarrow{\Delta} 5CO_2(g)+5H_2O(g)$

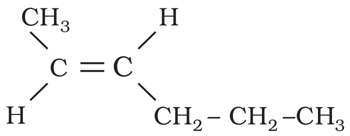
(c) $C_6H_{10}(g)+17/2\,O_2(g) \xrightarrow{\Delta} 6CO_2(g)+5H_2O(g)$

(d) $C_7H_8(g)+9O_2(g) \xrightarrow{\Delta} 7CO_2(g)+4H_2O(g)$

13.9



cis-Hex-2-ene



trans-Hex-2-ene

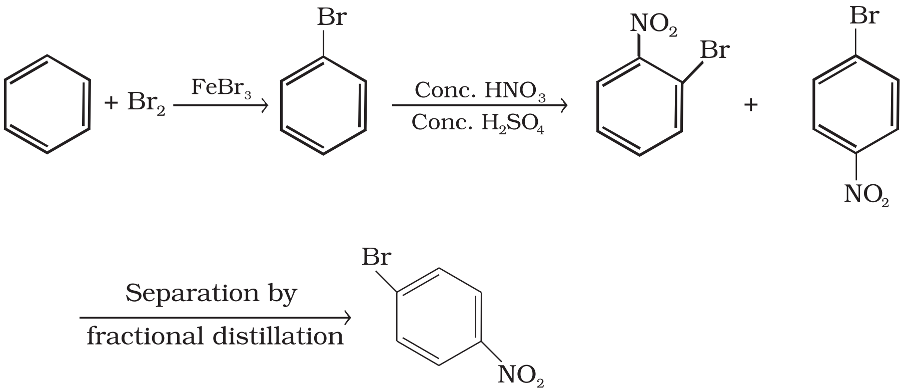
The cis form will have higher boiling point due to more polar nature leading to stronger intermolecular dipole–dipole interaction, thus requiring more heat energy to separate them.

13.10 Due to resonance

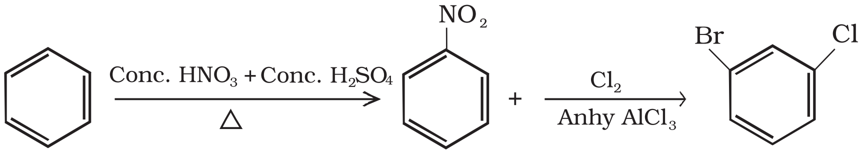
13.11 Planar, conjugated ring system with delocalisation of (4n+2) π electrons, where, n is an integer

13.12 Lack of delocalisation of (4n +2) π electrons in the cyclic system.

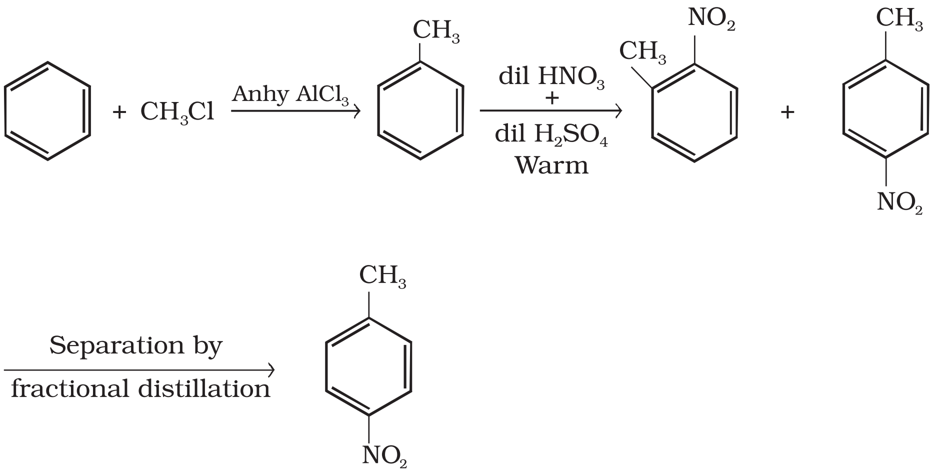
13.13 (i)



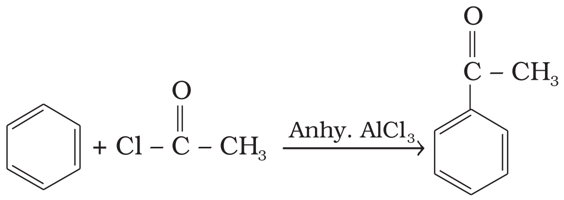
(ii)



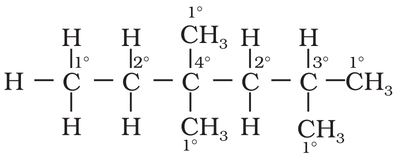
(iii)



(iv)



13.14



$$\begin{array}{ccccccccccc}
 & & & & & 1^\circ & & & & & \\
 & H & & H & & CH_3 & & H & & H & \\
 & |1^\circ & & |2^\circ & & |4^\circ & & |2^\circ & & |3^\circ & 1^\circ \\
H- & C & - & C & - & C & - & C & - & C & -CH_3 \\
 & | & & | & & | & & | & & | & \\
 & H & & H & & CH_3 & & H & & CH_3 & \\
 & & & & & 1^\circ & & & & 1^\circ &
\end{array}$$

15 H attached to 1° carbons

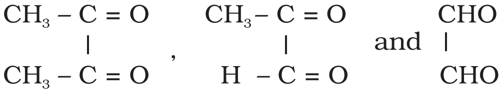
4 H attached to 2° carbons

1 H attached to 3° carbons

13.15 More the branching in alkane, lower will be the boiling point.

13.16 Refer to addition reaction of HBr to unsymmetrical alkenes in the text.

13.17



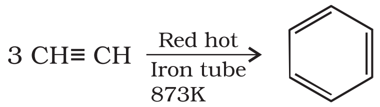
$$\begin{array}{c} CH_3-C=O \\ | \\ CH_3-C=O \end{array}, \quad \begin{array}{c} CH_3-C=O \\ | \\ H\ -C=O \end{array} \quad \text{and} \quad \begin{array}{c} CHO \\ | \\ CHO \end{array}$$

All the three products cannot be obtained by any one of the Kekulé's structures. This shows that benzene is a resonance hybrid of the two resonating structures.

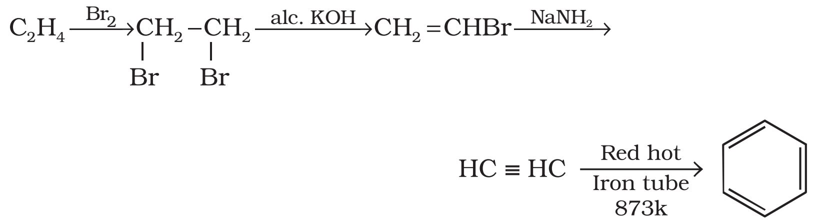
13.18 $H-C\equiv C-H > C_6H_6 > C_6H_{14}$. Due to maximum *s* orbital character in enthyne (50 per cent) as compared to 33 per cent in benzene and 25 per cent in *n*-hexane.

13.19 Due to the presence of 6 π electrons, benzene behaves as a rich source of electrons thus being easily attacked by reagents deficient in electrons.

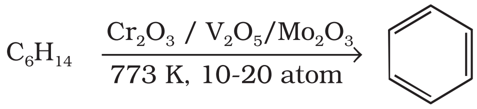
13.20 (i)



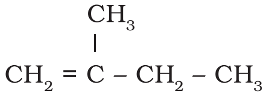
(ii)



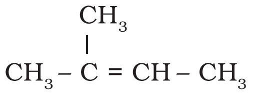
(iii)



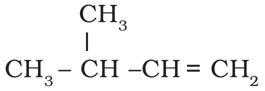
13.21



$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2-CH_3$ 2-Methylbut-1-ene



$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_3$ 2-Methylbut-2-ene



$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH=CH_2$ 3-Methylbut-1-ene

13.22 (a) Chlorobenzene>*p*-nitrochlorobenzene> 2,4 – dinitrochlorobenzene

(b) Toluene > *p*-CH_3-C_6H_4-NO_2 > *p*-O_2N–C_6H_4–NO_2

13.23 Toleune undergoes nitration most easily due to electron releasing nature of the methyl group.

13.24 $FeCl_3$

13.25 Due to the formation of side products. For example, by starting with 1-bromopropane and 1-bromobutane, hexane and octane are the side products besides heptane.