CHEMISTRY

Standard 11

(Semester II)

PLEDGE

India is my country.
All Indians are my brothers and sisters.
I love my country and I am proud of its rich and
varied heritage.
I shall always strive to be worthy of it.
I shall respect my parents, teachers and all my
elders and treat everyone with courtesy.
I pledge my devotion to my country and its people.
My happiness lies in their well-being and prosperity.

રાજ્ય સરકારની વિનામૂલ્યે યોજના હેઠળનું પુસ્તક

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PREFACE

The Gujarat State Secondary and Higher Secondary Education Board has prepared new syllabi in accordance with the new national syllabi prepared by N.C.E.R.T. based on N.C.F.-2005 and core-curriculam. These syllabi are sanctioned by the Government of Gujarat.

It is a pleasure for the Gujarat State Board of School Textbooks to place before the students this textbook of **Chemistry Standard 11 (Semester II)** prepared according to the new syllabus.

Before publishing the textbook, its manuscript has been fully reviewed by experts and teachers teaching at this level. Following suggestions given by teachers and experts, we have made necessary changes in the manuscript before publishing the textbook.

The Board has taken special care to ensure that this textbook is interesting, useful and free from errors. However, we welcome any suggestion, from people interested in education, to improve the quality of the textbook.

Dr. Bharat Pandit   **Sujit Gulati** IAS

Director   Executive President

Date : 05-08-2015   Gandhinagar

FUNDAMENTAL DUTIES

It shall be the duty of every citizen of India

(A)   to abide by the Constitution and respect its ideals and institutions, the National Flag and the National Anthem;

(B)   to cherish and follow the noble ideals which inspired our national struggle for freedom;

(C)   to uphold and protect the sovereignty, unity and integrity of India;

(D)   to defend the country and render national service when called upon to do so;

(E)   to promote harmony and the spirit of common brotherhood amongst all the people of India transcending religious, linguistic and regional or sectional diversities; to renounce practices derogatory to the dignity of women;

(F)   to value and preserve the rich heritage of our composite culture;

(G)   to protect and improve the natural environment including forests, lakes, rivers and wild life, and to have compassion for living creatures;

(H)   to develop the scientific temper, humanism and the spirit of inquiry and reform;

(I)   to safeguard public property and to abjure violence;

(J)   to strive towards excellence in all spheres of individual and collective activity so that the nation constantly rises to higher levels of endeavour and achievement.

(K)   to provide opportunities for education by the parent or the guardian, to his child or a ward between the age of 6-14 years as the case may be.

* Constitution of India : Section 51-A

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About This Textbook...

It has been decided by the Central Goverment of India, that only one competitive examination will be conducted at national level for the study of higher education. As a result of this planning, the formation of Core-Currilulum took place. The meaning of this was that there must be same syllabus in the subjects of Science Stream for national competitive examination. The same syllabus can be possible if the book is prepared according to NCF-2005.

Hence, by the Gujarat State Higher Secondary Education Board, a new Chemistry syllabus in Chemistry was prepared by experts and teachers on the basis of core-curriculum and NCF-2005.

Gujarat State Government being attempting for 'Education without Burden' plan will give comfort to students. Gujarat State Board of School Textbooks made positive arrangements for students to have advantage of the expertship of the teachers from Schools and Colleges having their own teaching experience, and experience in drawing questions for GUJCET examination as well as Higher Secondary Examination Board. The writers associated with the writing of this book have written units which are reviewed by other teachers, experts and reviewers and tried to prepare this book useful at national level by carrying out proper additions and alterations.

One important matter has been aded. Changes have been expected in different words in this new book viz. atomic mass instead of atomic weight, molecular mass instead of molecular weight, enthalpy instead of energy, bar instead of atmosphere as well use of unit pascal. The word like reactivity will appear to be unknown but its inclusion in the modern study was found to be essential. In addition to this, in this existing book, instead of the nomenclature, units etc. the modern SI units, method of nomenclature etc. as in NCERT book are used in the text. This will appear somewhat new but being very useful in competitive examinations and to counteract the new challanges and to obtain achievement in present education system, it should be accepted.

Competitive examinations like AIEEE, JEE, NEET are being conducted. SI units are used in the question papers. In our GUJCET examination, SI units not being used, students were finding it difficult at the above competitive examination but we are sure that the students will make the name of Gujarat, as a state of great pride at national level.

The subject content, presentation, examples are included in this book in such a way that the students will find easy in understanding. Attempt has been made at each level eventhen, if teacher, friend or anybody will send suggestion for attainment of completeness, the Gujarat State Board of School Textbook will acknowledge with thanks and will include in the revised edition or new re-print.

'To send proper suggestion is your work and to implement it is our work.' By keeping this goal, the students of Gujarat State may obtain success at national level being the object, all will join in these is our expectation and request.

It is a matter of great pleasure that **the year 2011 will be celebrated as International Year of Chemistry (IYC) in the memory of Madam Curie.**

– Authors

Chemical Bonding and Molecular Structure

1.1 Introduction

Matter is made up of one or more types of elements. Atoms of inert gases exist independently in nature, but under normal conditions the atoms of other element do not remain independent and so are obtained in combined form. The groups of atoms combine and exist as species having characteristic properties are known as molecules. There must be some attraction force which keeps the atoms present in the molecule combined with each other. Thus, **the attraction force that keeps the different components (atom/ion) combined together is called chemical bond.**

The chemical compounds that are formed as a result of this chemical bond creates some problems viz. Why do atoms combine? Why do they combine in definite proportion? Why do certain atoms combine with each other and not with other atoms ? Why do molecules possess some definite shapes ? The answers to these problems can be given by the principles like **Kossel-Lewis approach, VSEPR principle, valence bond theory, molecular orbital theory.**

1.2 Kossel - Lewis Approach of Chemical Bonding

Many attempts have been made to explain existence of chemical bond in relation to electron but, in 1916, Scientists Kossel and Lewis gave satisfactory explanation.

Lewis proposed atom as positively charged Kernel. In this Kernel, nucleus and electrons in the inner orbit are present, while eight electrons can be accomodated in outer shell. Thus, one electron of sodium element in the outermost shell is on the corner of a cube while all the eight electrons of inert gases (except helium) are arranged on the eight corners of the cube.

Lewis noted that when atoms are combined by chemical bond, they attain stable structure of octet of eight electrons. The atom of sodium element loses one electron (Na^+) and attain stable octet structure. While atom of chlorine element receives one electron (Cl^-) and attains stable octet structure. Molecules such as Cl_2, O_2, F_2 etc. attain stable octet structures by sharing of valence electrons (Exception H_2).

Lewis Symbols : In the formation of molecules by chemical bond, the electrons in the outermost shell only take part, and the electrons in the inner shells do not take part in the formation of bond because they are protected. Lewis utilised the following type of symbols. e.g. The valence electrons of the elements of second period of periodic table can be shown as below by Lewis Symbols :

$$\text{Li} \quad \text{Be} \quad \cdot\text{B}\cdot \quad \cdot\text{C}\cdot \quad \cdot\text{N}\cdot \quad \cdot\text{O}\cdot \quad \text{:F:} \quad \text{:Ne:}$$
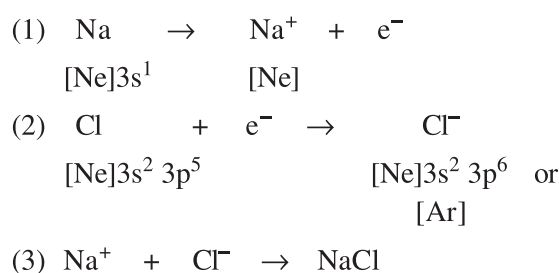
The number of dots around the symbol of the elements are considered as valence electrons of that element. The number of this valence electrons is useful in calculation of valency of the group.

Approach of Kossel for Chemical Bonding :

● The strongly electronegative halogen elements and strongly electropositive alkali elements in the periodic table differ from inert gases.

● Halogen elements receive one electron and become negatively charged ion, while alkali elements lose one electron and become positively charged ion.

● The positively charged and negatively charged ions formed this way attain stable electronic structure like inert gases (Except Helium) whose general electronic structure can be given as $ns^2 np^6$ (octet).

● This positive ion and negative ion are stable due to electrostatic attraction.

● In the formation of ionic compound, the atoms having less ionisation enthalpy combine with atoms having more electro-negativity and the bond formed by this combination is called **ionic bond.**

● The capacity of formation of ionic bond of an element is called **electrons lost or gained by element.**

The explanation of formation of ionic bond in sodium chloride compound is as follows :

(1) $Na \quad \rightarrow \quad Na^+ \quad + \quad e^-$
$[Ne]3s^1 \qquad\qquad [Ne]$

(2) $Cl \qquad + \quad e^- \rightarrow \qquad Cl^-$
$[Ne]3s^2 3p^5 \qquad\qquad [Ne]3s^2 3p^6$ or
$\qquad\qquad\qquad\qquad\qquad [Ar]$

(3) $Na^+ \quad + \quad Cl^- \quad \rightarrow \quad NaCl$

The bond formed by electrostatic attraction between positive ion and negative ion is called electrovalent bond. This approach of Kossel is not able to explain the formation of large number compounds.

1.3 Ionic Bond, Covalent Bond (including Lewis Structure), bond length, bond angle, bond energy, bond order, and their concept, Born-Haber Cycle

Ionic Bond : On the basis of approach of Kossel and Lewis, the formation of ionic bond depends on the following factors:

(1) Easy availability of positive ion and negative ion from neutral atoms.

(2) Arrangement of positive ion and negative ion in ionic bond.

The formation of positive ion from neutral atom or formation of negative ion from neutral atom depends on the values of ionisation enthalpy and electron gain enthalpy of atoms respectively.

$$M_{(g)} \quad \rightarrow \quad M^{n+} \quad + \quad ne^- \text{ (Ionisation)}$$

$$X_{(g)} \quad + \quad e^- \quad \rightarrow \quad X^-_{(g)} \text{(Electron gain)}$$
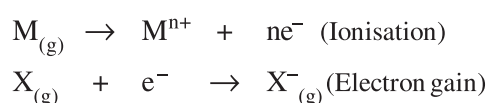
Ionisation reaction is endothermic (absorption of heat) while electron gain reaction is exothermic (evolution of heat). Thus elements having less ionisation enthalpy and more electro-negativity form ionic bonds easily.

In the crystal structure of ionic compounds, there is regular three dimensional arrangement of positive ions and negative ions. They are also strongly combined with each other by Coulombic attraction forces. Such an arrangement or structure is also called **crystal structure or crystal configuration.** The energy required to remove gaseous form of ions to infinite distance from ionic compound in one mole solid state is called **crystal lattice energy or enthalpy of lattice formation.** e.g. The lattice enthalpy of NaCl crystal is 788 kJmol^{-1}. Generally ionic solid compounds are soluble in water at room temperature and atmospheric pressure.

Covalent Bond : As we have seen earlier, electrons are shared in the formation of molecules. e.g. H_2, Cl_2, O_2, N_2 etc. Thus, **when two or more atoms of any (similar or dissimilar) elements attain octet structure by joint sharing of their valence electrons the bond formed is called covalent bond.** Thus, in the formation of covalent bond at least one electron is shared by each atom taking part in the bonding. If one-one electron is shared by atoms of elements then they form one covalent bond. e.g.

$$\text{H}\overset{\bullet}{\underset{\bullet}{}}\text{H},\quad \text{H}\overset{\times}{\underset{\times\,\times}{\overset{\times\,\times}{\text{Cl}}}}\text{,}\quad \text{H}\underset{\text{H}}{\overset{\text{H}}{\text{C}}}\text{H}$$

But when two-two electrons are shared by atoms combining by covalent bond, then formation of double bond between them is obtained. e.g.

$$:\overset{\bullet\bullet}{\text{O}}::\overset{\bullet\bullet}{\text{O}}:,\quad \overset{\bullet\bullet}{\text{O}}::\text{C}::\overset{\bullet\bullet}{\text{O}},\quad \overset{\text{H}}{}\text{C}::\text{C}\overset{\text{H}}{}$$

If three-three electrons are shared between atoms of combining elements, the formation of triple bond between them is obtained. e.g.

$$:\text{N}:::\text{N}:\quad \text{H}:\text{C}:::\text{C}:\text{H}$$
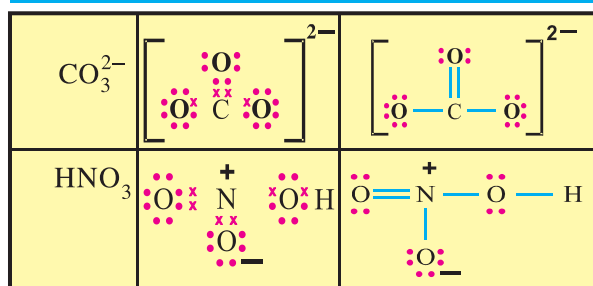
Lewis Dot Representation : To show Lewis Dot Representation of given molecule/ion :

- First of all the number of valence electrons of each atom taking part in the formation of molecule is taken into consideration and they are arranged as required around the symbol of that atom.

- If negative ion is formed, the number of electrons equal to negative charge is added but if positive ion is formed, the number of electrons equal to positive charge is deducted. e.g. CO_3^{2-} ion, as there are two units of negative charge, it has two electrons more (-2) in number than the valence electrons present in the neutral atom. Similarly in NH_4^+ ion, as there is one unit of positive charge, one electron is less $(+1)$ as compared to natural atom.

- Generally the atom of less electronegative element is taken as central atom and more electronegative atoms are arranged around it.

- **The electron pair which takes part by sharing in the formation of chemical bond is called bonding pair of electrons and the electron pair which does not take part in the formation of bond is called non-bonding pair of electrons or lone pair of electrons.**

Lewis Structures of certain molecules/ions are shown in Table 1.1.

Table 1.1 Lewis structure of certain molecules/ions

Molecule/ion	Lewis structure	
H_2	H:H*	H—H
O_2	:Ö::Ö:	:Ö=Ö:
O_3	(Lewis dot structure of ozone with O⁺ and O⁻)	(Lewis structure of ozone with O⊕ bonded to O and O⁻)
NF_3	(Lewis dot structure of NF_3)	(Lewis line structure of NF_3)

|		
CO_3^{2-}	Lewis structure	Lewis structure
HNO_3	Lewis structure	Structural formula

* **Each H atom attains the configuration of Helium (only two electrons.)**

With the help of the Lewis Approach, the shapes of molecule/ion cannot be known and also there are certain exceptions.

e.g. $BeCl_2$: Cl Be Cl (Lewis structure)

In the molecule of $BeCl_2$, the octet of the central Be atom is not completed; even then this compound is stable. Similarly, in certain examples like PCl_5, there are ten electrons around central phosphorus atom; even then the compound is stable.

Cl Cl Cl P Cl Cl Cl (Lewis structure of PCl_5)
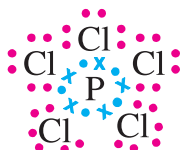
In certain cases, the stability decreases with increase in atomic size of central atom even though the octet structure is complete in the elements of the same group. e.g. $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. Electrons are shared in formation of covalent bond, but on the basis of the type of sharing and type of atom of combining element, it is divided into three parts :

(i) Polar Covalent Bond : In this type of covalent bond, atoms of element having different electropositivity or electronega-tivity take part in the formation of covalent bond. As a result, the property of polarity is Induced in moecules.

e.g. HCl   H Cl (Lewis structure)

(ii) Non-polar Covalent Bond : When a covalent bond is formed by sharing of elec-trons of atoms of the same element, the bond is called nonpolar covalent bond. Such compounds are nonpolar because the electropositivity or electro-negativity of their elemants is same.

e.g.   H H   Cl Cl (Lewis structures)

(iii) Co-ordinate Covalent Bond : For the formation of bond of this type, the required electron pair is donated by the atom of only one from the two elements. As a result the covalent bond formed is called **co-ordinate covalent bond.** This bond is shown by the sign of arrow ($\rightarrow$) and the direction of the arrow is from the atom donating the electron pair to the atom receiving the electron pair.

(Lewis structures showing $BF_3 + NH_3 \longrightarrow F_3B \leftarrow NH_3$)
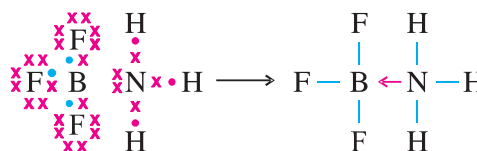
Bond Length : The equilibrium distance between the nuclei of two atoms conbined by bond in the molecule is called bond length. The bond length is measured by X-ray diffraction and spectroscopic methods. It is   expressed in picometer (pm = 10^{-12}m)

The bond lengths of some common molecules are shown in Table 1.2.

Table 1.2 Bond Lengths of some common molecules

Molecule	Bond Length (pm)
H_2 (H – H)	74
F_2 (F – F)	144
Cl_2 (Cl – Cl)	199
Br_2 (Br – Br)	228
I_2 (I – I)	267
N_2 (N – N)	109
O_2 (O – O)	121
HF (H – F)	92
HCl (H – Cl)	127
HBr (H – Br)	141
HI (H – I)	160

The less values of bond length mention greater stability.

Bond Angle : The angle between the orbitals possessing bonding electron pairs around central atom of the molecule/ion is called bond angle. Bond angle is expressed in degrees which can be determined by spectroscopic methods. With the help of the bond angle, the preliminary information about shapes of molecules

can be obtained. e.g. The bond angle in molecule of water can be shown as below :
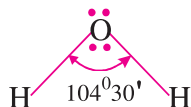

Bond Energy (Bond Enthalpy) : The energy required for breaking bond in one mole gaseous substance is called bond energy or bond enthalpy. The unit of bond enthalpy is kJmol^{-1}. e.g. The bond enthalpy of H–H bond in hydrogen molecule is 435.8 kJ mol^{-1}.

$H_{2(g)} \rightarrow H_{(g)} + H_{(g)}$ Bond enthalpy = 435.8 kJ mol^{-1}. More the value of bond enthalpy higher will be the stability of molecule/ion.

Bond Order : The number of bonds between atoms present in molecule is called bond order. e.g. In H_2 molecule, there is sharing of one electron pair. As a result, the two hydrogen atoms present in hydrogen molecule are combined by single bond, H–H. Similary, in O_2 and N_2 there are sharing of two and three electron pairs respectively and so double bond and triple bonds are formed. $\ddot{\underset{..}{O}} = \ddot{\underset{..}{O}}$, $:N \equiv N:$ Single bond, double bonds and triple bonds are respectively shown as $-$, $=$, and $\equiv$. With the increase in bond order, the values of bond enthalpy increase. As a result bond length decreases and so stability increases.

Born-Haber Cycle : The formation of ionic bond depends on lattice enthalpy. More the value of lattice enthalpy of the product easier will be the formation of ionic bond. The value of lattice energy will be more only when the attraction force between two atoms is more. Born-Haber first of all gave value of total enthalpy-lattice enthalpy by studying the enthalpies of different steps involved in the formation of ionic compounds by ionic bonds.

We shall try to explain Born-Haber Cycle by taking example of different enthalpy changes involved in the formation of NaCl crystalline compound from its components in standard state. Generally the simple equation for the formation of NaCl crystal can be written as follows:

$$Na_{(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow NaCl_{(s)}$$
$$\Delta_f H = -411 \ kJmol^{-1}$$
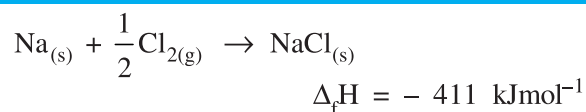
The different steps of formation of NaCl crystal are as follows :

(i) First of all, sodium element/atom which is in solid form at room temperature is sublimed and the value of sublimation enthalpy $(\Delta_s H)$ is 108 kJmol^{-1}.

$$Na_{(s)} \xrightarrow{\text{Sublimation enthalpy}} Na_{(g)}$$
$$\Delta_s H = +108 \ kJmol^{-1}$$
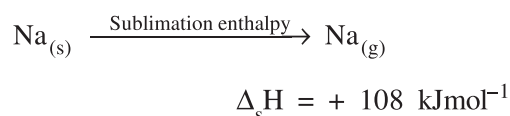
(ii) The value of ionisation enthalpy required to remove electron from one mole $Na_{(g)}$ atom to infinite distance is 496 kJmol^{-1}

$$Na_{(g)} \xrightarrow{\text{Ionization enthalpy}} Na^+_{(g)} + e^-$$
$$\Delta_i H = +496 \ kJmol^{-1}$$
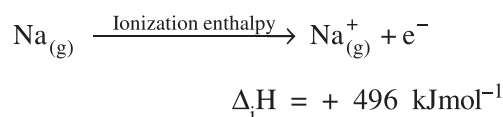
(iii) Gaseous chlorine element exists as diatomic molecule at room temperature. In one mole solid NaCl crystal structure formation only one chlorine atom is required. Hence decomposition of dichlorine molecule becomes essential. The enthalpy required for this is called decomposition enthalpy.

$$\frac{1}{2}Cl_{2(g)} \xrightarrow{\text{decomposition}} Cl_{(g)}$$
$$\Delta_{\frac{D}{2}}H = +121 \ kJmol^{-1}$$
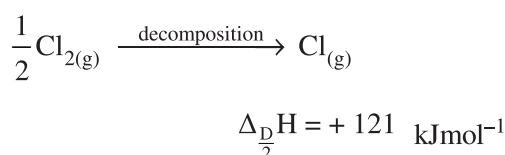
(iv) The gaseous atom of chlorine obtained this way accepts one electron and changes to chloride ion. The enthalpy released for this is called electron gain enthalpy $(\Delta_{eg}H)$

$$Cl_{(g)} + e^- \xrightarrow{\text{Electron gain enthalpy}} Cl^-_{(g)}$$
$$\Delta_{eg}H = -349 \ kJmol^{-1}$$
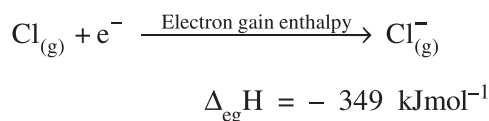
(v) One mole gaseous positive ion (Na$^+$) and one mole gaseous negative ion (Cl$^-$) combine with each other and form one mole of solid ionic crystal. The enthalpy released during this is called lattice enthalpy which is expressed as 'U'.

$$Na^+_{(g)} + Cl^-_{(g)} \xrightarrow{\text{Lattice enthalpy}} NaCl_{(s)}$$
$$\Delta_U H = -787 \ kJmol^{-1}$$
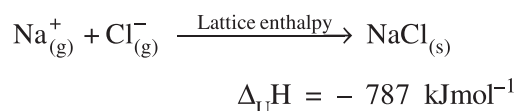
By the above method, the crystal structure of any ionic solid can be known by the study of each step of the different steps according to Born-Haber cycle, and the value of enthalpy of formation - lattice enthalpy can be obtained. The above different steps can be shown as below :
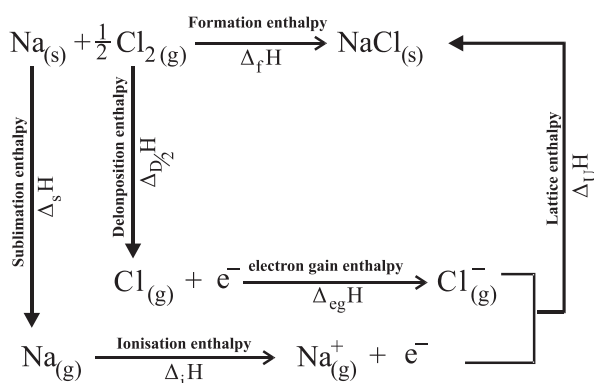
All the above different steps can be written in the form of equation as follows :

$$\Delta_f H = \Delta_s H + \frac{\Delta_D}{2} H + \Delta_i H + \Delta_{eg} H + \Delta_U H....(1.1)$$

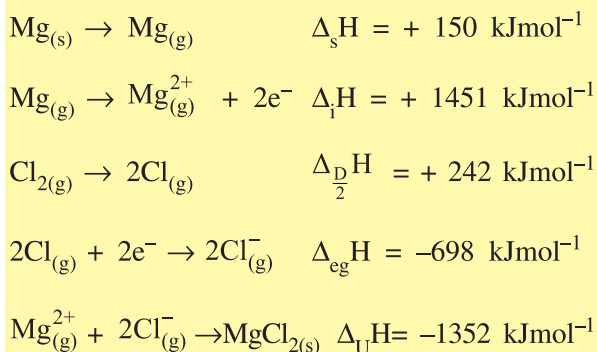The enthalpy of formation of crystal of one mole NaCl can be obtained by adding up the different enthalpies as below :

$$\Delta_f H = 108 + 121 + 496 + (-349) + (-787)$$

$$= -411 \text{ kJmol}^{-1}$$

Thus, the value of enthalpy of formation for one mole NaCl obtained is negative which indicates its stability.

Example 1.1 : Find the enthalpy of formation of $MgCl_2$ using the following values:

$Mg_{(s)} \rightarrow Mg_{(g)}$ $\Delta_s H = + 150$ kJmol^{-1}

$Mg_{(g)} \rightarrow Mg^{2+}_{(g)} + 2e^-$ $\Delta_i H = + 1451$ kJmol^{-1}

$Cl_{2(g)} \rightarrow 2Cl_{(g)}$ $\frac{\Delta_D}{2}H = + 242$ kJmol^{-1}

$2Cl_{(g)} + 2e^- \rightarrow 2Cl^-_{(g)}$ $\Delta_{eg} H = -698$ kJmol^{-1}

$Mg^{2+}_{(g)} + 2Cl^-_{(g)} \rightarrow MgCl_{2(s)}$ $\Delta_U H = -1352$ kJmol^{-1}

Solution :

$$\Delta_f H = \Delta_s H + \Delta_i H + \frac{\Delta_D}{2}H + \Delta_{eg} H + \Delta_U H$$

$$= 150 + 1451 + 242 + (-698) + (-1352)$$

$$= -207 \text{ kJmol}^{-1}$$

1.4   Rasonance Structures

The experimentally observed properties of the molecules cannot be explained only by Lewis Structure. This is its limitation. This means that Lewis Structure is incomplete to explain the experimentally observed properties of molecules e.g. Ozone molecule can be explained by following two structures :
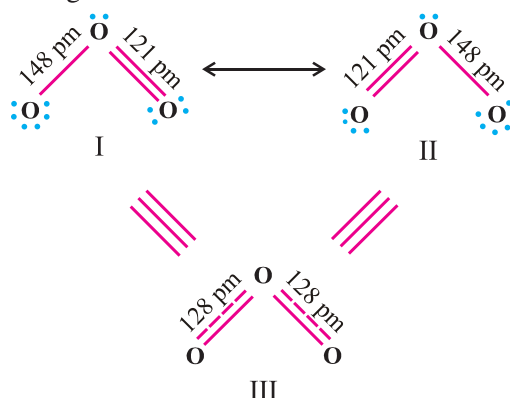

Fig. 1.1 The resonance structures of Ozone molecule

In both the structures, O – O single bond and O = O double bond are present. O – O single bond length is 148 pm (1 picometer (pm) = 10^{-12} meter) and O = O double bond length is 121 pm; but the bond length between any oxygen-oxygen in ozone molecule is same, and its value is 128 pm. Thus, the bond length between oxygen-oxygen in ozone molecule is in middle of single bond and double bond, which cannot be explained by any one of the structures I and II as shown in fig 1.1. Hence, the idea of resonance was presented to explain the real structures of molecules like ozone and others. You have studied about resonance structures of CO_2 molecule in Semester I. Thus, in resonance structure, same energy, same position of nucleus as well as bonding electron pairs and non bonding electron pairs are taken into consideration, the resonance structure which represents the molecule definitely. According to Fig 1.1, structures I and II, represent the resonance structures of structure III which is the real structure of ozone. Such structures are called hybrid resonance structures. Such similar examples like benzene; carbonate ion $\left(CO_3^{2-}\right)$ also can explain the resonance.

Resonance structures give stability to the molecule because the energy of resonance structure is less than those of structures shown separately. Thus decrease in energy is responsible for the stability of resonance structure.

1.5 Geometrical Structures of Molecules

Variety has been observed in geometric structures of molecules. The basis of diversity in geometrical structures of molecules in one type of molecules, the bonding and non-bonding electron pairs present in them as well as the magnitude of the attraction produced between them.

Table 1.3 Geometrical shapes of molecules in which central atoms of the molecule has no non-bonding electron pairs
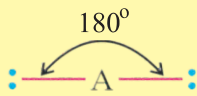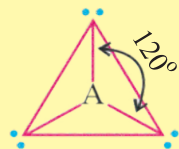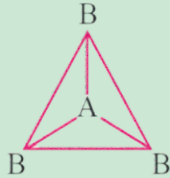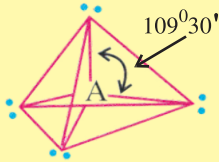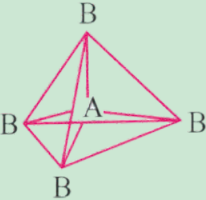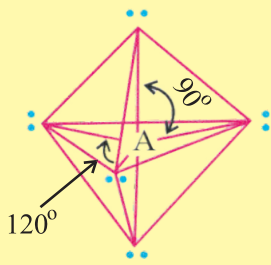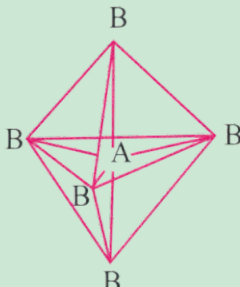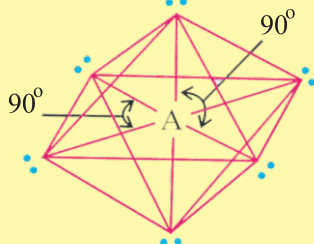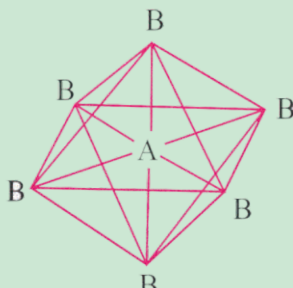
Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Hybridisation	Examples
2	Linear	Linear	sp	BeH_2, $BeCl_2$ $HgCl_2$
3	Trigonal planar	Trigonal planar	sp^2	BF_3, BCl_3
4	Tetrahedral	Tetrahedral	sp^3	CH_4, NH_4^+ BF_4^-, CCl_4
5	Trigonal bipyramidal	Trigonal bipyramidal	sp^3d	PCl_5
6	Octahedral	Octahedral	sp^3d^2	SF_6

Table 1.4 Geometrial shapes of molecules in which the central atom of molecule has one or more non-bonding electron pairs
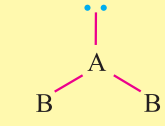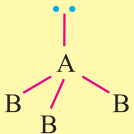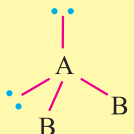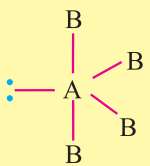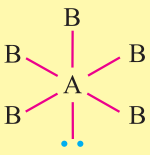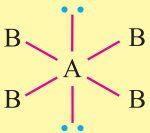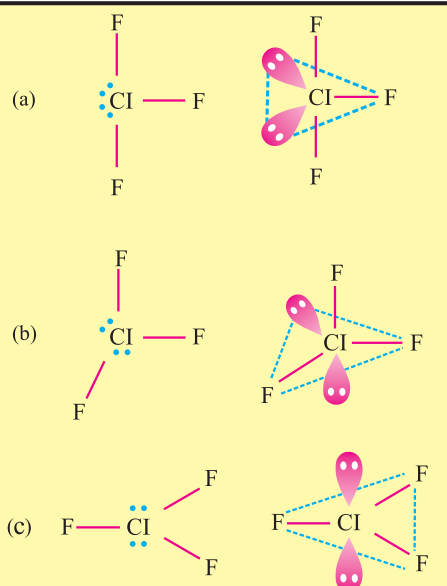
Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB_2E	2	1	Trigonal planar	Bent	SO_2, O_3
AB_3E	3	1	Tetrahedral	Trigonal pyramidal	NH_3 PCl_3
AB_2E_2	2	2	Tetrahedral	Bent	H_2O F_2O
AB_4E	4	1	Trigonal bipyramidal	See saw	SF_4
AB_3E_2	3	2	Trigonal bipyramidal	T- shape	ClF_3
AB_5E	5	1	Octahedral	Square pyramidal.	BrF_5
AB_4E_2	4	2	Octahedral	Square planar	XeF_4

Table 1.5 Geometrical shapes of molecules having bonding and non-bonding electron pairs

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Example
AB_2E	2	1		Bent	SO_2
AB_3E	3	1		Trigonal pyramidal	NH_3
AB_2E_2	2	2		Bent	H_2O
AB_4E	4	1	(a) ... (b) ... (More Stable)	See saw	SF_4

AB_3E_2	3	2		T- shape	ClF_3
			(a) Cl with F (top), F (right), F (bottom) and lone pairs		
			(b) Cl with F (top), F (right), F (bottom-left) and lone pairs		
			(c) $F-Cl$ with F (upper right), F (lower right) and lone pairs		

1.6   VSEPR Principle (Principle of Valence Shell Electron Pair Repulsion)

Lewis Aproach was incomplete to explain shapes of molecules. Only the hypotheses about the structures of molecules containing covalent bond can be made. First of all, in 1940, Sidgwick and Powell presented the theory of repulsion existing between electron pairs present in valence shells of atoms. In 1957, Nyholm and Gillespie presented this theory in the developed form. The main hypotheses of this theory are as follows :

- The shape of the molecule depends upon the number of electron pairs (bonding and non-bonding electron pairs) in valence shells around the central atom.

- The electron pairs present in valence shell being negatively charged, repel each other.

- These electron pairs possess the tendency of obtaining such an arrangement in the space that the repulsion between them is minimum and as a result there is maximum distance between them.

- If there are two or more than two resonance structures in the molecule, VSEPR principle can be applied to any of the structures.

- The magnitude of the repulsion produced between electron pair is as follows :

Thus, **VSEPR principle is helpful in determining geometrical shapes produced due to presence of electron pair in the molecule.** Especially, the geometric structures of compounds of elements of p-block can be explained by this principle.
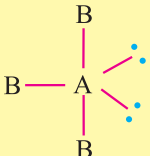
The molecule of sulphur dioxide is angular and bond angle is 119.5^0 instead of 120^0. This is due to repulsion produced between bonding and non-bonding electron pairs. In the same way, in methane, ammonia and water molecules there is similar type of hybrid orbitals (sp^3), even then the repulsion forces are produced in different magnitudes due to different numbers of electron pairs and as a result different bond angles are obtained.

The electronic structure of central carbon atom in methane molecule in ground state is as follows :

$$_6C : 1s^2 \ 2s^2 \ 2p_x^1 \ 2p_y^1 \ 2p_z^0$$

Repulsion produced between non-bonding and non-bonding pair of electron (Lp – Lp)	Repulsion produced between non-bonding pair of electron and bonding pair of electron (Lp – Bp)	Repulsion produced between bonding pairs of electrons (Bp – Bp)
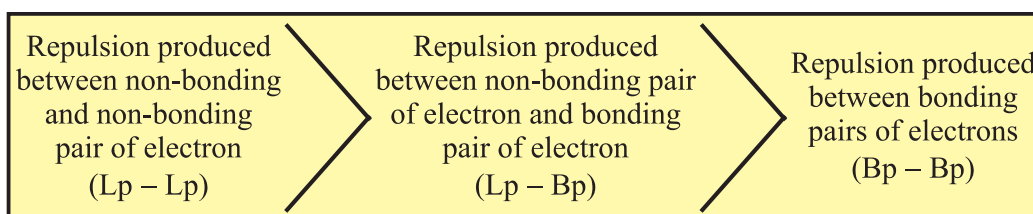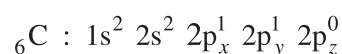
As four hydrogen atoms are combined with central carbon atom, four half filled orbitals will be requied. For this, writing the electron structure of carbon in excited state will be.

$$_6C^* \; : \; 1s^2 \; 2s^1 \; 2p_x^1 \; 2p_y^1 \; 2p_z^1$$
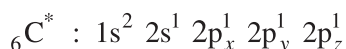
Thus, carbon atom in its excited state utilises sp^3 hybrid orbitals, combines with half filled $1s^1$ orbitals of hydrogen atom and forms four covalent bonds.
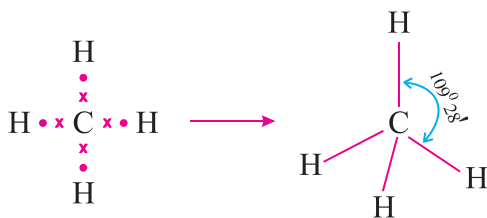
Thus, in methane molecule, there are four bonding electron pairs (Bp) between carbon and hydrogen atoms. According to Sidgwick-Powell rule, there is minimum repulsion between these four bonding electron pairs. As a result, tetrahedral structure corresponding to sp^3 hybridisation is observed in which the bond angle as in regular tetrahedral structure that is $109^0 28'$is observed.

In the molecule of NH_3, nitrogen atom has five valence electrons, out of which three electrons combine with electrons of 1s orbital of three hydrogen atoms by sharing and form three covalent bonds. Even after that nitrogen atoms has two electrons or one electron pair which remains uncombined even after formation of bonds. Thus one non-bonding pair of electrons remains.
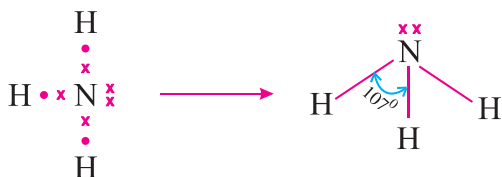
This non bonding electron pair of nitrogen atom repels the two bonding electron pairs around nitrogen according to Sidgwick-Powell rule. As a result, both these electron pairs are pushed inside. As a result the bond angle between them decreases or instead of regular tetrahedral bond angle $109^0 28'$ it is obtained as 107^0.

In H_2O molecule, there are total six valence electrons around central oxygen atom, out of which, two valence electrons form covalent bond with 1s orbital electrons of two hydrogen atoms but remaining four electrons or two electron pairs become non bonding electron pairs.
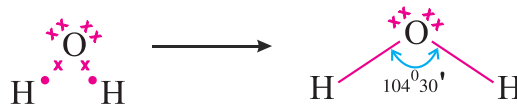
According to Sidgwick-Powell rule there is maximum repusion force between these two non bonding electron pairs and as a result they remain away from each other. When it happens so, they go near the bonding electron pairs and repulsion is produced between them. Because of this, bonding electron pairs are pushed inside, in more proportion and there is noticeable decrease in the bond angle. In H_2O molecule, even though there is sp^3 hybridisation but bond angle formed is 104^0 30' by decreasing from bond angle $109^0 28'$.

1.7 Polarity of Bond

Any chemical bond does not possess completely ionic or completely covalent nature. In the molecules like H_2, N_2, O_2, Cl_2 etc. the covalent bond is formed by sharing of electrons between its two atoms; but when the experimental values of bond lengths and bond enthalpies are studied, it is found that there is some contribution of ionic bond. Heteronuclear diatomic molecules like hydrogen fluoride (HF), the electron pair of covalent bond remains dragged more towards atom of fluorine element because the electronegativity of fluorine (in comparison to hydrogen atom) is more. As a result the partial negative charge $(-\delta)$ is produced on atom of fluorine element and partial positive charge $(+\delta)$ is produced on atom of hydrogen. Its real structural formula can be written as below :

Dipole Moment is found in the molecule due to this property of polarity. In the same way in the molecule of water, one oxygen atom and two hydrogen atoms combine to form two covalent bonds. The electronegativity of oxygen

element being more relative to that of atom of hydrogen element, the electron pairs remain dragged towards atom of oxygen. This produces partial positive charge $(+\delta)$ on hydrogen atom and partial negative charge $(-\delta)$ on oxygen atom. In addition due to the two non-bonding electron pairs on atom of oxygen element, property of polarity is as shown below :

$$2(-\delta) \quad O$$
$$(+\delta)\,H \qquad H\,(+\delta)$$
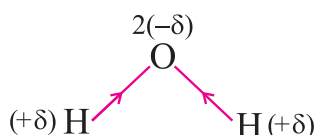
In linear molecule like beryllium flouride (BeF$_2$) polarity of the same magnitude exists between beryllium and each fluorine atom but in opposite directions. As a result, the resultant value of polarity becomes zero and the value of dipole moment becomes zero.

$$\overset{-\delta}{F} \longleftarrow \overset{2(+\delta)}{Be} \longrightarrow \overset{-\delta}{F}$$
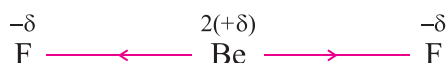
The value of dipole moment of ammonia (NH$_3$) is not zero, so it is not linear but the structure of the molecule is pyramidal.

$$2(-\delta) \quad N$$
$$(+\delta)\,H \qquad\qquad H\,(+\delta)$$
$$(+\delta)\,H$$
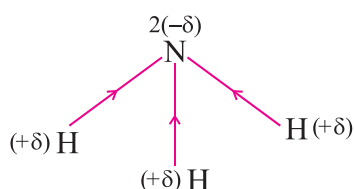
The electronegativity of flurine element being more than that of the electronegativity of hydrogen, the value of dipole moment of NH$_3$ molecule is more than the value of dipole moment of NF$_3$. In both these molecules, one non bonding electron pair is on central nitrogen atom. In the molecule of NH$_3$ the polarily of all the three N–H bonds is towards nitrogen atom. (The electronegativity of nitrogen is more than that of hydrogen). Thus, the polarity of three bonds is concentrated on central nitrogen atom and so the resultant value of dipole moment increases while, in NF$_3$ molecule, the polarity of N–F bond is towards F atom (The electronegativity of fluorine is more than that of nitrogen). Thus in NF$_3$ three N–F bonds in different directions and so the resultant value of dipole moment is less in comparison to NH$_3$ molecule.
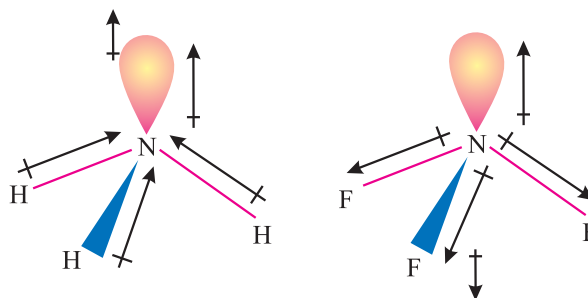
The values of dipole moments of some molecules and their geometrical shapes are in Table 1.6.

Table 1.6 Dipole moments of some selected compounds and their geometrical shapes

Type of molecule	Example	Dipole moment μ (D)	Geometrical shape
Molecule AB	HF	1.78	Linear
	HCl	1.07	Linear
	HBr	0.79	Linear
	HI	0.38	Linear
	H$_2$	0	Linear
Molecule AB$_2$	H$_2$O	1.85	Bent
	H$_2$S	0.95	Bent
	CO$_2$	0	Linear
Molecule AB$_3$	NH$_3$	1.47	Trigonal pyramidal
	NF$_3$	0.23	Trigonal pyramidal
	BF$_3$	0	Planar trigonal

Molecule AB_4	CH_4	0	Tetrahedaral
	$CHCl_3$	1.04	Tetrahedaral
	CCl_4	0	Tetrahedaral

1.8 Approach to Covalent Bond

The explanation of covalent bond can be given by Lewis theory but the shapes of molecules and polarity of bonds cannot be explained by this theory. The modern theory of covalent bond formation is based on the quantum mechanics. For explanation of this, there are two major approaches-Valence Bond Theory and Molecular Orbital Theory.

Heitler and London had presented the theory of valence bond in 1927 which was later developed by scientist Pauling with some changes. According to this theory, the bond is formed by overlapping of valence orbitals of atoms. e.g. Dihydrogen molecule is formed by combination of two hydrogen atoms. Each hydrogen atom possesses one proton in the nucleus and one electron in its orbit. According to valence bond theory, one covalent bond between two hydrogen atoms H—H is formed by the overlapping of 1s orbital of each hydrogen atom. The directions of the spin of electron in 1s orbital of each hydrogen, which is overlapping are opposite to each other. In the formation of hydrogen molecule, the electron pair obtained by overlapping of two 1s orbitals, and having opposite spins remain in between nuclei of two hydrogen atoms and this bonding electron pair experiences similar attraction by both the nuclei.

1.9 Valence Bond Theory

In 1927, Heitler and London first of all presented the valence bond theory. Its detailed study and devlopment were carried out by scientists Linus Pauling and Slater. According to this theory, when half filled atomic orbitals come near to each other, then they get overlapped, and as a result the formation of covalent bond

is attained. Thus, one half filled orbital of one atom overlaps with half filled orbital of other atom and forms bond. Thus, the combining atoms share their valence electrons and form covalent bond. Sometimes, out of the two combining atoms, the orbital of one atom may be completely filled and the other orbital of the other atom may be vacant, even then they both overlap and form special type of covalent bond (which is called co-ordinate covalent bond).

Two atoms A and B of hydrogen element which possess nuclei N_A and N_B. Suppose, they go near to each other. The electrons in the two atoms are shown as e_A and e_B. When these two atoms are at very far distance, there is no interattractive force between them. When they come nearer to each other, the attractive and repulsive forces are produced between them.

The attractive forces are produced because of following factors :

(i) The attractive forces produced between nucleus of the atom itself and its own electron or $N_A - e_A$ and $N_B - e_B$.

(ii) The attractive force produced by nucleus of one atom and electron of other atom. $N_A - e_B$ and $N_B - e_A$.

In the same way, repulsive forces are produced because of the following factors :

(i) Repulsive force produced between electron-electron of two atoms $e_A - e_B$.

(ii) Repulsive force produced between nuclei of two atoms or $N_A - N_B$.

Attractive forces try to take both the atoms near to each other while repulsive forces try to push each other. This is shown in Fig 1.2.

Attractive Forces

- - - - - - - **Old force**
—————— **New force**
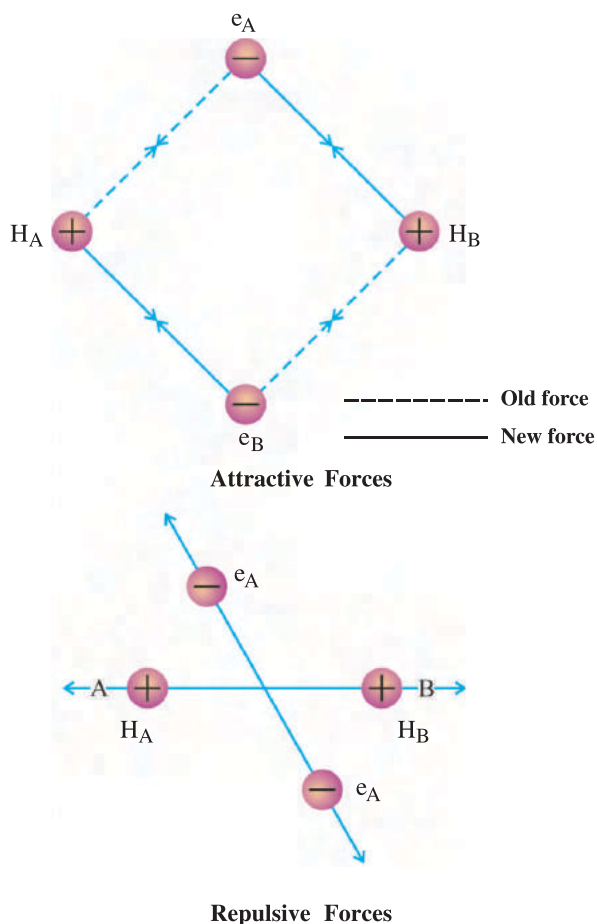
Repulsive Forces

Fig. 1.2 Forces of attraction and repulsion during the formation of H$_2$ molecule

It is proved from the experiments that the magnitude of attractive forces is more than that of repulsive forces. As a result both the atoms go near to each other and their potential energy decreases. Both the atoms go near to each other to such an extent that attractive forces are balanced by repulsive forces and the system attains minimum energy. At this stage, both hydrogen atoms combine with each other and remain at certain definite distance and forms stable hydrogen molecule. This distance or bond length is 74 pm.

Assumptions of Valence Bond Theory :
According to valence bond theory, the half filled atomic orbitals (and having same symmetry) having same energy overlap with each other and form covalent bond. As a result there is pairing of electrons in valence orbitals. The strength of covalent bond is directly proportional to the magnitude of overlapping of orbitals or if the overlapping of valence orbitals of atom is more, then stronger will be the covalent bond

The assumptions of valence bond theory can be given as follows :

(i) Generally there must not be much difference in energies of overlapping atomic orbitals.

(ii) The overlapping orbitals must be half filled and the spin of the electrons in them must be in opposite direction to each other.

(iii) There must be overlapping of atomic orbitals to proper extent, so that chemical bond formation can take place.

Overlapping of atomic orbitals : When two atoms come near to each other, there is overlapping of atomic orbitals. This overlapping can be positive, negative or zero wich depends upon the properties of the overlapping atomic orbitals. The different overlapping arrangements of s and p orbitals are shown in Fig. 1.3.
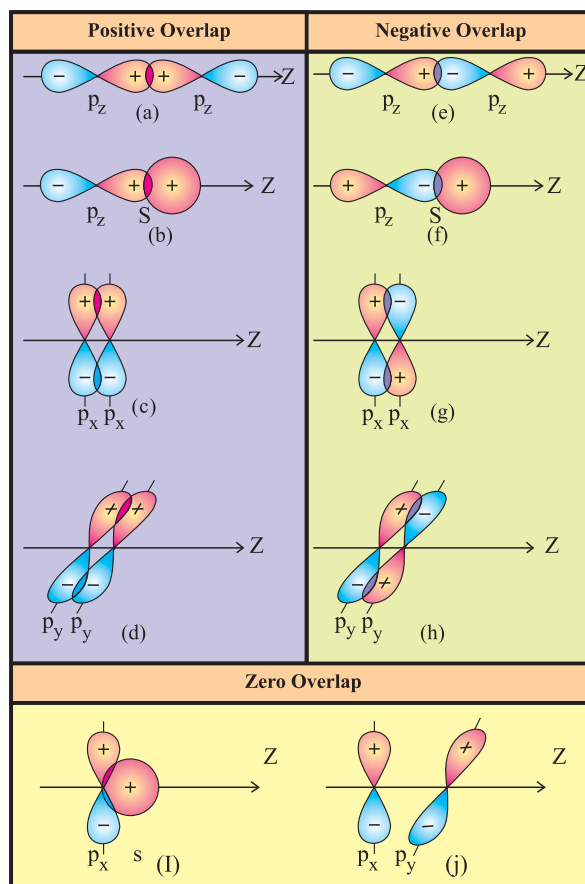
Fig. 1.3 Positive, negative and zero overlapping of s and p atomic orbitals

The assumptions of overlapping of atomic orbitals are applicable similarly to homonuclear, heteronuclear, diatomic and polyatomic molecules. The chemical bonding in molecules having

polynuclear atoms like CH_4, NH_3 and H_2O can be explained with the help of valence bond theory. Their shapes and bond angles can also be known. We know that the shapes of the molecules CH_4, NH_3 and H_2O are tetrahedral, pyramidal and bent respectively. These geometrical shapes can be explained with reference to overlapping of atomic orbitals.

The electronic structure of central atom carbon in CH_4 molecule, in its ground state is [He] $2s^2 \ 2p_x^1 \ 2p_y^1 \ 2p_z^0$, and in excited state it is [He] $2s^1 \ 2p_x^1 \ 2p_y^1 \ 2p_z^1$. Thus, four half filled orbitals of carbon atom overlap with 1s orbitals of four hydrogen atom, which are also half filled and form four C − H bonds. Three p-orbitals of carbon atom are at 90^0 to one another and so three C − H bonds are found at 90^0 to one another. But 2s orbital of hydrogen atom are symmetrically spherical, hence, they overlap with each other in any direction. Hence, the fourth C − H bond is not determined clearly. But this assumption is not consistent with tetrahedral molecular structure in which bond angle is $109^0 28$. Hence, it can be said that the overlapping of atomic orbitals does not possess vector properties. In the similar way the shapes of molecules of NH_3 and H_2O and their bond angles can be explained.

Types of Overlapping and Nature of Covalent Bond : The covalent bond formed by overlapping of atomic orbitals can be divided in to two types.

(i) σ bond : This type of σ - covalent bond is obtained by end to end overlapping of the ends of two atomic orbital having internuclear axis. It is also called axial overlapping. This type of overlapping is obtained by overlapping of atomic orbitals as shown below :

Overlapping of s—s orbitals : In this type, overlapping of two half filled orbitals having one axis is observed.

s-Orbital   s-Orbital   s-s Overlapping
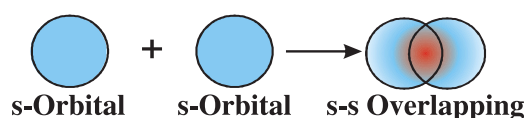
Overlapping of s—p orbitals : In this type, there is overlapping between half filled atomic

s-orbital of one atom and half filled atomic p-orbital of other atom.

s-Orbital   p-Orbital   s-p Overlapping
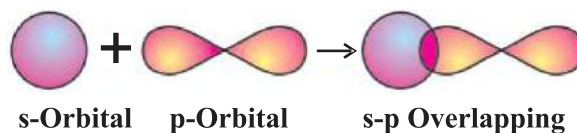
Overlapping of p—p orbitals : Here it is found that when the two atoms go near to each other the overlapping of p-p orbitals due to overlapping of half filled p-orbital of two atoms is observed.

p-Orbital   p-Orbital   p-p Overlapping
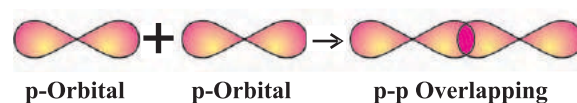
(ii) π− bond : In this type of π−covalent bond formation, the axes of atomic orbitals that are overlapping remains parallel to each other and it is perpendicular to internuclear axis.

p-Orbital p-Orbital   p-p Overlapping
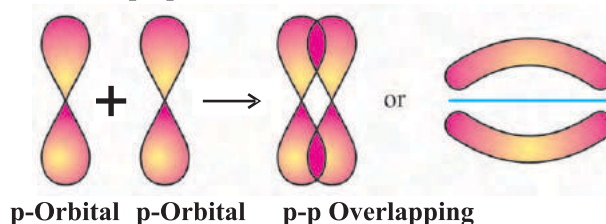
The strength of any type of σ or π bond is proportional to the magnitude of overlapping of atomic orbitals. In σ bond formation, overlapping of atomic orbitals is more and as a result σ− bond is strong. In π− bond formation the megnitude of overlapping is less because of overlapping of atomic orbitals is sidewise and as a result π− bond is weaker relative to σ− bond.

1.10 Molecular Orbital Theory

The molecular orbital theory was first of all presented by Mulliken and Hund in 1932. According to them, the description of molecular orbital is similar to that of atomic orbital. As electrons of atom are arranged in atomic orbitals (such as s,p,d...etc) in the same way the electrons of the molecule are arranged in molecular orbitals. The probability distribution of electrons around the nucleus of the atom can be shown by atomic orbitals. Similarly, the probability distribution of electrons around the nucleus of molecule can be shown by molecular orbitals is carried out obeying Auf bau principle, Pauli's Exclusion principle and Hund's rule of maximum multiplicity.

Important points of molecular orbital theory :

(i) As the electrons of the atom are arranged in different atomic orbitals, similarly electrons of the molecule are arranged in different molecular orbitals.

(ii) The atomic orbitals having similar energy and proper symmetry combine with each other in some definite way and forms molecular orbitals.

(iii) The electrons in the atomic orbital are under the effect of only one nucleus, while the electrons in the molecular orbitals are under the effect of two or more nuclei. It depends on how many atoms are there in the molecule. Thus atomic orbitals are monocentric, while molecular orbitals are polycentric.

(iv) The number of atomic orbitals that combine with each other is the same for molecular orbitals. Half the number these molecular orbitals are called Bonding Molecular Orbitals (BMO) and remaining half number of molecular orbitals are called Anti-bonding Molecular Orbitals (ABMO).

(v) The energy of the bonding molecular orbitals obtained by combination of respective atomic orbitals is less in comparison to the anti-bonding molecular orbitals.

Linear Combination of Atomic Orbitals (LCAO) and Formation of Molecular Orbitals : According to quantum mechanics, the formation of molecular orbitals between any two atoms is the linear combination of acceptable wave functions or Linear Combination of Atomic Orbitals. When two hydrogen atoms combine and H_2 molecule is formed, acceptable wave functions of each hydrogen atom $\Psi_{1s(1)}$ and $\Psi_{1s(2)}$ takes place by linear combination in two ways as follows : Hence two acceptable wave functions Ψ_{MO} and Ψ^*_{MO} are formed.

$$\Psi_{MO} = \Psi_{1s(1)} + \Psi_{1s(2)}$$
$$\Psi^*_{MO} = \Psi_{1s(1)} - \Psi_{1s(2)}$$

Here, (1) and (2) are the numbers used for two atoms of hydrogen. Two molecular wave functions formed here describe two molecular orbitals. The molecular orbital indicated by Ψ_{MO} is called bonding molecular orbital and by Ψ^*_{MO} is called antibonding molecular orbital.

When the molecular orbital is formed by complementary overlapping of two 1s orbital, it is spread over the nuclei of both the atoms. The total energy of this molecular orbital is less than the total energy of both the atomic orbitals. It is called bonding molecular orbital. When the molecular orbital formed by opposing overlapping of two 1s orbitals has total energy more than the total energy of both the atomic orbitals, is formed, it is called antibonding molecular orbital.
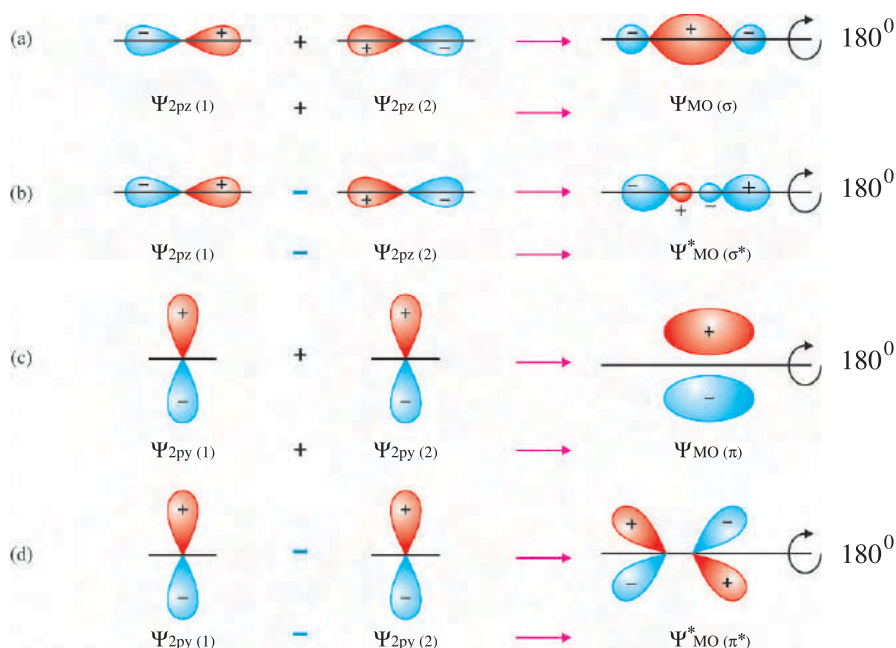

Fig. 1.4 Bonding and anti-bonding molecular orbitals

In the Figure 1.4, the horizontal line is the bond axis. (+) and (−) signs are the signs of wave function; they do not indicate electric charge. If the rotation of axis is carried out by 180^0 angle, the positions of (+) and (−) signs in (a) and (b) do not change. Hence, these molecular orbitals possess cylindrical symmetry. These orbitals are expressed by σ− symbol. In (a) the probability of electron in the field between two nuclei is maximum and so such type of molecular orbitals are (σ). In (b) the probability of electron being in the field between two nuclei is less and so this type of molecular orbitals resist the entry of electrons. Hence, they are called anti-bonding molecular orbitals (σ*). The molecular orbitals shown by (c) and (d) are of π−type because, the positions of the signs of wave functions change by rotation of bond axis by an angle of 180^0. In (c) the probability of electron in the field between two nuclei is more and so it is π-type bonding molecular orbital (π), while in (d) the probability of electron in the field between two nuclei is decreasing and so it is π− type anti-bonding molecular orbital (π*). In this type of molecular orbital the nodal plane between the two nuclei is plane. The probability of getting electron in the nodal plane is zero.

Conditions for the Combination of Atomic Orbitals :

When the molecular orbitals are formed by linear combination of atomic orbitals, some of the requirements should be satisfied. These requirements are also called the conditions for the linear combination of atomic orbitals. They are as follows :

(i) The atomic orbitals of the combining atoms must possess similar energies.

(ii) The combining atoms must be as near as possible so that the overlapping can be maximum on the axis of atomic orbitals.

(iii) The symmetry of the atomic orbitals of combining atoms must be same.

1.11 Types of Molecular Orbitals

The molecular orbitals of diatomic molecule are generally expressed as σ and π. The σ−type molecular orbitals possess symmetry around the bond axis, while π-type molecular orbitals do not possess symmetry around the bond axis. Generally σ−type molecular combination of s − s orbitals and s − p type orbitals, while by linear combination of $p_z - p_z$ atomic orbitals σ−type molecular orbitals are obtained. By linear combination $p_x - p_x$ and $p_y - p_y$ atomic orbitals, π−bond is obtained.

1.12 Molecular Orbitals and Their Relative Energies

When two atoms come near to each other and form molecular orbitals, the number of molecular orbitals is equal to the total number of atomic orbitals of those two atoms. The types of molecular orbitals, formed when diatomic molecule is formed by bringing two atoms of elements from hydrogen to neon when brought near to each other and their relative energy can be shown as in Fig 1.5.
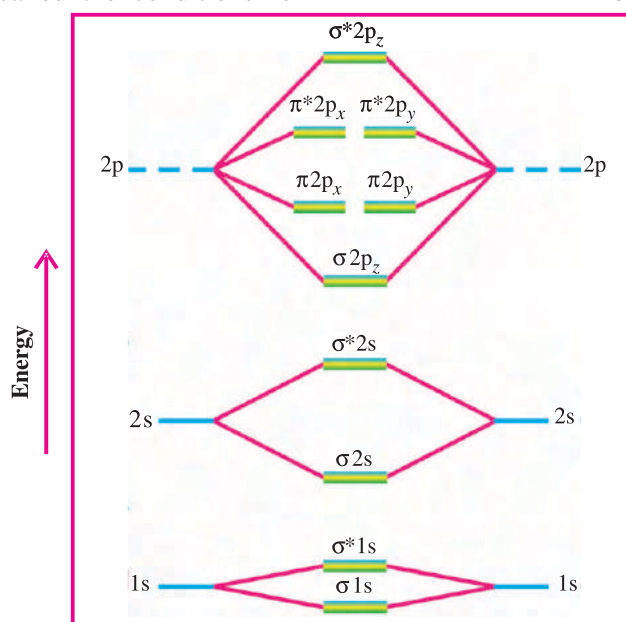
Fig. 1.5 Energy levels diagram of molecular orbital

The increasing order of molecular orbitals for molecules from H_2 to N_2 is as follows :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

But the order is changed for molecules from O_2 to Ne_2, which is as follows :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

1.13 Molecular Orbitals and their Relative Energies

The distribution of electrons in different molecular orbitals is called molecular electronic configuration. Some important information is obtained from electronic configuration of molecule.

Stability of Molecule : Suppose N_b is the number of electrons in bonding molecular orbital and N_a is the number of electrons in anti-bonding molecular orbitals, then :

(i) For $N_b > N_a$, molecule is more stable.

(ii) For $N_b < N_a$, molecule becomes unstable.

Bond Order and Stability : The stability of molecule is directly proportional to the value of bond order. The difference between total number of electrons in bonding molecular orbitals (N_b) and the number of electrons in anti-bonding molecular orbitals (N_a) when divided by two, the value of bond order is obtained i.e.

$$\text{Bond order} = \frac{1}{2}\left[N_b - N_a\right]$$

If the value of bond order is positive $(N_b > N_a)$ the molecule becomes stable but negative or zero value of bond order $(N_b < N_a$ or $N_b = N_a)$ indicates instability of molecule.

If unpaired electrons are there in electronic configuration of atomic orbitals, the molecule/ion becomes paramagnetic and if all the electrons are paired it becomes diamagnetic.

1.14 Energy Level Diagram Bond Order, Stability and Magnetic Properties of Homonuclear Diatomic Molecules Like He_2 to Ne_2

The energy level diagram of molecular orbitals of any homonuclear diatomic molecule can be drawn as shown in Fig 1.5 and the bond order can be calculated by arranging electrons in them. The energy level diagrams of molecular orbitals of H_2 molecule and O_2 molecule are shown as illustration in Fig 1.6 (a) and (b) respectively.

H_2
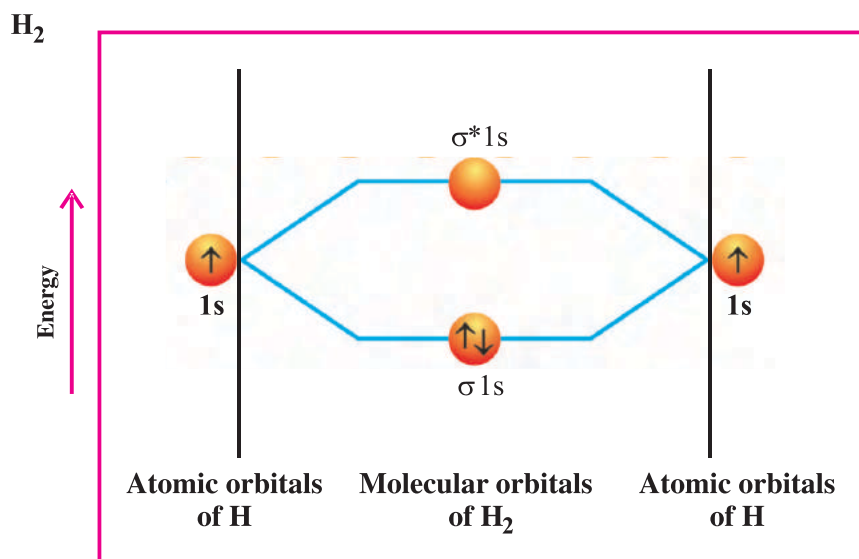
Fig. 1.6 (a) Energy level diagram of molecular orbital of H_2
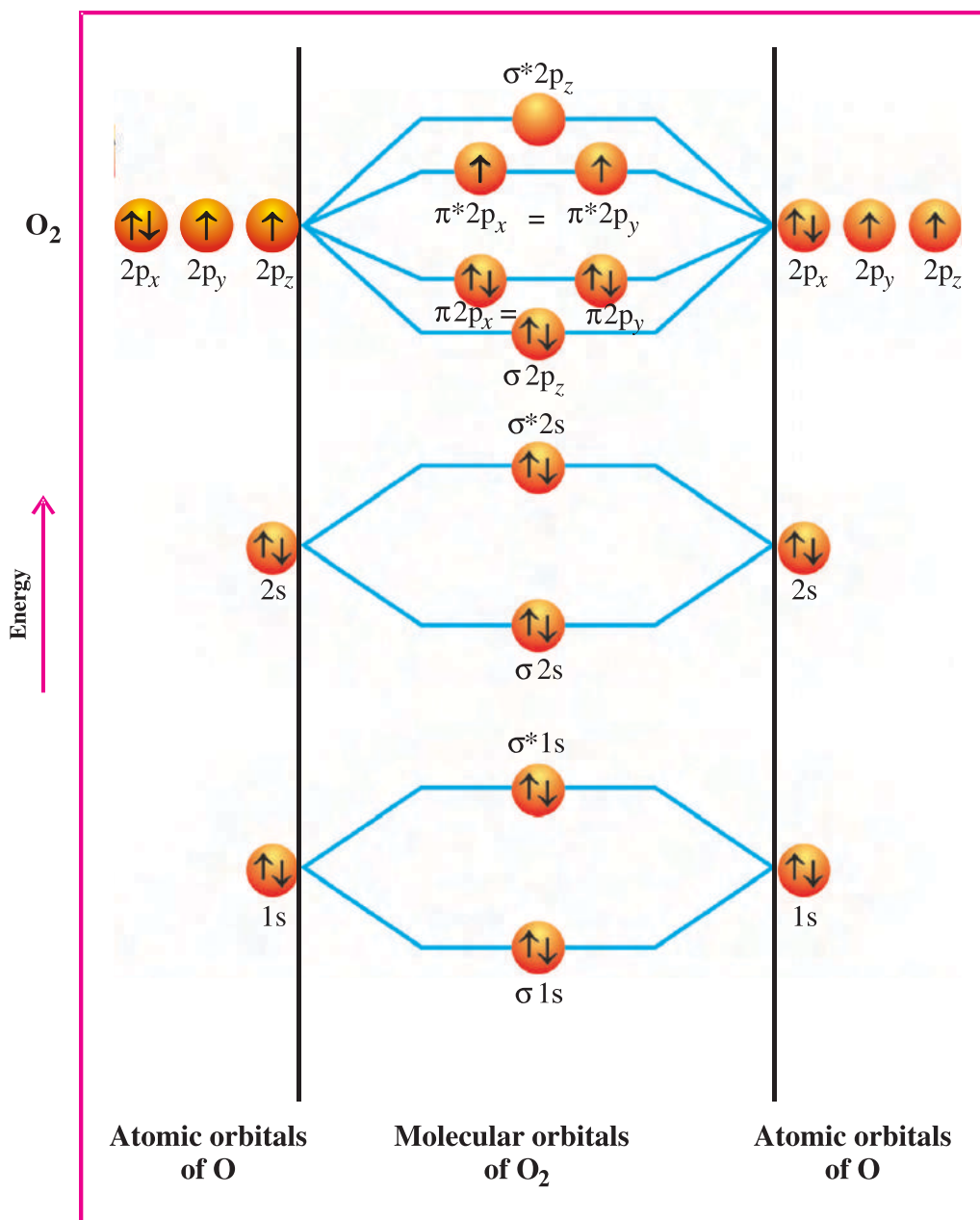
Fig. 1.6 (b) Energy level diagram of molecular orbitals of O_2

(1) H_2 molecule : The electronic configuration of H-atom is $1s^1$. Hence, there are two electrons in H_2 molecule. The molecular electronic configuration of these two electrons will be as follows :

$$H_2 = (\sigma 1s)^2$$

$$\text{Bond order} = \frac{1}{2}\left[N_b - N_a\right]$$

$$= \frac{1}{2}\left[2 - 0\right]$$

$$= 1$$

Hence, H − H is in H_2.

(2) He_2 molecule: The electronic configuration of He atom is $1s^2$. Total four electrons are there in He_2 molecule, whose molecular electronic configuration can be shown as follows :

$$He_2 = (\sigma 1s)^2 \, (\sigma^* 1s)^2$$

$$\text{Bond order} = \frac{1}{2}\left[N_b - N_a\right]$$

$$= \frac{1}{2}\left[2 - 2\right] = 0$$

Here, the value of bond order obtained is zero which indicates that He_2 molecule is unstable and so He_2 molecule is not possible.

(3) Li$_2$ molecule : The electronic configuration of Li atom is $1s^2\ 2s^1$. Thus, there are six electrons in Li$_2$ molecule whose arrangement in molecular orbitals can be made as follows :

$$Li_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2$$

$$Bond\ order = \frac{1}{2}\ [N_b - N_a]$$

$$= \frac{1}{2}\ [4 - 2] = 1$$

Hence, Li $-$ Li is there in Li$_2$.

(4) Be$_2$ molecule : The electronic configuration of Be atom is $1s^2\ 2s^2$. Thus, there are totally eight electrons in Be$_2$ molecule which will be arranged in molecule orbitals as follows :

$$Be_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2$$

$$Bond\ order = \frac{1}{2}\ [N_b - N_a]$$

$$= \frac{1}{2}\ [4 - 4] = 0$$

Thus, the value of bond order of Be$_2$ is zero which indicates unstable molecule.

(5) B$_2$ molecule : The electronic configuration of B atom is $1s^2\ 2s^2\ 2p^1$. Thus, in boron molecule there are ten electrons which will be arranged as follows in molecular orbitals.

$$B_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2$$

$$(\pi 2p_x)^1 = (\pi 2p_y)^1$$

$$Bond\ order = \frac{1}{2}\ [N_b - N_a]$$

$$= \frac{1}{2}\ [6 - 4] = 1$$

Hence, B $-$ B is in B$_2$. Here, there are two unpaired electrons and so B$_2$ molecule is paramagnetic.

(6) C$_2$ molecule : The electronic configuration of carbon atom is $1s^2\ 2s^2\ 2p^2$. Hence the total number of electronic configuration will be as follows :

$$C_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2$$

$$(\pi 2p_x)^2 = (\pi 2p_y)^2$$

$$Bond\ order = \frac{1}{2}\ \left[N_b - N_a\right]$$

$$= \frac{1}{2}\ \left[8 - 4\right] = 2$$

Hence C = C is in C$_2$. All the electrons are paired and so C$_2$ molecule is diamagntic.

(7) N$_2$ molecule : The electronic configuration of N atom is $1s^2\ 2s^2\ 2p^3$. Hence there are totally 14 electrons in N$_2$ molecular orbitals will be as follows :

$$N_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2$$

$$(\pi 2p_x)^2 = (\pi 2p_y)^2\ (\sigma 2p_z)^2$$

$$Bond\ order = \frac{1}{2}\ [N_b - N_a]$$

$$= \frac{1}{2}\ [10 - 4] = 3$$

Hence, N $\equiv$ N is in N$_2$ molecule. As all the electrons are paired, N$_2$ molecule is diamagnetic.

(8) O$_2$ molecule : The electronic configuration of O atom is $1s^2\ 2s^2\ 2p^4$. Hence, there are 16 electrons in O$_2$ molecule. The electronic configuration in molecular orbitals will be as follows :

$$O_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2$$

$$(\pi 2p_x)^2 = (\pi 2p_y)^2\ (\pi^* 2p_x)^1 = (\pi^* 2p_y)^1$$

$$Bond\ order = \frac{1}{2}\ [N_b - N_a]$$

$$= \frac{1}{2}\ [10 - 6] = 2$$

Hence, O = O is in O$_2$ molecule. As two unpaired electrons are there in O$_2$ molecule, it is paramagnatic. This result expresses the importance of molecular orbital theory because O$_2$ molecule is diamagnetic according to valence bond theory.

(9) F$_2$ molecule : The electronic configuration of F atom is $1s^2\ 2s^2\ 2p^5$. Hence 18 electrons are there in F$_2$ molecule whose arrangement in molecular orbitals can be shown as follows.

$$F_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2$$

$$(\pi 2p_x)^2 = (\pi 2p_y)^2\ (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$$

Bond order $= \dfrac{1}{2} \left[N_b - N_a \right]$

$= \dfrac{1}{2} \left[10 - 8 \right] = 1$

Hence F — F is in F_2. As all the electrons in F_2 molecule are paired, the molecule will be diamagnetic.

(10) Ne_2 molecule : The electronic configuration of Ne is $1s^2 \, 2s^2 \, 2p^6$. Hence 20 electrons are there in Ne_2. The arrangement of it can be as follows :

$Ne_2 = (\sigma 1s)^2 \, (\sigma^* 1s)^2 \, (\sigma 2s)^2 \, (\sigma^* 2s)^2 \, (\sigma 2p_z)^2$

$(\pi 2p_x)^2 = (\pi 2p_y)^2 \, (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$

$(\sigma^* 2p_z)^2$
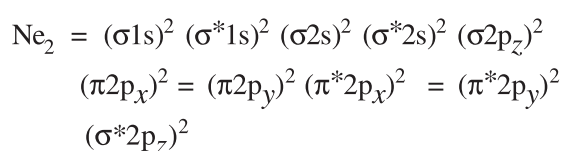
Bond order $= \dfrac{1}{2} \left[N_b - N_a \right]$

$= \dfrac{1}{2} \left[10 - 10 \right] = 0$

Here, the value of bond order is zero. Hence, Ne_2 molecule is not possible.

1.15 The Energy Diagram, Bond Order, Stability and Magnetic Properties of Heteronuclear Diatomic Molecules like CO and NO

CO (carbon monoxide) molecule : CO is a heteronuclear diatomic molecule. Atoms of two different elements carbon and oxygen take part in its formation. There is difference in energy levels of atomic orbitals of carbon and oxygen atoms. As compared to carbon atom, the energy level of respective orbitals of oxygen atom is at lower level i.e. possess less energy. As a result it is more stable. Total fourteen electrons (six electrons of carbon atom and eight electrons of oxygen atom) are there in carbon monoxide molecule. These fourteen electrons are arranged in molecular orbitals obtained by combination of atomic orbitals of carbon and oxygen. It can be seen from the energy diagram of carbon monoxide that all the electrons in it are paired and so it is diamagnetic. The energy diagram of CO molecule is shown in Fig 1.7.
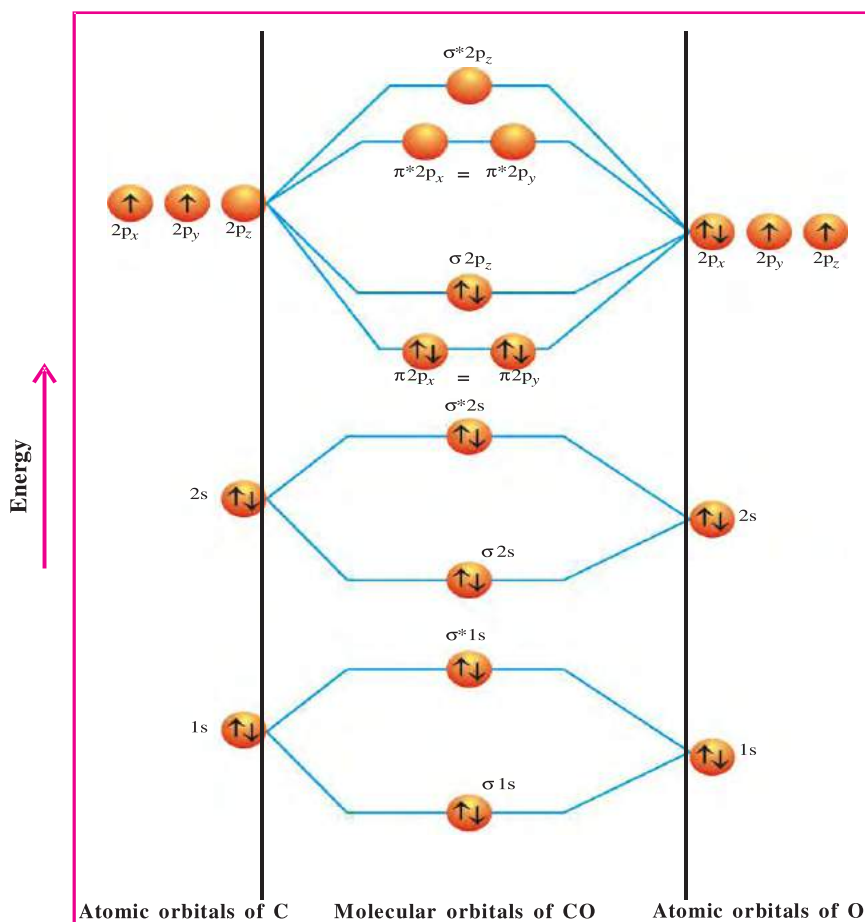
Fig. 1.7 Energy leval diagram of CO molecule

The arrangement of fourteen electrons present in carbon monoxide molecule, can be written in molecular orbitals as follows :

CO : $(\sigma 1s)^2 \ (\sigma^* 1s)^2 \ (\sigma 2s)^2 \ (\sigma^* 2s)^2$

$(\pi 2p_x)^2 = (\pi 2p_y)^2 \ (\sigma 2p_z)^2$
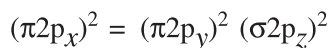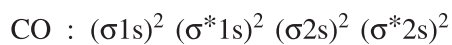
$$\text{Bond order} \quad = \frac{1}{2} \left[N_b - N_a \right]$$

$$= \frac{1}{2} \left[10 - 4 \right]$$

$$= 3$$

Hence, $C \equiv O$ will be in CO.

NO (Nitric oxide) molecule : NO is a heteronuclear diatomic molecule. Atoms of two different elements nitrogen and oxygen take part in its formation. There is difference in the energy of oxygen atom is less than corresponding to that of nitrogen atom.

There are total 15 electrons (seven electrons of nitrogen atom and eight electrons of oxygen atom). The arrangement of these 15 electrons can be made in molecular orbitals as shown in Fig 1.8.

The arrangement of electrons of NO molecule in molecular orbitals can be written as follows :

NO : $(\sigma 1s)^2 \ (\sigma^* 1s)^2 \ (\sigma 2s)^2 \ (\sigma^* 2s)^2 \ (\sigma 2p_z)^2$

$(\pi 2p_x)^2 = (\pi 2p_y)^2 \ (\pi^* 2p_x)^1$
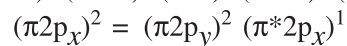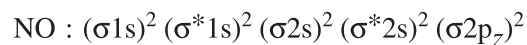
$$\text{Bond order} = \frac{1}{2} [N_b - N_a]$$

$$= \frac{1}{2} [10 - 5] = 2.5$$

As there is one unpaired electron in NO molecule, it is paramagnetic and as the bond order is a fraction, NO molecule is unstable.

The electrons of 1s orbitals (inner shells) do not take part in formation of bond and so they are called non-bonding electrons.
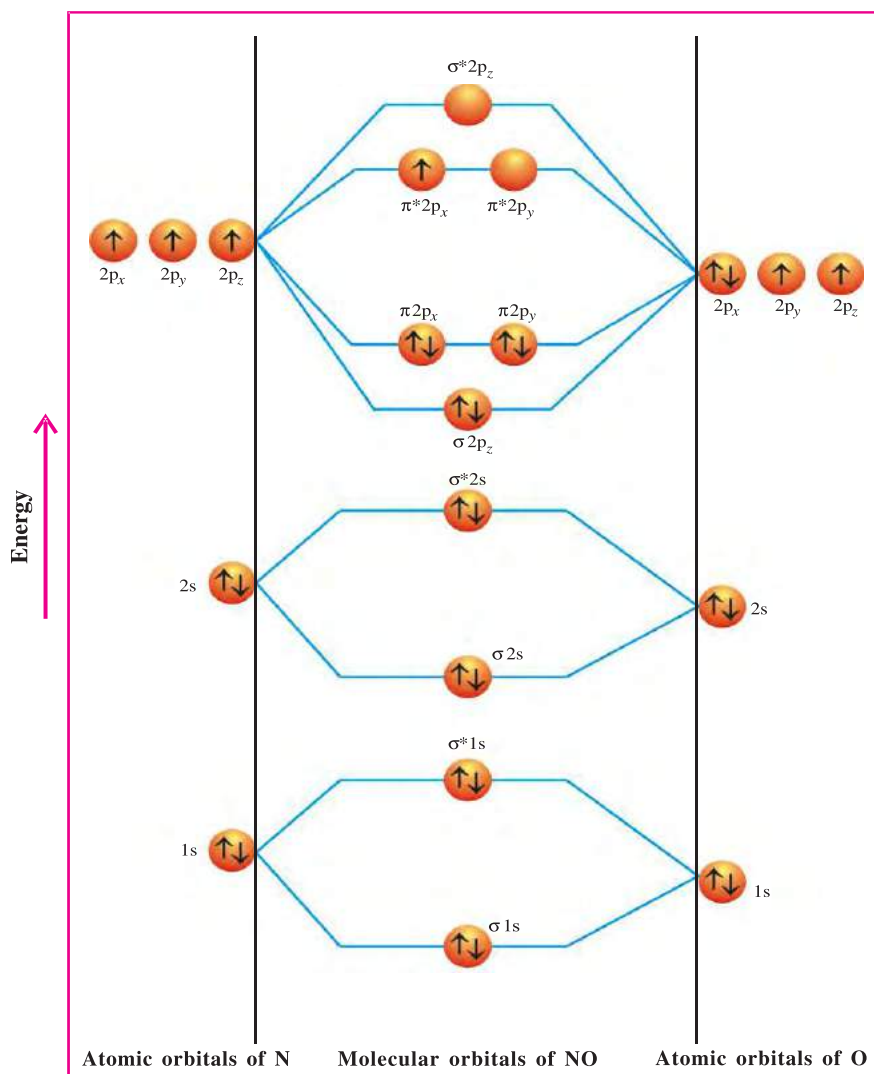
Fig. 1.8 Energy level diagram of NO molecule

1.16 Intermolecular Attraction Forces

Scientist van der Waals mentioned weak attraction force existing between molecule-molecule on the basis of the study of deviation from ideal behaviour of gas. The existence of this weak attraction force cannot be explained by any other chemical attraction force. It is called van der Waals attraction force. This phenomenon is universal. There is presence of van der Waals attraction force in components of ionic substances and also in components of covalent substances. As its dimension is very less about 42 kJ mole^{-1} in relation to other attraction force, it is mostly covered by other attraction forces. This attraction force prevails upto a very less distance about 4.5 $\overset{0}{A}$. The electrons on the surface of molecule experience attraction of nucleus of other molecule. Hence, van der Waals attraction force is produced. As the strength of this attraction force is different between molecules of different substances, the difference in melting points and boiling points of different substances is observed. The intermolecular forces depend upon the following factors :

(i) Shapes of molecules

(ii) Number of electrons in molecules

(iii) Contact surface of molecules

(iv) Average intermolecular distance

The study of these four factors can be understood from the molecule of nitrogen (N_2) and phosphorus (P_4) viz. At normal temperature, from amongst the elements of the same group nitrogen is in gaseous form while phosphorus is in solid form.

Hydrogen Bond : Nitrogen, oxygen and fluorine are strong electronegative elements. When such elements combine with hydrogen atom through covalent bond, the electrons combined by sharing in covalent bond remains dragged towards more electronegative element. Thus, partial positively charged hydrogen atom of one hydride forms strong attraction bond with more electronegative element of the other hydride which is called hydrogen bond (H-bond). Hydrogen bond is weaker than covalent bond. Thus, **the attraction force produced between electronegative elements having non-bonding electron pair with positively charged hydrogen atom is called hydrogen bond.**

Hydrogen bond is shown by dotted (.........) line. e.g. In molecule of HF, hydrogen atom of one molecule and fluorine atom of other molecule has formed H—bond shown as below :

$$\cdots\cdots\cdots \overset{\delta+}{H}\text{———}\overset{\delta-}{F}\cdots\cdots\cdots\overset{\delta+}{H}\text{———}\overset{\delta-}{F}\cdots\cdots\cdots$$

Here, hydrogen bond works as a bridge between two atoms in which it forms covalent bond with one atom and forms hydrogen bond with other atom. The hydrogen bonds in NH_3, H_2O and HF molecule can be shown as in Fig. 1.9

H-Bond in liquid NH$_3$

H-Bond in H$_2$O liquid

H-Bond in liquid HF
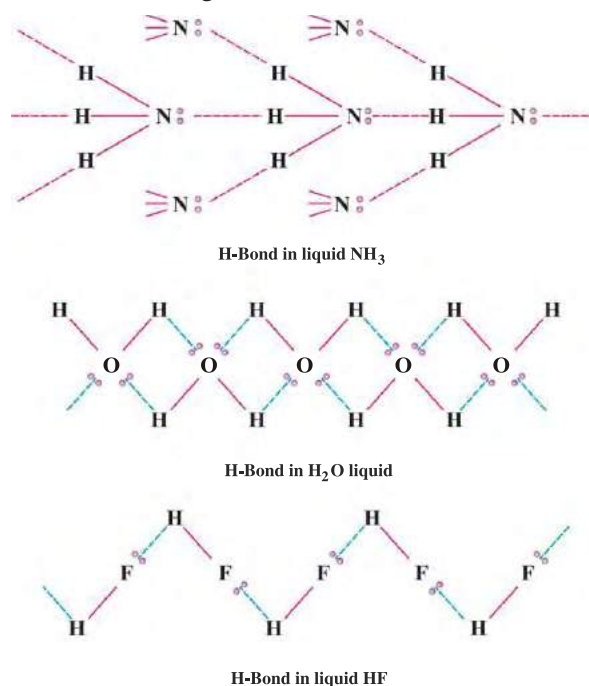
Fig. 1.9 Hydrogen bond

NH_3, H_2O and HF in their liquid states possess strong hydrogen bond. Hence their boiling points and melting points are very high in expectation to those of hydrides of other elements of the same group viz. the higher melting points and boiling points of hydrides of first elements of group 15, 16 and 17 (NH_3, H_2O, HF) support presence of hydrogen bond in them. The energy of hydrogen bond is about 40 kJmol^{-1}, which is higher than the van der Waals' forces.

The density of water is maximum at 277 K In the temperature interval of 273 K to 277 K the density of water being more than that of ice, ice floats on water. Ice is a solid crystal of water having hydrogen bond. The magnitude of hydrogen bond is maximum in solid state of a substance and is minimum in gaseous state of a

substance. The effect of hydrogen bond is observed on the structures and the properties of the compounds.

Importance of Hydrogen Bond :

(i)   As hydrogen bond is formed in water, its evaporation is slow at normal temperature. Hence, water on the surface of the earth is retained in large proportion.

(ii) The storage of water in animal and vegetative cell is due to hydrogen bond.

(iii) Molecules of water forms hydrogen bond with components of the soil. Hence, the moisture is retained in the soil.

(iv) Hydrogen bond is formed in protein molecules in the muscles of living ones through amide (–CONH–) group. Hence, certain functions of muscles are due to hydrogen bond.

(v)   The effectiveness of medicines increases and becomes faster due to hydrogen bond.

(vi) Hydrogen bond plays an important role in living cells of biochemical molecules in nucleic acid, DNA, RNA etc.

(vii) The clothes of synthetic fibres (nylon, terrylene etc) dry faster than cotton clothes because of hydrogen bond formation by water with cellulose of cotton clothes.

Types of Hydrogen Bonds :

Hydrogen bond is mainly of two types :

(i) Intramolecular Hydrogen Bond

(ii) Intermolecular Hydrogen Bond

If hydrogen bond is formed between atoms of same molecule, then that type of hydrogen bond is called intramolecular hydrogen bond. e.g.

o-Chlorophenol   Ethane 1,2-diol

The hydrogen bond formed between two or more different molecules of the same compound is called intermolecular hydrogen bond. e.g.

p – Chlorophenol
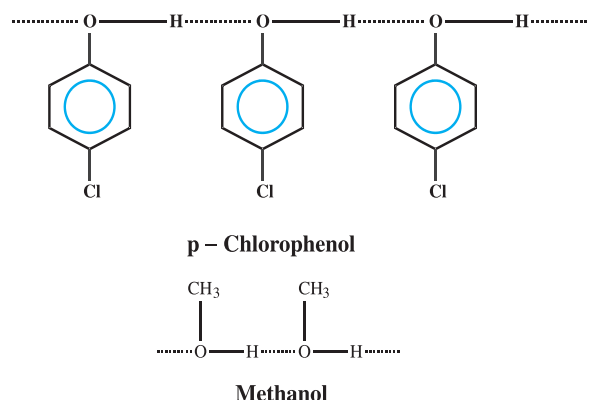
Methanol

As the intermolecular hydrogen bond is formed with more than one molecules of the same compound, the number of such hydrogen bonds is more. As a result, the melting points and boiling points of such compounds are comparatively higher.

The intramoleaclar hydrogen bond is formed internally between atoms of the same molecule. As a result, the number of such hydrogen bonds is limited. Hence, the melting points and boiling points of the compounds having intramolecular hydrogen bond are relatively lower.

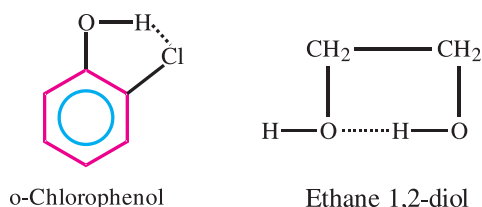E.g. The boiling point of p-chlorophenol is higher than that of o-chlorophenol because intramolecular hydrogen bond is present in o-chlorophenol and intermolecular hydrogen bond is present in p-chlorophenol.

1.17 Concept of Metallic Bond

The less ionisation energy of metal indicates that metal atom has less attraction for valence electron. Also, it has less number of valence electrons (generally 1, 2 or 3) to form covalent bond. Hence, covalent bond between two atoms of metal is not formed. As a result, the directional property is not observed in metals. The valence electrons of atoms of metal are considered not specific for any nucleus but same for the whole crystal. These electrons are called delocalized electrons. The delocalized electrons can change their positively charged kernel (positively charged part of the atom with the nucleus except valence orbit). This can be described as positively charged sphere in the delocalized electron cloud. According to Laws of Electrostatics, the atomic kernel being positively charged, there must be repulsion between each other. Even then, the atomic kernel arranged very near to each other. The attraction between

atomic kernel and the delocalized electrons keep the atomic kernels together. The attraction between positively charged atomic kernel and the delocalised electrons arranged around it is the metallic bond. It makes the arrangement in such a way that atomic kernel can be accommodated in least possible space and also keeps parallel distance between each pair of spherical atomic kernel of any two nearby kernels.

The explanation of metallic bond can be given with the help of Electron Sea Model. According to this model, the metal crystal is considered as sea of delocalised valence electrons. The positively charged kernel is imagined to be floating in it. They are arranged near to each other. Because of the presence of delocalised electrons between such positively charged kernels, these delocalised electrons possess very strong attraction forces with positively charged kernels. Such an attraction force is called metallic bond. All the electrons which are delocalised, have attraction between electron sea and positively charged kernel.

Positively charged kernel
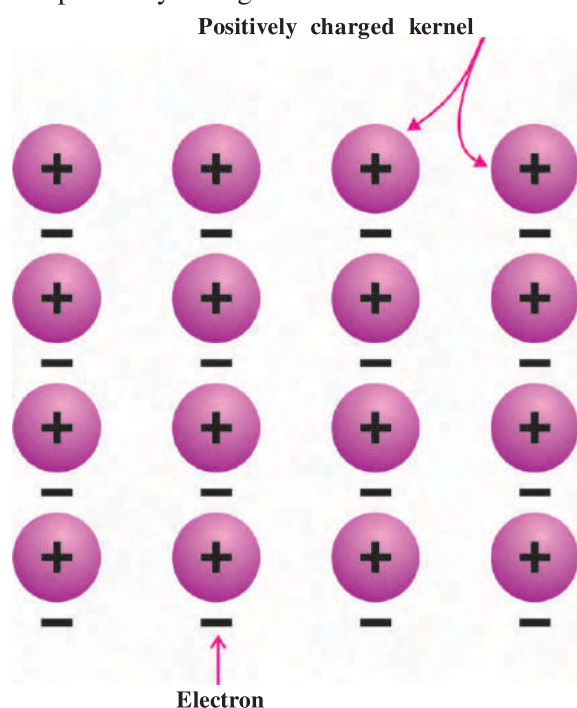
Electron

Fig.1.10 Electron - Sea model of metallic bond.

1.18 Co-ordinate Covalent Bond

Co-ordinate covalent bond is one type of covalent bond. In the formation of covalent bond,

the atoms combining with bond give same number of electrons for sharing. e.g. H_2 molecule. But sometimes the electron pair required for sharing in the formation of molecule/ion, one of the atoms from the combining atoms donates the electron pair and bond is formed. The sharing of the electrons in this type of bond formation is called covalent bond. But the electron pair required for sharing are donated by atom of only one element, special type of covalent bond is formed which is called **co-ordinate covalent bond.** This bonding is expressed by the sign of arrow $(\rightarrow)$ and the direction of arrow is from the atom donating the electron pair towards the atom receiving the electron pair.

Generally, the molecules having one or more non-bonding electron pairs form this type of bond by donating electron pair. Thus, this type of bond is formed between completely vacant orbitals of the atom of the element and atoms possessing non-bonding electron pairs by sharing the electrons easily.

(1) e.g. In NH_4^+ ion, there are three covalent and one co-ordinate covalent bonds.

$$NH_3 + H^+ \longrightarrow NH_4^+$$

$$NH_4^+$$
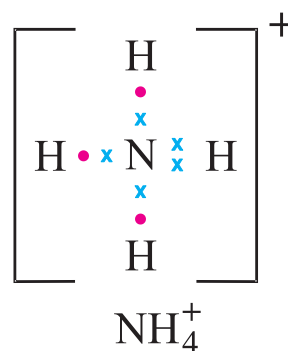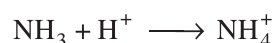
1.19 Hybridisation in BeH_2, BCl_3, CH_4, PCl_5, SF_6, by s, p and d Orbitals

The information of hybridisation in BeH_2, BCl_3, CH_4, PCl_5, SF_6 etc. through s, p and d orbitals is included in the table 1.3.

SUMMARY

In this unit, the study of chemical bonding and formation of molecule from the atoms are included. The smallest particle of element is atom and the smallest particle in a compound is molecule. The force or the binding that keeps the atoms in the molecule combined during the formation of molecule is called chemical bonding. The concepts like that of Kossel-Lewis, VSEPR principle, valence bond theory, molecular orbital theory have been presented. In chemical bonding, it has more relation with orbitals around the nucleus and especially the valence orbitals. We do not think about the nucleus but we take into consideration the effect due to its positive charge. Scientists Lewis and Kossel have mentioned the approach of chemical bonding. In this, the atom obtains the octet either by losing or by gaining the electron, which is chemically inert. This is called law of octet. Such bonds are called ionic bonds e.g. NaCl. Also, some atoms share electrons with each other and obtain octet structure resulting into stable covalent molecule. e.g. Cl_2. To explain the structures of such molecules he mentioned dot and cross symbols and explained the stability of the molecules. Such a bond is called covalent bond. The approach of Kossel Law is explained in detail in the unit.

When any bond is formed, the distance between their atoms is called bond length and the angle is called bond angle. As you know the bond lengths of single (−) bond, double (=) bond and triple (≡) bond are different. The bond angle gives geometrical shapes to molecules viz.180^0- linear, $109^028'$ tetrachedral. You will study in detail about covalent bond which can be of three types. Polar covalent bond in which the electron remains dragged towards the more electronegative atom and $+\delta$ charge on electropositive atom and $-\delta$ charge on electronegative atoms are shown. As a result the molecule becomes polar. If the electronegativities of the two atoms are same or the difference between them is less, than non-polar bonds, formed by both the atoms sharing the electrons. In co-ordinate covalent bond, one of the two atoms sharing a pair of electrons and the second atom completes the octet with the help of this gained electron pair. viz. $F_3B \leftarrow NH_3$. Bond ← indicates co-ordinate covalent bond. Over and above, bond length, bond angle, bond enthalpy (bond energy) is also an important concept. Shorter the bond length, more will be the stability and so more energy will be required to break it. Thus, the values of enthalpy may be different according to bond formation. The number of bonds is called bond order which we have studied in detail and also the formula to determine it. Born-Haber showed that the enthalpy evolved in formation of compound is the mathematical results of the enthalpies of several reactions of atoms. It is explained in the unit by discussing the formation of compound like NaCl.

Sometimes, it so happens that the electron pair instead of being localised on any molecule it localises towards other molecule. Thus, the bonds in the molecule can be shown at different positions in the compounds having same molecular formula. Such structures are called resonance structures and energy associated with the changes of these resonance forms is called resonance energy. This can be studied through the molecules of ozone, carbon dioxide, benzene etc.

As we have seen earlier, structures like linear, tetrahedral etc, can be obtained on the basis of bond angle. This study can be used to show the shapes of the molecule by hybridisation of atoms in them, geometrical structures etc. viz. linear $BeCl_2$ - 180^0, trigonal BCl_3 - 120^0, tetrahedral CH_4 - $109^028'$.

Lewis approach being insufficient to explain the shapes of molecules, Sidgwick and Powell proposed one principle which is known as VSEPR principle which was developed

by Nyholm and Gillespie and they proposed certain assumptions. In this it is important to note that when non-bonding electron pairs are there, then they show deviation in geometrical structure and bond angle due to repulsion between electron pairs. e.g. Molecule of water has sp^3 hybridisation and so its bond angle must be $109^0 28'$ but it becomes $104^0 30'$ due to repulsion by two non-bonding electron pairs. Hence, it is called distored tetrachedral. The polarity of bond is a vector quantity. Hence, if a polar bond is formed due to difference in electronegativities but another bond of the same type is formed in its opposite direction, then polar bond will be formed but the resultant polarity of the molecules becomes zero and molecule will be non-polar.

e.g $\quad$ F ⟵+ Be +⟶ F $\quad$ or
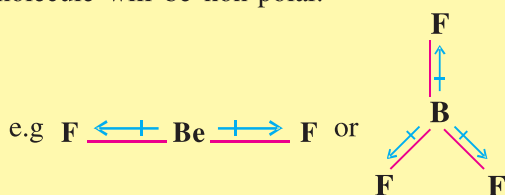
The dipole momentes of polar substances can be calculated for which both the charges $+\delta$ and $-\delta$ and the distance between them is to be utilised. More the value of dipole moment, more will be the polar bond and more will be the ionic bond. One important aspect is that polar substances dissolve only in polar solvents and non-polar substances dissolve in nonpolar solvents. e.g. NaCl will dissolve in water. Napthalene will dissolve in benzene. New hypotheses have been presented affter taking into consideration the limitations of the principles for the approach of covalent bond. Two are main from them : (1) Valence Bond Theory and (2) Molecular Orbital Theory. These concepts are based on quantum mechanics. Heitler and London first of all gave the idea of valence bond theory and it was developed by Pauling and Slater.

In the assumptions of valence bond theory the attraction - repulsion forces between positively charged nuclei of two atoms and the electrons arranged in the orbits around them. According to Coulomb's Law if attractive forces are more than repulsive forces then the bond will be formed and molecule will be formed. In this theory, on the basis of the overlapping of valence orbitals different overlaps can be formed. In this type of overlapping the excitation of electrons in valence orbitals can be shown and then formation of molecule by covalent bond with other atoms. viz. In carbon, the electrons of valence orbital $1s^2\ 2s^2\ 2p^2$ will be excited to give $1s^2\ 2s^1\ 2p_x{}^1\ 2p_y{}^1\ 2p_z{}^1$ containing four orbitals with one electron in each and four hydrogen atoms, and hence will give stable molecule like CH_4. The geometrical structure, and bond angle can be expressed from the hybridisation associated with it. In such valence bonds, two types of bonds–σ and π are also observed. σ bond is a covalent bond; it attains axial overlap of internuclear axis. The stability of this bond is more than that of π bond. In the π–bond the axis of the atomic orbitals undergoing overlapping remains parallel to each other and is perpendicular to internuclear axis. $\pi-$ bonds are less stable in comparison to $\sigma-$bonds or they are weaker. Valence bond theory is based on overlapping of valence orbitals. It explains properties like the geometrical shapes, the bond angle etc. very simply but cannot explain magnetic properties.

Scientists Mulliken and Hund suggested molecular orbitals like atomic orbitals and proposed molecular orbital theory. Amongst its important points, the idea that atomic orbitals can also form molecular orbitals was taken into consideration. As many atomic orbitals take part in the formation, same number of molecular orbitals, their energy, symmetry etc. were taken into consideration. The formation of these types of atomic orbitals can be shown in the formation of homonuclear molecules like H_2, Be_2, F_2 etc. and heteronuclear molecules like CO, NO etc. Molecular orbitals are formed by linear combination of atomic orbitals–LCAO principle. On the basis of these types of combination

two types of molecular orbitals are formed which are known as Bonding Molecular Orbitals (BMO) and Anti-Bonding Molecular Orbitals (ABMO). In the formation of rules these types of BMO and ABMO the principles like Hund's rule of maximum spin multiplicity, Pauli's exclusion principle, Aufbau principle etc. which are applicable in formation of atomic orbital are also obeyed and maintained. In the unit the molecular orbital diagrams of construction of molecular orbitals from the atomic orbitals for formation of homonuclear molecules from H_2 to Ne_2 elements as well as for formation of heteronuclear molecules like CO, and NO are shown. From these diagrams, important property like bond order can be calculated. Bond order

$= \dfrac{1}{2}$ {electron in bonding molecular orbitals − electrons in anti−bonding orbital} viz. for N_2

molecule bond order $= \dfrac{1}{2} (10-4) = 3$ i.e. there will be triple bond $N \equiv N$. In the same

way, in NO molecule bond order will be $= \dfrac{1}{2} [10 - 5] = 2.5$. Here, we will note that if the value of bond order becomes zero, the bond will not be formed e.g. He_2. If the value of bond order is integer, the bond will be formed and according to the integer 1, 2, or 3, there will be single (−), double (=) or triple (≡) bonds respectively. If the value of **bond order is fraction, then molecule will attain unstable structure.** The molecular orbital theory can explain the magnetic properties e.g. In O_2 molecule two unpaired electrons are there and so it is paramagnetic and in N_2 molecule, all the electrons are paired and so it is diamagnetic. Thus molecular orbital theory is superior to valence bond theory in this matter.

Above this, one important phenomenon is hydrogen bond. The first element of 15, 16, and 17, groups N, O, F being higer electronegative than the other elements of the group it can form covalent molecules like NH_3, H_2O and HF with hydrogen. Afterwards the molecule like H————F⋯⋯⋯H————F combines with each other H − F molecule through hydrogen bond H————F⋯⋯⋯H————F where H .... (dotted line) indicates hydrogen bond formation. HF, NH_3, H_2O possess hydrogen bonds and so their properties are different from those of other elements in the group. Hydrogen bond is of two types (1) Intermolecular and (2) Intramolecular hydrogen bonds. When hydrogen bond is formed between two molecules it is called intermoleculer hydrogen bond e.g. p-chlororphenol and between two groups in the same molecule, it is called intramoleculer hydrogen bond e.g. o-chlorophenol. Intermolecular hydrogen bond is stronger than in-tramolecular hydrogen bond. The presence of hydrogen bond is the reason for specific properties of the compounds. Viz the retaining of water in the soil, drying of terrylene clothes is faster than that of cotton clothes.

After knowing about ionic bond, covalent bond, co-ordinate covalent bond, we shall study the special type of bond present in metals which is called metallic bond. As there are 1, 2 or 3 electrons in the outermost orbit of the metals, they are not able to form covalent bonds. Their ionisation energy is less and attraction of electron towards the nucleus is less. One, two or three electrons are arranged around the nucleus of the atom. Hence, the positively charged nucleus or kernel is there. The electrons around it have attraction towards other nuclei of the atoms in the lattice. Thus, the electron instead of being localised for any one atom, remains delocalised in the whole metal crystal. For this theory Electron Sea model was proposed. In this, the atomic kernel is imagined as floating in the sea, delocalised electrons are arranged around kernel possessing positive charge. Because of this type of metallic bonds, the specific properties of metals, like density, ductility, malleability etc. are different.

Co-ordinate covalent bond is a type of covalent bond as seen earlier. The characteristic in it is that from the two atoms undergoing sharing of electrons, only one of the atoms provides a pair of electrons, and is shared by both the atoms. Hence, it is called co-ordinate covalent bond. e.g. In BF_3, three F atoms were bonded with B-atom through three covalent bonds but the octet of B is not complete. Similary in NH_3 molecule, three H atoms are bonded with N through three covalent bonds. But N has one non-bonding pair of electrons, which it gives to BF_3 molecule and is shared by both the molecules. Hence $F_3B \leftarrow NH_3$ Co-ordinate covalent bond is formed. In this, the molecule which gives pair of electrons is shown by arrow $(\rightarrow)$ from the molecule which donates it towards the molecule or atom which accepts and shares gained electron pair. You will study more about co-ordinate covalent bond in the unit of complex salts in Standard-12.

EXERCISE

1. **Select the proper choice from the given multiple choices :**

   (1) Mention the relationship between bond order and stability of a compound ?

   (A) Directly proportional   (B) Inversely proportional

   (C) Equal   (D) Opposite.

   (2) Which type of the bond from the following is obtained by combination of the ions of strongly electropositive and strongly electronegative elements ?

   (A) Ionic   (B) Covalent

   (C) Co-ordinate covalent   (D) Metallic

   (3) In which of the following compounds the rule of octet is not obeyed ?

   (A) CH_4 (B) PCl_5 (C) NH_3 (D) H_2O

   (4) Which from the following is the magnetic property of oxygen molecule on the basis of valence bond theory ?

   (A) Diamagnetic   (B) Paramagnetic

   (C) Ferromagnetic   (D) Antiferromagnetic

   (5) Which from the following is the magnetic property of oxygen molecule on the basis of molecular orbital theory ?

   (A) Diamagnetic   (B) Paramagnetic

   (C) Ferromagnetic   (D) Antiferromagnetic

   (6) Who presented the valence bond theory ?

   (A) Linus Pauling   (B) van der Waals

   (C) Mulliken   (D) Heitler and London

   (7) Who presented the molecular orbital theory ?

   (A) Linus Pauling   (B) van der Waals

   (C) Lewis   (D) Mulliken

   (8) The water on the surface of the earth is mostly retained, the reason for which is

   (A) Density of water is 1.0 gml^{-1} (B) Hydrogen bond is present in water

   (C) Water is neutral   (D) Water is used in large proportion

(9)   Which type of bond is observed in p-chlorophenol ?

(A) Intermoleculer hydrogen   (B) Intramoleculer hydrogen

(C) van der Waals   (D) Metallic

(10) Which of the following molecular orbitals possess minimum energy ?

(A) $\sigma 2p_z$ (B) $\sigma 1s$ (C) $\sigma 2s^*$ (D) $\pi 2p_x$

2.   Answer the following questions in brief :

(1)   Write Lewis structures of following molecules/ions :

BeF_2, PH_4^+

(2)   Write the rule of Octet.

(3)   Write resonance structures of NO_3^- ion

(4)   Mention types of hydrogen bond.

(5)   Give the values of bond angles of molecules of CH_4 and NH_3.

(6)   What is the value of bond order in H_2 molecule ?

(7)   On what depends the strength of hydrogen bond ?

(8)   Metals are good conductors of heat and electricity. On which type of bond does this property of metals depend ?

3.   Answer the following questions :

(1)   Explain with suitable example, the formation of polar and non-polar covalent bonds.

(2)   Explain co-ordinate covalent bond.

(3)   Give definitions : Lattice enthalpy, Enthalpy of formation.

(4)   Give Lewis structures of PCl_5, NH_4^+ , SF_6, H_2SO_4.

(5)   Give explanation of σ and π bonds. Mention by overlapping of which orbitals are σ and π bonds formed ?

(6)   Mention the condition for linear combination of atomic orbitals

(7)   Write the relative order of moleculer orbitals for homonuclear diatomic molecules H_2 to N_2 and O_2 to Ne_2 .

(8)   Explain the calculation of bond order in Be_2 molecule on the basis of molecular orbital theory.

(9)   Explain the factors affecting the intermolecular attraction forces.

(10) Mention importance of hydrogen bond.

4.   Answer the following questions :

(1)   Write a note on Kossel-Lewis approach for chemical bonding.

(2)   Explain bond angles of CH_4, NH_3, and H_2O molecules on the basis of VSEPR principle.

(3)   Explain polarity of bonds in NH_3 and NF_3 molecules.

(4)   Give explanation of LCAO with example.

(5)   Give explanation of bond order and magnetic property of O_2 molecule by drawing its energy level diagram according to M. O. theory.

(6) Give explanation of bond order and magnetic property of NO molecule by drawing its molecular orbital energy level diagram.

(7) Write short note on intermoleculer attraction forces.

(8) Give brief account of metallic bond.

(9) Justify the following statements :

(i) The clothes of nylon dry faster than those of cotton.

(ii) The boiling point of o-chlorophenol is lower than that of p-chlorophenol.

(iii) Amongst H_2O, H_2S, H_2Se, only H_2O is obtained in liquid form.

(iv) O_2 molecule is paramagnetic.

(v) σ–bond is stronger than π–bond.

●

Dr. Prafulla Chandra Ray
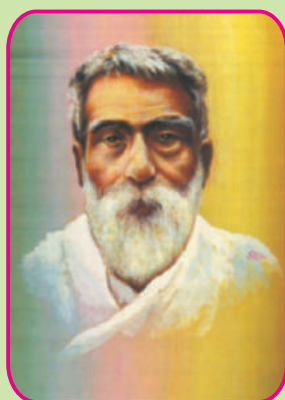
Dr. Prafulla Chandra Ray was born on August 2, 1861 in the village Radauli of East Bengal. He obtained his primary education in the primary school of his village. He had read the life sketches of some scientists, Newton, Galelio, Benjamin Franklin, during his young age. He got inspiration from it. He went to England in 1882 and got admission in science faculty of Edinburgh University. After completing his study for B.Sc. in 1887, he obtained the D.Sc. degree on the subject of Inorganic Chemistry. He worked on analysis of ores. He returned to India in 1888 and joined the Calcutta Presidency College, as a lecturer. Here he studied nitrite compounds. He was awarded the prestigious honour of 'Master of nitrite' by Prof. Armstrong because of his research work on nitrite compounds. In 1911, he became Senior Professor, After some years be retired from the post of professor but he continued the research work. As a result of this he prepared an unstable substance - mercurous nitrate in the laboratory. The other scientists of the world were astonished by this research. He wrote a book 'The History of Indian Chemistry' with a purpose that the whole world may be aware of ancient Indian chemistry. This book was admired by the whole world. After fifteen years, he published the second part of this book. These two books have given important contribution in the devlopment of chemistry. The important research of Dr. Ray was the discovery of mercury nitrate and preparation of its derivatives. Over and above he had prepared a series of compounds of mercury alkyl, and mercury aryl ammonium chlorides. He established Indian Chemical Society in 1924 for the canvass and development of chemistry. He remained as Director of this institute for two years. He also co-operated the university for the scholarship and award to encourage students studying there. He had the first visit with Mahatma Gandhi in 1902 and became strong supporter of Non-violence Movement. In 1932, he wrote his autobiography- 'The Life and Experiences of a Bengali Chemist. He expired on 14th June 1944.

States of Matter - Gas and Liquid

2.1 Introduction

It is not possible for any chemist to study a single molecule, but she/he can study a group of molecules existing in nature. **A group of molecules is called the matter.** The matter is made up of small particles. Matter is in three states, solid, liquid and gas, the other two states are known as plasma an Bose Einstein condensate.

Solid substances have fixed volume, definite shape and surface. Liquid subtances have fixed volume and surface. They do not possess shape of their own, but take up the shape of the container in which they are poured. Gases do not have fixed volume, definite shape or surface. They acquire the shape and volume of the container. The physical state of matter can be changed by changing temperature. e.g. at 273 K temperature the H_2O is in solid state (ice), at higher than that temperature H_2O is in liquid state (water) and at 373 K temperature in gaseous state (vapour). The physical properties of a subtance can be changed by changing its physical state, but the chemical properties cannot be changed. Sometimes the rate of chemical reaction changes by changing the physical state. During the chemical calculation, it is most (important) essential to have the infromation about the physical state of subtances (reactant or product), and hence, it is essential to study the physical state of matter, factors affecting it and some important laws related to that.

The deciding factors of the physical state of matter are intermolecular forces, molecular interaction and effect of thermal energy on the motion of particles. We shall study the gaseous and liquid state of matter in this unit, so let us study these factors.

States of matter and intermolecular attractive forces : Very weak attractive forces existing between molecules are called inter-molecular attractive forces (van der Waals'

attractive force). It is universal and exists in all the physical states of matter. However this type of weak attractive force are hidden under strong attractive forces (chemical bonds) present in a substance. van der Waals' forces depend upon the following factors.

(1) shape of molecule (2) number of electrons present in (3) contact surface area of a molecule (4) average intermolecular distance.

These factors affect the physical properties of a substance viz. melting point and boiling point. e.g. (1) Melting point of yellow phosphorus (P_4) is less than that of Rhombic sulphur (S_8).

The reason for this can be understood by the following structures. Yellow phosphorus (P_4) a molecule having four P atoms and it has $4 \times 15 = 60$ electrons. Rhombic sulphur (S_8) is a molecule having 8 S atoms and it has $8 \times 16 = 128$ electrons. Thus the size (volume) and contact surface area of yellow phosphorus is less than that of rhombic sulphur (S_8); hence the existing van der Waals' force in P_4 is weaker than S_8 hence the melting point of yellow phosphorus is less than that of rhombic sulphur.
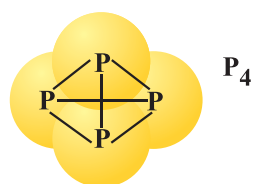
Yellow phosphorus (P_4)
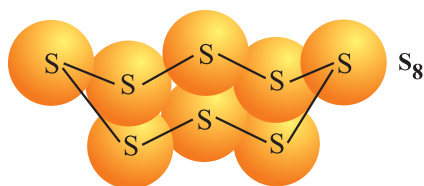
Rhombic sulphur (S_8)

The van der Waals' forces of attraction are different like (1) Dispersion forces or London forces (2) Dipole-dipole forces and (3) Dipole-induced dipole forces.

(1) Dispersion forces or the London forces : This force of attraction was first proposed by the German scientist Fritz London, so it is known as the London forces. Generally, in atoms of non-polar molecules, their electronic charge cloud is distributed symmetrically. Now, in such atoms or molecules the temporary
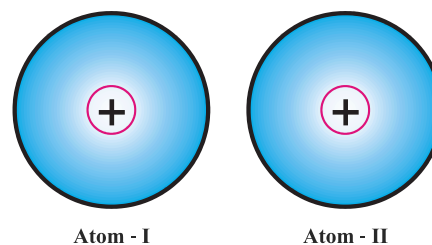
Fig 2.1 (i) The charge cloud is distributed equally in both the atoms
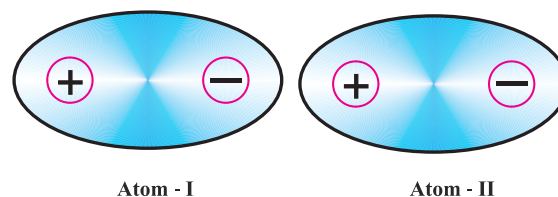
Fig 2.1 (ii)The electron density is more on right hand side in atom I. Its effect is experienced in atom II
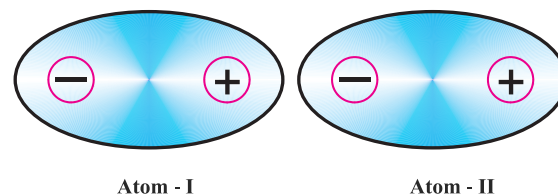
Fig 2.1 (iii) The electron density is more on left hand side. Its effect is experienced in Atom II

dipolarity is developed which can be explained as below. As shown in Figure 2.1 two atoms (atom-I and atom-II), the electron cloud is distributed symmetrically. When two such atoms come close to each other, it so happens that in one atom (atom-I) momentarily, the electronic charge density of atom-I undergoes the dispersion as shown in Figure 2.1 (ii). Hence, electron density will move towards the right hand side pole. So, the left hand side pole will be in shortage of that, therefore atom-I becomes temporarily dipolar. Now, the other atom (atom-II) which comes in its contact, it realises its effect and hence, the dispersion in the symmetrical electron density and the dipole character is induced in atom-II. The pole of right hand side of atom-I where the electron density is more and the atom II which comes in contact of that pole realises the shortage of electron density, so that, at another pole the electron density increases. Thus, the temporary dipolarity is created in atom. The opposite pole of atom-I and II comes in contact, that develops temporary force of attraction. Similarly, as shown in Figure 2.1 (iii) the temporary

can be explained. Such a force of attraction can also be explained in two molecules. This type of force of attraction in atoms or molecules, there is a temporary dispresion in electron density that affects the electron density of nearby atom or molecules. So the force of attraction develops due to such effect is called dispersion force.

(2) Dipole-Dipole forces : The molecules which are made up of the atoms having more difference in their electronegativities are always dipolar. In such molecules, which are permanently dipolar, the atom having higher electronegativity becomes partially negatively charged ($-\delta$) and atom having less electronegativity becomes partially positively charged ($+\delta$). The value of partial charges is always less than unit electronic charge 1.6×10^{-19} C. In such dipolar molecules there is a force of attraction between the poles of atoms having partially opposite charges, which is shown in Figure 2.2. In HCl molecule the chlorine atom is more electro-negative than hydrogen atom, so the chlorine atom aquires partial negative charge and hydrogen atom acquires partial positive charge, hence there is a dipolar interactive attraction between two HCl molecules and such attractive forces are called dipole-dipole forces of attraction. There is also interactive London forces between such molecules so the cummulative effect of both the forces is observed. In these molecules these forces are stronger than London forces.
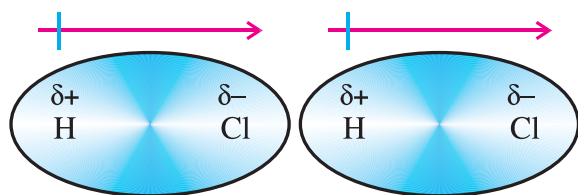
2.2 Dipole-Dipole mutual attractive forces in HCl molecules

(3) Dipole-Induced dipole forces : When dipolar molecules come closer to non-polar molecules, then, this type of force of attraction is observed. In dipolar molecule the density of electron cloud always distributed unevenly, also when non-polar molecule comes closer to such polar molecule, the electron density is induced unevenly in non-polar molecule, which can be explained as given below. As shown in Figure

2.3 the non-polar molecule comes in contact with B^- pole of polar molecule AB. There is an induced positive charge towards the pole of non-polar molecules which is in contact with them and the opposite pole becomes partially negative, so the dipolarity is induced in them. As a result, dipolarity can be induced between the polar molecule and non-polar molecule. They get attracted. This type of force of attraction is called dipole-induced dipole force of attraction. This type of molecules also have interactive London forces and hence, in such molecules the cumulative effect of both forces can be observed.
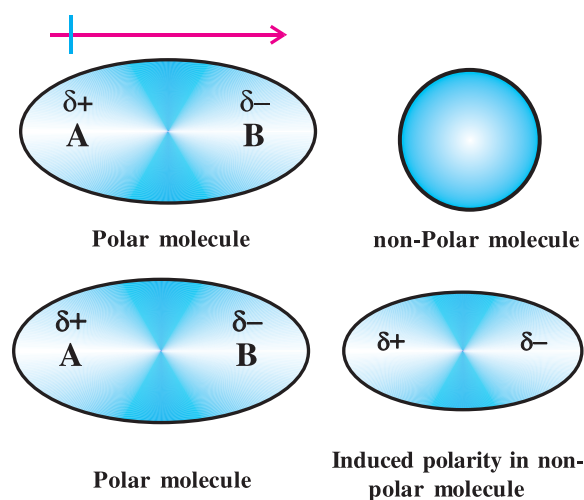
Fig. 2.3 Dipolar - Induced dipolar forces

Hydrogen bond : In intermolecular forces hydrogen bond is an important force of attraction. The first elements of group 15, 16 and 17 due to their high electronegativity, combine with hydrogen to form hydride compound in which hydrogen bond is observed. Hence, such molecules have interactive dipolar attractive forces and due to that elements of these groups show deviation in some properties. The hydrogen bond enthalpy is 10 to 100 kJ mol^{-1}. Thus, it is a weak attractive force.

Now, let us study the inermolecular repulsive forces. When two atoms or molecules come near, they repel due to same type of charges in their electron cloud. There is also repulsion between their nuclei. As the distance decreases between the two atoms or molecules, the repulsive forces rise very rapidly. Therefore, the effect of pressure is more on gas, while less in liquid and very less or negligible in solid, compared to that of gas. So if presure is applied on solid state, the molecules do not come closer

because the molecules are close enough, so there is a repulsion in them, and if they are brought closer, then the repulsion increases more which resists the molecules to come nearer. Therefore, in solid state the effect of pressure is very less. Now, in liquid state compared to solid, the molecules are arranged little far from each other, so applying pressure on the molecules, they come closer to each other, hence effect of pressure is observed in liquid. At 293 K temperature and 1000 bar pressure applied on water, then the volume reduced only by 4%. Now, in gaseous state molecules are arranged far away and hence applying pressure, the molecules come nearer, and hence the effect of pressure is maximum on gaueous state.

The most important factor which decides the physical state of matter is the effect of thermal energy on motion of molecules. Due to this motion of molecules or atoms the energy produced is called thermal energy. It depends on the temperature of substances. On increasing the temperature the motion of molecules or atoms is increased and this motion is also called thermal motion.

Now, the inermolecular forces have tendency to keep the molecules near to each other, while the thermal energy has tendency to keep the molecules away from each other. So by balancing combinaton of the two opposite factors, the physical state of matter as solid, liquid or gas is decided. The gaseous molecules are arranged near to each other only by force of attracton, so they are not converted into solid or liquid spontaneously, because it is also necessary to have a change in thermal energy related to liquid and solid state. Thus, only the compression of gas will not convert gas into solid or liquid but by decreasing the temperature of gas its thermal energy can be decreased. So it can be liquefied easily. The characteristics of weak forces of attraction between the molecules of gaseous state are given below :

(i) The volume, surface and shape of gases are not fixed but they assume the volume and shape of the container in which they are poured.

(ii) Due to this characteristic of compression, gases show the effect of pressure and also the effect of temperature on them.

(iii) The gaseous molecules exert equal pressure in all directions and expansion in all directions equally.

(iv) The gaseous molecules spontaneously mix into each other easily and evenly.

(v) The density of gas is very less compared to the density of solid or liquid.

Out of three physical states, the gaseous state is very simple because in this state the force of attraction is negligible and also indicate similarity in behaviour. Different gases have different chemical properties, still they have similarity in their behaviour. Their behaviour is described by the quantitative relation between mass, volume, temperature and pressure, and these relations can be discovered by experimental observations and such relations are called laws of gases. A number of laws of gases can be derived, while for liquid such laws derived are limited and very few for solid.

2.2 The Gas Laws

The volume of a fixed amount of gas depends upon its temperature and pressure. Both factors are different at different places and also they change with the change in atomsphere. So it is necessary to understand the relation between the volume of gas and the affecting factors and the laws of gas are derived from the study of such relations.

Boyle's law : In 1662, scientist Robert Boyle carried out experiments to study the relation between pressure and volume for fixed amount of gas and finally on the basis of experimental observations, the relation between pressure and volume of a gas was stated and it is known as Boyle's law which is given below :

"At constant temperature the pressure of a fixed amount of gas varies inversely with its volume." Mathematically Boyle's law can be written as given below :

$P \propto \dfrac{1}{V}$ (constant temperature, fixed amount)

$\therefore \;\; P = K \cdot \dfrac{1}{V}$

(where K is proportionality constant and it depends on the temperature and amount of the gas)

$PV = K$

So from Boyle's law it is said that "At constant temperature for fixed amount of gas the product of its pressure and volume is constant."

Now, suppose at the initial stage, at constant tempartatue the fixed amount of gas has its pressure and volume as P_1 and V_1 respectively and at final stage they become P_2 and V_2 then according to Boyle's law

$$P_1V_1 = K \qquad\qquad (I)$$

$$P_2V_2 = K \qquad\qquad (II)$$

From equations I and II

$$P_1V_1 = P_2V_2$$

(constant temperature and fixed amount)

Boyle's law can be shown by following graphs : Figure 2.4 indicates the relation between pressure and volume of gas at different constant temperature and fixed amount of gas.
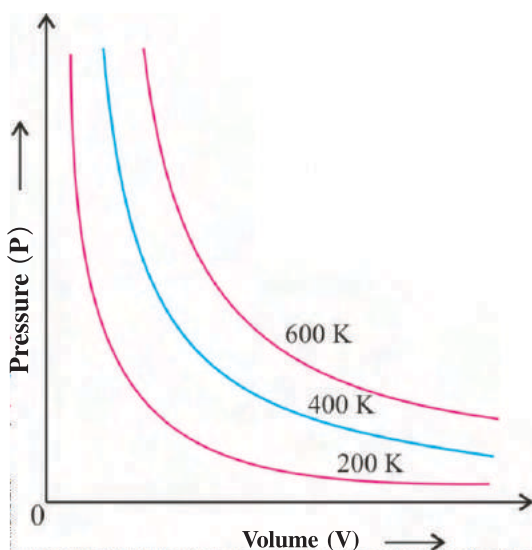
Fig. 2.4 Graph I
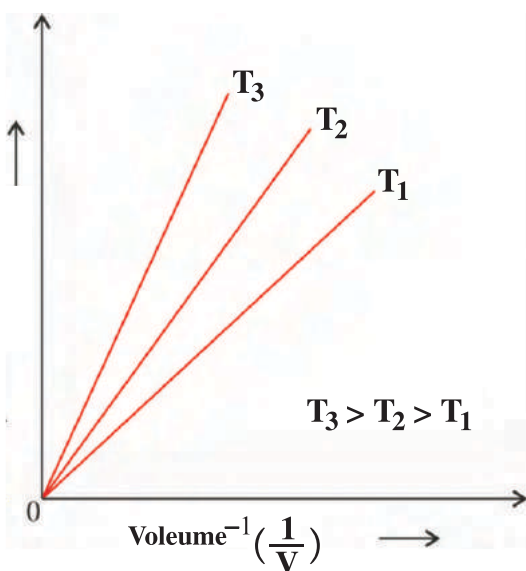
Fig. 2.5 Graph I
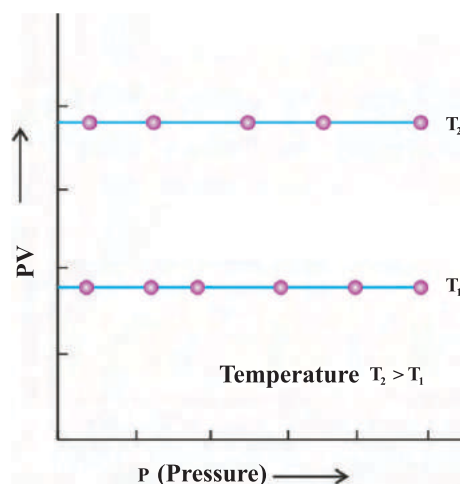
Fig. 2.6 Graph I

This graph is also called isotherm. It is clear from the isotherm graphs that at any constant temperature if the pressure increases its volume gets decreased and if the volume increases, its pressure gets decreased. This means that the product of pressure and volume becomes constant. But if the temperature changes, then, PV = K in which the value of K changes which is clear from the graph in Figure 2.4.

The formula to indicate the relation between density and pressure of a gas derived from Boyle's law given below :

According to Boyle's law PV = K.... (2.1)

Now, density

$$\therefore V = \frac{m}{d} \quad \text{(Putting this value in Boyle's law equation)}$$

$$P \cdot \frac{m}{d} = K$$

$$\therefore d = \left(\frac{m}{K}\right) \cdot P$$

Now, for fixed amount of a gas m is constant and so the value of $\frac{m}{K}$ is also constant, which is indicated by K'

$$d = K' P$$

$$\therefore d \propto P$$

$$\therefore \frac{d}{P} = K' \text{ so } \frac{d_1}{P_1} = \frac{d_2}{P_2} \text{ can be written.}$$

Hence, the relation between density and pressure of a gas which is derived from Boyle's law can be expressed as follows :

"At constant temperature for a fixed amount of gas the density of a gas varies directly as its pressure."

The application of this relation is useful to understand the practical illustration. The pressure of air decreases on Mount Abu (nearly 0.5 bar). So, as the pressure of air decreases the density also decreases. This means that the density of O_2 in air also decreases and it becomes difficult to breath. In the same way, same type of difficulty is observed in the plane flying at height. So, in a plane attempt is made to maintain the pressure of air artficially. Eventhough by chance if any difficulty arises in breathing, then the facilities of O_2 is also available.

Example 1 : At constant temperature fixed amount of Cl_2 gas sample is filled in 2.5 litre container having pressure 4 bar. If the pressure is made 10 bar find its volume.

Solution :

According to Boyle's law

$$P_1V_1 = P_2V_2$$

$$P_1 = 4 \text{ bar, } V_1 = 2.5 \text{ litre}$$

$$P_2 = 10 \text{ bar, } V_2 = ?$$

$$\therefore V_2 = \frac{P_1V_1}{P_2}$$

$$= \frac{4\text{bar} \times 2.5\text{litre}}{10 \text{ bar}} = 1 \text{ litre}$$

The volume of Cl_2 gas will be 1 litre.

Example 2 : At constant temperature fixed amount of O_2 gas having pressure 200 millibar is filled in 200 ml bottle. If the same amount of O_2 gas is filled in 2 litre bottle, find its pressure.

Solution : According to Boyle's law

$$P_1V_1 = P_2V_2$$

$$P_1 = 200 \text{ millibar, } V_1 = 200 \text{ ml}$$

$$P_2 = ?, \ V_2 = 2 \text{ litre} = 2000 \text{ ml}$$

$$P_1V_1 = P_2V_2$$

$$\therefore P_2 = \frac{P_1V_1}{V_2}$$

$$= \frac{200 \times 200}{2000}$$

$$= 20 \text{ millibar}$$

The pressure of O_2 gas will be 20 millibar.

Example 3 : If the density of a gas at sea-level is 1.5 mg lit^{-1}, find the density of that gas on Mount Abu, having pressure 0.5 bar.

Solution : On sea level the pressure of gas is 1 bar. According to Boyle's law :

$$\frac{d_1}{P_1} = \frac{d_2}{P_2}$$

$$d_1 = 1.5 \text{ mg lit}^{-1}, d_2 = ?,$$
$$P_1 = 1 \text{ bar, } P_2 = 0.5 \text{ bar}$$

$$\therefore d_2 = \frac{d_1 \, P_2}{P_1}$$

$$= \frac{1.5 \times 0.5}{1}$$

$$= 0.75 \text{ mglitre}^{-1}$$

The density of gas will be 0.75 mglitre^{-1}

Absolute Zero Temperature : For fixed amount of gas at constant pressure, to understand the change in volume by changing the temparature, experiments were carrited out and observations were noted. On the basis of the observations, relation between volume and temperature for gas is obtained which is known as Charles' law. From the analysis of the results the idea of absolute scale for temperature was obtained. Plotting the values of temperatures and volumes obtained from the observatons as shown in Figure 2.7 graph is obtained. For the fixed
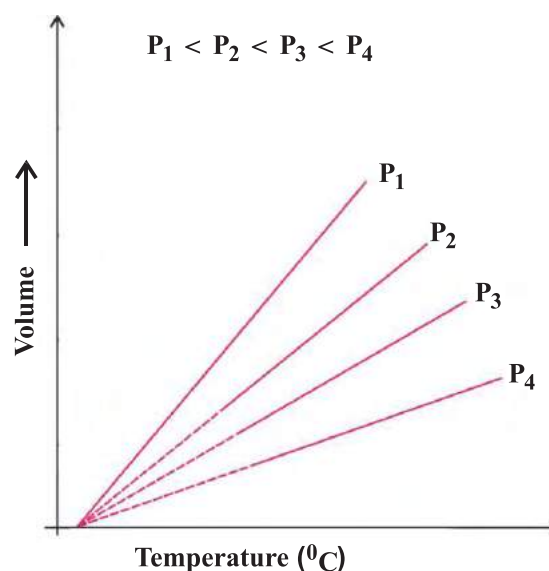

Fig. 2.7 Volume $\rightarrow$ Temperature (^{0}C)

amount of gas, at constant pressure, if the temperature is decreased then the volume will decrease and if temperature is increased the volume will increase. Hence the volume varies directly with its temperature. The graph indicating experimentally observed values of volume and

temperature is extended towards the lower temperatures, then it touches the X-axis at -273.15^0C, which indicates that theoretically at -273.15^0C temperature the volume of gas should be zero and at further low temperatures the volume of gas becomes negative which is meaningless and thus at -273.15^0C temperature at which the volume of gas is believed to be zero; the temperature is called absolute zero temperature. The idea of absolute zero temperature was first given by British scientist Kelvin and so this absolute zero temperature is also called Kelvin temperature. It is indicated by symbol K. When writing the Kelvin temperature, the sign for degree is not mentioned. Now, for the comparison between ^{0}C and K scale, the relation obtained is given below.

-273.15^0C = 0 K

now, add 273.15 on both sides

0 ^{0}C = 273.15 K

similarly

1 ^{0}C = (1+273.15) K

t ^{0}C = (t + 273.15) K is obtained which is the relation between K and ^{0}C temperature. From this relation a new scale can be derived for indicating temperature, which is also known as Kelvin scale. On the basis of experimental observations a relation between absolute temperature and volume is obtained which is known as Charles' law. For convenience 273.15 value is taken nearly equal to 273 so that t ^{0}C = (t + 273) K.

The Kelvin temperature is accepted as the SI unit.

Charles' law : In 1787, scientist Charles had carried out some experiments and relation was obtained. For the fixed amount of gas at constant pressure, the relation of absolute temperature and volume of gas is known as Charles' law.

Charles' and Gay-Lussac performed several experiments and found that "At comstant pressure and for fixed amount of a gas the change in volume by increasing or decreasing 1 ^{0}C temperature is $\frac{1}{273}$ of the original volume of a gas."

Now, suppose at 0 ^{0}C temperature the volume of gas is V_0. So by increasing temperature by 1 ^{0}C the change in volume of a gas is ($V_0 \times \frac{1}{273}$). Now if the temperature increased by t ^{0}C, then the change in volume is ($V_0 \times \frac{t}{273}$). So at t ^{0}C temperature the volume of a gas is $\left(V_0 + \frac{V_0 \times t}{273} \right)$

$$V_t = \left(V_0 + \frac{V_0 \times t}{273} \right)$$

$$= V_0 \left(1 + \frac{t}{273} \right) = V_0 \left(\frac{273 + t}{273} \right)$$

but t + 273 = T_t K and for 273 is T_0, putting this value in above equation then,

$$V_t = V_0 \left(\frac{T_t}{T_0} \right)$$

$$V_t = \left(\frac{V_0 T_t}{T_0} \right)$$

$$\frac{V_t}{V_0} = \frac{T_t}{T_0} = K \quad \text{or} \quad \frac{V_t}{T_t} = \frac{V_0}{T_0} = K$$

$$\therefore \frac{V}{T} = K, \quad V = KT \quad \text{or} \quad V \propto T \text{ (fixed}$$
amount of gas, constant pressure)

So the Charles' law can be written in this way.

"At constant pressure the volume of a fixed amount of gas varies directly to its absolute temperature."
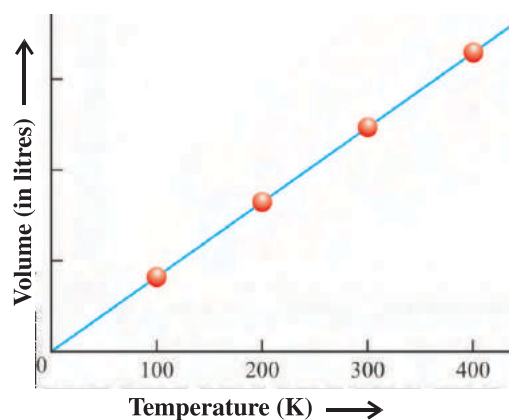
Fig. 2.8 Charles' law : volume → Temperature (K)

Now, suppose at initial stage at constant pressure, for fixed amount of gas its volume and absolute temperature are V_1 and T_1 respectively and at final stage they are V_2 and T_2 then according to Charles' law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Charles' law can be explained by garph given in Figure 2.8. It can be said that at constant pressure the volume of a fixed amount of gas varies directly with its absolute temperature which is indicated by a straight line. At different pressures $\dfrac{V}{T} = K$. The values of constant K are different which is also indicated in Figure 2.9 in $P_1 < P_2 < P_3 < P_4$.
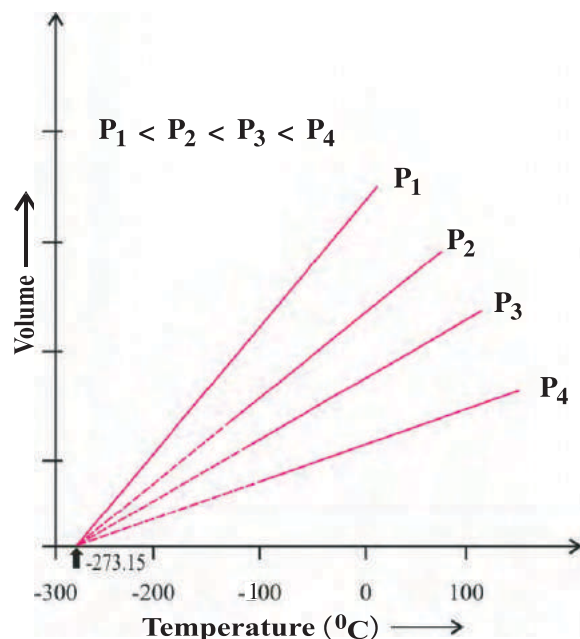
Fig. 2.9 Volume → Temperature (^{0}C)

Example 4: At 127 °C temperature the volume of O_2 gas is 3 litre. At which temperature the volume of O_2 gas will be halved ?

Solution : According to Charles' law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 = 3 \text{ litre, } V_2 = \frac{3}{2} \text{ litre}$$

$$T_1 = 127 + 273 = 400 \text{ K, } T_2 = ?$$

$$\therefore T_2 = \frac{V_2\, T_1}{V_1}$$

$$= \frac{1.5 \times 400}{3} = 200 \text{ K}$$

$$t_2\,^0C = T_2 - 273 = 200 - 273 = -73^0C.$$

The temperature of O_2 gas will be $-73\ ^0$C.

Example 5 : At constant pressure and 125 ^{0}C temperature Helium is filled in a container having volume 2 litre. If the temperature in ^{0}C is doubled then find the volume of helium gas at that temperature.

Solution : According to Charles' law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 = 2 \text{ litre, } V_2 = ?$$

$$T_1 = 125 + 273 = 398 \text{ K,}$$

$$T_2 = 250 + 273 = 523 \text{ K}$$

$$\therefore V_2 = \frac{V_1\, T_2}{T_1}$$

$$= \frac{2 \times 523}{398} = 2.628 \text{ litre}$$

$\therefore$ The volume of helium gas will be 2.628 litre.

Gay-Lussac's law : For a fixed amount of gas and at constant volume, to find the relation between pressure and absolute temperature, Gay-Lussac carried out experiments and from the observatons the relation is obtained which is given below. It is known as Gay-Lussac's law. This can be stated as follows :

"For constant volume, the pressure of a fixed amount of gas varies directly with its absoulte temperature."

Gay-Lussac's law is written mathematically as $P \propto T$ (constant volume of gas, fixed amount)

$$\therefore \ P = KT$$

$$\therefore \ \frac{P}{T} = K$$

At constant volume for a fixed amount of gas if at the initial stage the pressure and absolute temperature are P_1 and T_1 respectively and at final stage it is P_2 and T_2, then according to Gay-Lussac's law $\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$

Gay-Lussac's law can also be explained by garph. The relation between pressure and

absolute temperature is obtained as shown in Figure 2.10. Now, at cosatant volume and fixed amount of gas, the values of $\frac{P}{T}$ obtained are constant at different tempeatures i.e. $\frac{P}{T} = K$. The constant K is different at different constant values $V_1 < V_2 < V_3 < V_4$. This is clear from the Figure 2.10.

$$V_1 < V_2 < V_3 < V_4$$
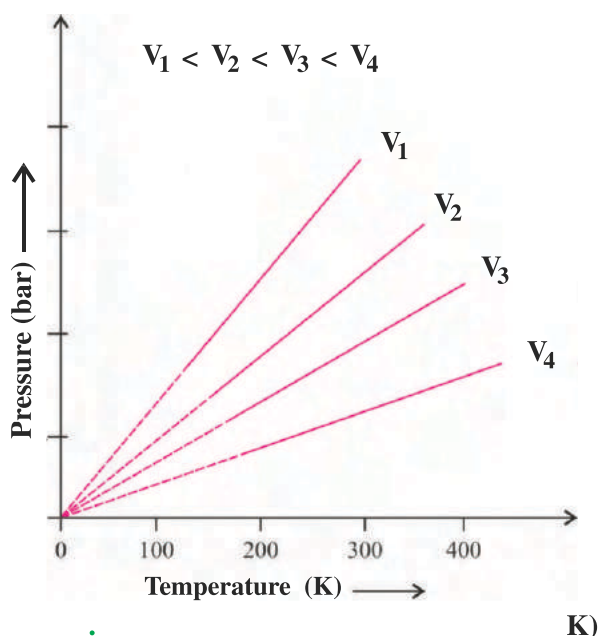
Fig. 2.10 Pressure (bar) → Temperature (K)

Solution :

According to Gay-Lussac's law,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_1 = 2 \text{ bar, } P_2 = ?$$
$$T_1 = 27 + 273 = 300 \text{ K,}$$
$$T_2 = 77 + 273 = 350 \text{ K}$$

$$\therefore P_2 = \frac{P_1 T_2}{T_1}$$

$$= \frac{2 \times 350}{300}$$

$$= 2.33 \text{ bar}$$

$\therefore$ The pressure of N_2 gas 2.33 bar.

Example 7 : In a colsed vassel of 400 K temperature the pressure of Cl_2 gas is 4 bar. At which ^{0}C temperature the gas is having pressure 5 bar.

Solution :

According to Gay-Lussac's law

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_1 = 4 \text{ bar, } P_2 = 5 \text{ bar,}$$
$$T_1 = 400 \text{ k, } T_2 = ?$$

$$\therefore T_2 = \frac{P_2 T_1}{P_1}$$

$$= \frac{5 \times 400}{4} = 500 \text{ K}$$

Now, $t^0 C = T_2 - 273 = 500 - 273 = 227^0$ C.

$\therefore$ The temperature of Cl_2 gas will be 227^0 C.

Avogadro's law : In 1811, Avogadro tried to combine the conclusions of Dalton's law and Gay-Lussac's law of combning volumes. The relation between volume of a gas and the number of molecules were given by Avogadro which is known as Avogadro's law. According to Avogadro's law, **"Equal volumes of all gases at same temperature and pressure contain equal number of molecules."** So, at constant temperature and pressure the volume of gas (V) varies directly to the number of molecules (n).

$$\therefore V \propto n...$$

$\therefore V = Kn....$ (Mathematical form of Avogadro's law)

2.3   Standard Temperature and Pressure

The volume of a fixed amount of gas depends upon its temperature and pressure. So 0 ^{0}C or 273 K temperature and 1 bar pressure. (10^5 Pa) are accepted as standard values by SI system, and hence, these values of temperature and pressure are known as standard temperature and pressure. **So 1 mole of any gas has same volume (for ideal gas 22.71098 litre mole^{-1}) at standard temperature and pressure (STP). The volume at STP is known as molar volume.** The molar volumes of some gases at STP are given in table 2.1.

So, normally at STP 22.413996 litre means nearly 22.4 litre is accepted as molar volume of gas and in one mole of gas the number of molecules are 6.022×10^{23}. This constant value is known as Avogadro's number. So, at STP 22.4 litre of gas contains 6.022×10^{23} molecules.

Table 2.1

Molar volume of some gases

Gas	Volume (litremole^{-1})
Argon	22.37
Carbon dioxide	22.54
Dinitrogen	22.69
Dioxygen	22.69
Dihydrogen	22.72
Ideal Gas	22.71

Combined Gas Equation : Boyle's law and Charles' law state the relation of volume with pressure and with temperature respectively. So, by combining these two laws an equation is obtained which indicates the combined effect of temperature and pressure on volume for fixed amount of gas. This is known as combined gas equation or it is also called gas equation.

According to Boyle's law $V \propto \dfrac{1}{P}$ (Fixed amount of gas, constant temperature)

According to Charles' law $V \propto T$ (Fixed amount of gas, constant temperature)

On obtaining combined relations from both the laws, then

$$V \propto \dfrac{T}{P}$$

$$\therefore \ PV \propto T$$

$$\therefore \ PV = KT$$

$$\therefore \ \dfrac{PV}{T} = K \ ..... \ \text{(Combined gas equation)}$$

Now, for fixed amount of gas at its initial stage the pressure, volume and absolute temperature are P_1, V_1 and T_1 respectively and at final stage the values are P_2, V_2 and T_2 respectively, then according to combined gas equation $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

Example 8 : At $27 \ ^0C$ temperature and 4 bar pressure CO is filled in 2 litre vessel. Find the pressure if it is filled in 4 litre vessel at $77 \ ^0C$ temperature.

Solution :

According to combined gas equation,

$$\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$$

$$P_1 = 4.0 \text{ bar, } P_2 = ?$$

$$V_1 = 2 \text{ litre, } V_2 = 4.0 \text{ litre}$$

$$T_1 = 27 + 273 = 300 \text{ K,}$$

$$T_2 = 77 + 273 = 350 \text{ K}$$

$$\therefore \ P_2 = \dfrac{P_1V_1}{T_1} \times \dfrac{T_2}{V_2}$$

$$= \dfrac{4 \times 2 \times 350}{300 \ \times 4} = 2.33 \text{ bar}$$

$\therefore$ The pressure of CO gas will be 2.33 bar.

Example 9 : At 400 K temperature, 200 ml N_2 has pressure 1.5 bar. Find the volume of N_2 gas at STP.

Solution : According to combined gas equation,

$$\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$$

$$P_1 = 1.5 \text{ bar, } P_2 = 1 \text{ bar}$$

$$V_1 = 200 \text{ ml, } V_2 = ?$$

$$T_1 = 400 \text{ K, } T_2 = 273 \text{ K}$$

$$V_2 = \dfrac{P_1V_1}{T_1} \times \dfrac{T_2}{P_2}$$

$$= \dfrac{1.5 \times 200 \times 273}{400 \times 1} = 204.75 \text{ ml}$$

$\therefore$ The volume of N_2 gas at STP will be 204.75 ml.

Example 10 : Find the pressure of a gas when 6.022×10^{22} molecules are placed in 2 litre vessel at $27 \ ^0C$ temperature.

Solution :

At STP 6.022×10^{22} molecules = 22.4 litre.

CO_2 gas 6.022×10^{22} molecules having volume at STP

$$= 22.4 \times \frac{6.022 \times 10^{22}}{6.022 \times 10^{23}} = 2.24 \text{ litre}$$

According to combined gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_1 = 1 \text{ bar}, \quad P_2 = ?$$

$$V_1 = 2.24 \text{ litre}, \quad V_2 = 2 \text{ litre}$$

$$T_1 = 273 \text{ K},$$

$$T_2 = 27 + 273 = 300 \text{ K}$$

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{1 \times 2.24 \times 300}{273 \times 2} = 1.231 \text{ bar}$$

$\therefore$ The pressure of CO_2 gas will be 1.231 bar.

2.4   Ideal Gas Equation

By combining Boyle's law, Charles' law and Avogadro's law, the relation obtained is called Ideal gas equation. In this equation four variables like temperature, pressure, volume and amount of gas describe gaseous state and the equation which indicates the quantitative relation between them is also called **equation of state,**

$$V \propto \frac{1}{P} \quad \text{(Boyles' law)}$$

$$V \propto T \quad \text{(Charles' law)}$$

$$V \propto n \quad \text{(Avogadro's law)}$$

$$\therefore V \propto \frac{nT}{P}$$

$$\therefore PV \propto nT$$

$$\therefore PV = nRT$$

(where R is proportionality constant)

R is also called universal constant because the values of R is the same for all the gases. It is also the same for any temperature, pressure or volume which means it has the same constant value. The value is not changed eventhough R has different values related to difierernt unit systems.

The ideal gas equation can also be written as below, in which it indicates the relation with density and molecular mass.

Ideal gas equation $PV = nRT$

where n is the number of moles

but $n = \dfrac{m}{M}$ where m is mass of gas. M = molecular mass. Putting this value in above equation.

$$PV = \frac{mRT}{M}$$

$$\therefore P = \left(\frac{m}{V}\right)\frac{RT}{M}; \quad \text{but } \left(\frac{m}{V}\right) = d$$

$$P = \frac{dRT}{M} \quad \text{(where } d = \text{density)}$$

m = molecular mass.

The values of gas constant R : In different unit systems the values of R gas constant (Universal constant) are different because R has unit of work energy mole^{-1} K^{-1}. The unit of work is differernt in different systmes.

Now, let us understand the unit of R. Ideal gas equation,

$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{\text{pressure} \times \text{volume}}{\text{mole} \times \text{temperature}}$$

But pressure = force ÷ area

$$R = \frac{[\text{force} \div \text{area}] \times \text{volume}}{\text{mole} \times \text{temperature}}$$

$$= \frac{[\text{force} \div (\text{length})^2] \times (\text{length})^3}{\text{mole} \times \text{temperature}}$$

$$= \frac{\text{force} \times \text{length}}{\text{mole} \times \text{temperature}}$$

$$= \frac{\text{work energy}}{\text{mole} \times \text{temperature}}$$

$$(\because \text{force} \times \text{length} = \text{work energy})$$

So the unit of R is work energy mole^{-1} K^{-1}. The calculation of values of R in different units are as given below :

(1) If the unit of pressure and volume are in atmosphere and litre respectively, then the unit of R will be in litre atmosphere $mole^{-1}$ K^{-1}.

volume of 1 mole gas at STP is 22.4 L.

so, $R = \dfrac{PV}{nT} = \dfrac{1 \text{ atmosphere} \times 22.4 \text{ litre}}{1 \text{ mole} \times 273 \text{ K}}$

$= 0.0821$ litre atmosphere $mole^{-1}K^{-1}$

(2) If the unit of pressure and volume are atmosphere and cm^3 respectively, then the unit of R will be atm cm^3 $mole^{-1}$ K^{-1}.

$R = \dfrac{PV}{nT} = \dfrac{1 \text{ atmosphere} \times 22400 \text{ cm}^3}{1 \text{ mole} \times 273 \text{ K}}$

$= 82.1$ atm cm^3 $mole^{-1}$ K^{-1}

(3) If the unit of pressure and volume are dyne cm^{-2} and cm^3 respectively, then the unit R will be erg $mole^{-1}$ K^{-1}.

$R = \dfrac{PV}{nT} = \dfrac{76 \text{ cm of Hg height} \times 22400 \text{ cm}^3}{1 \text{ mole} \times 273 \text{ K}}$

$= \dfrac{76 \times 13.6 \times 981 \times 22400}{1 \times 273}$

where 13.6 is the density of Hg and g = 981 dyne.

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

8.314 joule K^{-1} $mole^{-1}$

(1 joule = 10^7 erg)

(4) Now, 4.184 J = 1 calorie

$R = \dfrac{8.314}{4.184} = 1.987$ calorie $K^{-1}mole^{-1}$

≈ 2 calorie $mole^{-1}$ K^{-1}

$= 2 \times 10^{-3}$ kilocalorie $mole^{-1}$ K^{-1}

(5) If the unit of pressure and volume are bar and litre respectively, for ideal gas then unit of R will be bar litre $mole^{-1}$ K^{-1}.

$R = \dfrac{PV}{nT} = \dfrac{1 \text{ bar} \times 22.71 \text{ litre}}{1 \text{ mole} \times 273 \ 15 \text{ K}}$

$= 8.314 \times 10^{-2}$ barlitmole$^{-1}K^{-1}$

$= 8.314$ joulemole$^{-1}K^{-1}$

Thus, the units of R are different according to the different units of pressure and volume which are given in Table 2.2

Table 2.2 Different values of R

Sr.	Value of R	Unit	Unit of P and V
1	0.0821	litre atm $K^{-1}mol^{-1}$	(P in atm, V in litre)
2	82.1	ml atm $K^{-1}mol^{-1}$	P in atm, V in cm^3
3	8.314×10^7	erg $K^{-1}mol^{-1}$	P in dynes cm^{-2}, V in cm^3
4	1.987	cal $K^{-1}mol^{-1}$	P in dynes cm^{-2}, V in cm^3
5	8.3144	J $K^{-1}mol^{-1}$	P in Pa or N m^{-2}, V in m^3
6	8.314×10^{-2}	bar lit $K^{-1}mol^{-1}$	P in bar, V in litre

Example 11 : Find the pressure of 5 mole Cl_2 gas filled in a 2 litre vessel at 27^0C temperature.

Solution :

$PV = nRT$

$$\therefore P = \frac{nRT}{V}$$

$P = ?$, $n = 5$ mole

$R = 8.314 \times 10^{-2}$ barlitmole^{-1}K^{-1}

$T = 27 + 273 = 300$ K, $V = 2$ litre

$$= \frac{5 \times 8.314 \times 10^{-2} \times 300}{2}$$

$$= 62.355 \text{ bar}$$

$\therefore$ The pressure of Cl_2 gas will be 62.355 bar.

Example 12 : Find the moles of O_2 gas having pressure 250 bar in 500 ml vessel at 350 K temperature.

Solution :

According to ideal gas equation

$PV = nRT$

$$\therefore n = \frac{PV}{RT}$$

$P = 250$ bar, $n = ?$

$R = 8.314 \times 10^{-2}$ barlitmole^{-1}K^{-1}

$T = 350$ K, $V = 500$ ml $= 0.5$ litre

$$= \frac{250 \times 0.5}{8.314 \times 10^{-2} \times 350} = 4.296 \text{ mol}$$

$\therefore$ The mole of O_2 gas will be 4.296.

Example 13 : Find the temperature in ^0C for 6.4 gm O_2 gas filled in a 200 ml vessel having pressure 50 bar.

Solution :

According to ideal gas equation,

$PV = nRT$

$$\therefore PV = \frac{gRT}{M} \quad (\because n = \frac{g}{M})$$

$$\therefore T = \frac{PVM}{gR}$$

$P = 50$ bar, $M = 32$ grammole^{-1}

$R = 8.314 \times 10^{-2}$ barlitmole^{-1}K^{-1}

$g = 6.4$ gram

$V = 200$ ml $= 0.2$ litre, $T = ?$

$$T = \frac{50 \times 0.2 \times 32}{8.314 \times 10^{-2} \times 6.4}$$

$$= 601.4 \text{ K}$$

$$\therefore t^0 \text{ C} = T - 273$$

$$= 601.4 - 273 = 328.4^0 \text{ C}$$

$\therefore$ The temperature of O_2 gas will be 328.4^0 C.

Example 14 : Find the pressure of neon gas having density 0.9 gm lit^{-1} at 350 K temperature.

Solution : According to ideal gas equation

$$P = \frac{dRT}{M} \quad (\because n = \frac{d}{M})$$

$P = ?$, $d = 0.9$ gm lit^{-1}

$R = 8.314 \times 10^{-2}$ bar litmole^{-1} K^{-1}

$T = 350$ K, $M = 20$ gm mol^{-1}

$$P = \frac{0.9 \times 8.314 \times 10^{-2} \times 350}{20}$$

$$= 1.309 \text{ bar}$$

$\therefore$ The pressure of Neon gas will be 1.309 bar.

Concept of Ideal Gas : Deviation from Ideal Gas Behaviour : In ideal gas equation, the word ideal is used, but in fact there is not a single gas which follows this equation completely. However, it is believed that real gas behaves as ideal gas at high temperature and low pressure.

The gases which obey the ideal gas equation and gas laws at all temperatures and pressure are called ideal gases. Actually not a single gas is found as an ideal gas. If the temperature is lowered and at high pressure the deviation is observed in gas laws and ideal gas equation. Hence, the gases at all temperatures and pressures do not follow the ideal gas equation and these gases are called non-ideal gases or

real gases. Generally all the gases are real gases. They show ideal behavior in different proportions and out of them most of gases at low pressure and high temperature show ideal behavior. Some scientists studied gases extensively and at last concluded that all real gases at all conditions of temperature and pressure do not follow laws of ideal gas and the behaviour of real gas is deviated from an ideal gas and its study is carried out by effect of pressure and temperature.

Effect of pressure : To study the deviation in the behaviour of real gas from that of ideal gas, its idea can be obtained by plotting graph $\frac{PV}{nRT} \rightarrow P$, $\frac{PV}{nRT}$ is called **compressibility factor,** which is indicated by Z. For ideal gas the value of Z is one, because PV = nRT for ideal gas equation. Hence $\frac{PV}{nRT} = 1$, while for a real gas Z > 1, Z < 1, are possible, means that PV ≠ nRT. As shown in figure 2.11 for H_2 and He gases always Z > 1 so it is called positive
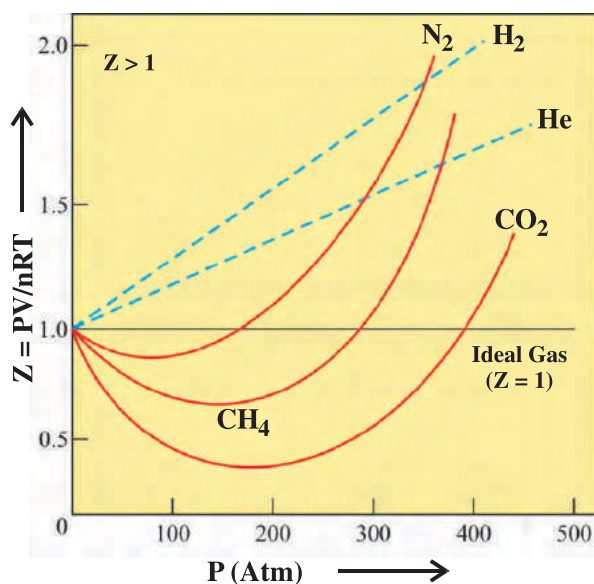
Fig. 2.11 Z → P

deviation and it indicates that for all values of pressure they are less compressive than ideal gas, while for N_2 and CO_2 gases at low pressure Z < 1 is called **negative deviation.** It indicates that, they are more compressive than ideal gas and at high pressure Z > 1 is called **positive deviation** which indicates that at high pressure, they are less compressive than ideal gases shown

in figure 2.11. For all gases the pressure is reduced and when it becomes zero, at that time Z = 1 means at zero pressure all gases behave as an ideal gas.

To study the deviation, the experimental data obtained for volumes of real gas at different pressures and theoretical data obtained for volumes of an ideal gas by calculation on the basis of Boyle's law at different pressures can be plotted against volume as shown in Figure 2.12. It is clear from the graph that at very high pressure, value obtained for volume of a real gas is higher than the value obtained for
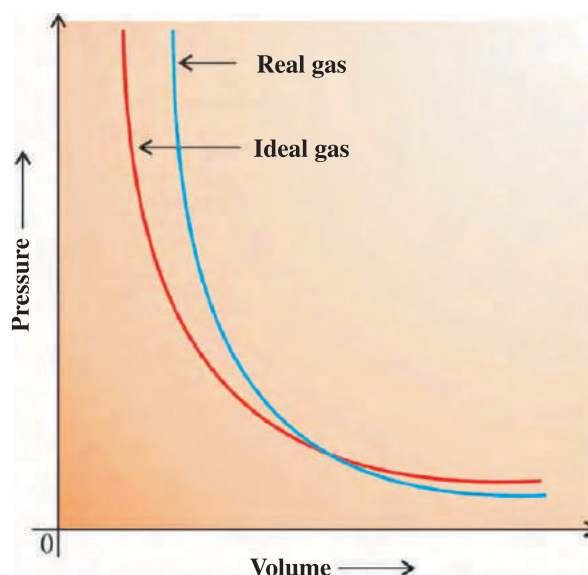
Fig. 2.12 Pressure → Volume

volume of ideal gas and as the pressure decreases means at low pressure the volume difference for both types of gases go on decreasing and at the end, it becomes zero and so both the graphs cross each other and after that as the pressure decreases once again the difference in volume of both types of gases are observed.

Effect of temperature : The effect of temperature can be explained by comparing the real behaviour of N_2 gas and its ideal behaviour at different temperatures. As shown in Figure 2.13 at different temperatures for N_2 the values of PV and P are plotted. In the figure, the dotted line indicates the ideal behaviour of the gas at the same temperature. It is clear from the figure that as the temperature incerases ($T_1 < T_2 < T_3 < T_4$), the depth of curved portion goes on decreasing, hence, as the temperature increases
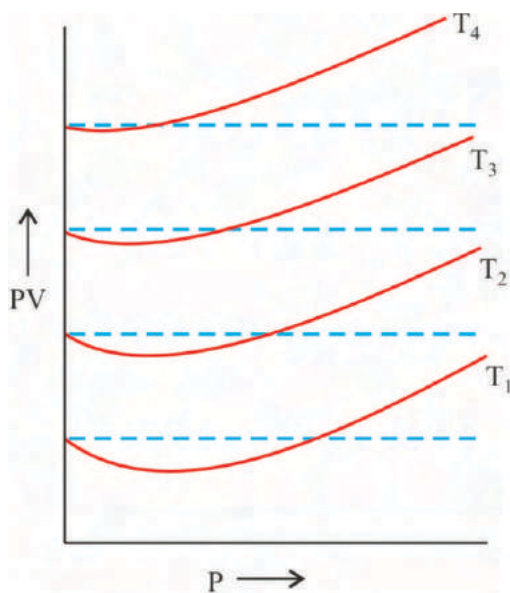
Fig. 2.13 PV → P

the deviaton of real gas compared to ideal gas behiviour goes on decreasing and at definite temperature the curved portion of graph becomes minimum and finally becomes straight line for appreciable range of pressures and at such definite temperature N_2 gas shows ideal behaviour and at this definite temperature, it follows Boyle's law. So this temperature of the gas is known as Boyle's temperature. Its values are different for different gases. For example, for N_2 gas it is 332 K and for H_2 gas it is 108 K.

Therefore, it is said that at low pressure and high temperature real gas shows ideal behaviour and at low temperature and high pressure there is a remarkable difference in its behaviour. The real gas shows devitaion from ideal gas behaviour. Why ? Because, out of the assumptions made in kinetic theory of gases two are not proper. These two assumptions are

(1) The force of attraction beween the gaseous molecules is negligible.

(2) The volume of a molecule is negligible (which can be avoided) compared to total volume of gas.

Now, if the assumption (1) is correct then there is a negligible force of attraction so, by cooling or compressing by the effect of pressure, the molecules will never be arranged close to each other and hence, the liquefaction of gas is not possible. Similarly, liquid cannot be converted into solid by effect of temperature or pressure.

Now, if asumption (2) is correct then the theoretical and experimental graphs of volume and pressure will be same, but in fact, it is not true. The deviation is observed. So it is neceassary to have correction in both the assumptions.

Now, if the force of attraction existing between gaseous molecules is as shown in Figure 2.14, then any molecules in the middle of the container have force of attraction evenly by the neighbouring molecules which are arranged in all directions. Hence, the resultant force of attraction becomes zero. Now, molecules when move towards the wall of container and ready to hit the wall means they are ready to touch the wall of container, at that time, as shown in Figure 2.14, the molecules have resultant force of attraction towards one side, i.e. it does not become zero and it tries to pull them in opposite direction from the wall. Thus with the inward
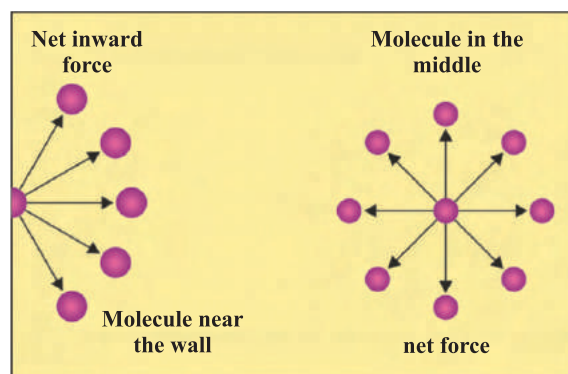
Fig. 2.14 Attraction force in molecules of gases

force of attraction, resistance is created in striking the molecules with the wall; so the measured real pressure is less than ideal pressure. So to obtain ideal pressure some correction is required in measured pressure P. (something to be added) Such suggestion is given by van der Waals and the total pressure (attraction) varies directly to square of density or inversely varies with square of its volume(V^2) so for any gas the ideal pressure value is equal to sums of real pressure and $\dfrac{an^2}{V^2}$

$$\therefore \text{ Ideal pressure of gas} = P_{real} + \frac{an^2}{V^2}$$

where a is constant and n is number of moles of gas.

Now, if the volume of gas molecule is taken into consideration, then the total volume

occupied by the gas molecules is not available for the motion of these molecules, so to obtain the effective or ideal volume (available volume), the volume occupied by the molecules is to be subtracted from the measured volume of the gas, and thus, the volume occupied by n mole of gas is nearly nb (where b is constant) which is subtracted from total volume (V). This correction is made in ideal gas equation and so the ideal gas equation is written as given below :

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

This equation is known as **van der Waals equation** where a and b are constants and they depend on the characteristics of gas. The constant a indicates the measurement of intermolecular attractive forces which is free from effect of temperature and pressure.

At very low temperature the intermolecular attractive forces become significant when molecules are moving with low avarage velocity. Due to this force of attraction the molecules are pulled towards each other and hence, it creates resistance in striking with wall of container. Due to this, measured value of pressure is less than ideal pressure. So it is said that the behaviour of real gas is ideal when intermolecular forces are such that it becomes practically negligible.

Liquefaction of gas : Gas can be liquefied by lowering the temperature and increasing the preassure but for liquefaction of gas, effect of temperature is more important than effect of pressure because all gases after cooling to certain fixed temperature are liquefied under effect of pressure but in addition to that temperature, however, the pressure may be applied, eventhough, they are not liquefied. These temperatures are different for different gases. Hence, **the maximum temperature at which the gas gets liquefied is known as critical temperature, (T_C).** Above the critical temperature, however, the pressure is applied eventhough the liquefaction of gas is not possible. So, at higher than critical temperature, the liquid state is not possible but below the critical temperature under the effect of pressure gas liquefaction is possible. **At critical temperature, the pressure is applied on gas for liquefaction, that pressure is called critical pressure (P_C) of that gas. At critical temperature and critical pressure, the**

volume occupied by 1 mole of gas is called critical volume (V_C) and this state is called critical state. Every gas has its P_C, T_C and V_C values fixed. So they are known as critical constants which are different than other gas constants. In 1869 Thomas Andrews studied the relation between pressure, volume and temperature for CO_2 gas and obtained experimental data for gaseous and liquid state of CO_2 gas. For this, he had taken a hard glass tube at constant temperature and filled with CO_2 gas. At different pressures the volume of gas was measured. After that he plotted a graph (isotherm) indicating effect of pressure on volume of gas at different constant temperature as shown in Figure 2.15. At lower temperature i.e. 13.1^0 C temperature and lower pressure, at point X the
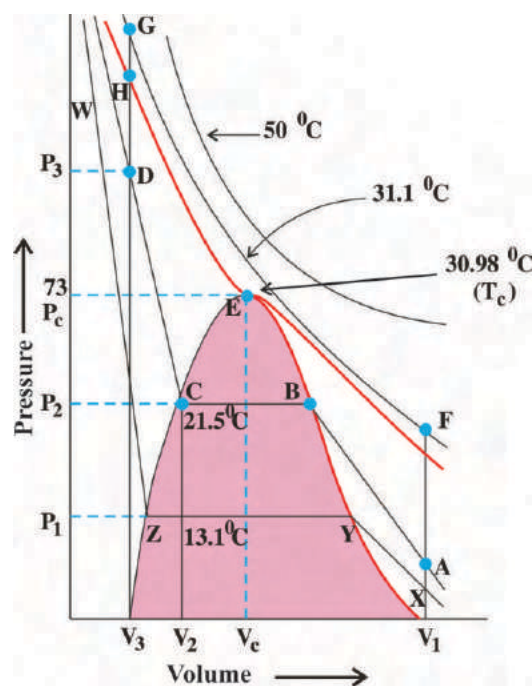
Fig. 2.15 Liquefaction of gas

CO_2 is in gaseous state. Now with increasing pressure volume of CO_2 gas decreases which is shown by XY curve. Now, at point Y, at given pressure, the liquefaction of gas starts and at point Z total gas is converted into liquid state. During this the pressure remains costant, which is clear from the figure. After that the curve ZW rises straight which indicates that after increasing the pressure on volume of liquid is very less. Thus, the isotherm obtained at 13.1^0 C the XY indicates gaseous state, YZ indicates equilibrium between liquid and ZW only liquid state. YZ is horizontal which indicates that during the liquefaction of gas the pressure remains

constant. This pressure is the vapour pressure of liquid gas. Now, the isotherm obtained at 21.5^0 C temperature, on basis of experimental data, is the same as the isotherm obtained at 13.1^0 C but the horizontal portion BC which indicates the liquefaction is smaller than YZ. As the temperature increases the portion which indicates the liquefaction becomes smaller and finally at 30.98^0 C temperature, this portion becomes only a point E and above this temperature, i.e. 31.1^0 C this portion is lacking in the isotherm. So at this point of temperature the liquefaction of CO_2 is not possible. Thus at 30.98^0 C temperature the portion is just a point only indicating that at this point there is a liquefaction. So this temperature is known as critical temperautre of CO_2 gas. Above this temperature, however, the pressure is applied, still the liquefaction of CO_2 is not possible but at 30.98^0 C or less than that temperature liquefaction is possible under pressure.

According to molecular kinetic theory of gases on lowering the temperature the kinetic energy of the molecules decreases and as a result slow moving molecules come closer to each other. At sufficiently low temperature some of the slow moving molecules cannot resist the force of attraction and they come closer and closer and ultimately the gas changes into the liquid state. In the same way increasing pressure, the volume decreases and so by the increase in pressure gas can also be liquefied. Thus, the combination of temperature and pressure means at critical temperature or lower than that temperature by increasing pressure the gas gets liquefied. In Table 2.3 critical temperature of some gases are given.

Table 2.3 Critical Constants

Gas-Substance	T_C (K)	P_C (Bar)	V_C dm^3mol^{-1}
H_2	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N_2	126	33.9	0.0900
O_2	154.3	50.4	0.0744
CO_2	304.10	73.9	0.0956
H_2O	647.1	220.6	0.0450
NH_3	405.5	113.0	0.0723

In the mixture of two gases having different critical temperatures one gets liquefied faster because on cooling the mixture, the gas starts liquefying whose critical temperature comes first so the H_2 gas starts liquefying first and at that time He gas is not liquefied.

Kinetic Energy and Molecular Speed : Molecules are made up of particles of the substance having gaseous state. These particles are far away from each other in a large area. These particles are continuously moving in all directions. The continuous moving particles collide with each other and also with the wall of container. At that time the speeds and directions are changed, so that all particles in a container do not have same speed, but have different speeds which are continuously changing. However, at one temperature the distribution of speed of molecules is same. Maxwell and Boltzmann had studied the distribution of molecules between different possible speeds. They studied the speed of molecules and the fraction of molecules with a given speed and a graph was plotted. The graph is known as Maxwell's distribution curve as shown in Figure 2.16. The feature of molecular speed is shown below.
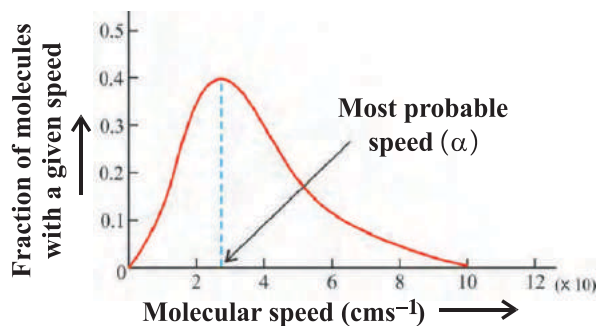
Fig 2.16

Fraction of molecules with given speed → Molecular speed

(1) The fraction of molecules with very high or low speed is very small.

(2) Increasing the speed of molecules, fraction of molecules also increases which becomes maximum and then decreases.

(3) The top portion of curve indicates maximum fraction of molecules and the speed of molecules is called most probable speed which is indicated by α. On increasing temperature the collision of molecules increases and the speed of molecules changes. On increasing temperature the most probable speed also increases which is clear from the graph in Fig 2.17. The graph is

shifted towards right side as the temperature increases and becomes more flat. If the temperature remains constant, curve of speed distribution does not change. There are three main types of speed of molecules.

(1) most probable speed

(2) average speed

(3) root mean square speed.

The molecules have different kinetic energies with different types of speed.
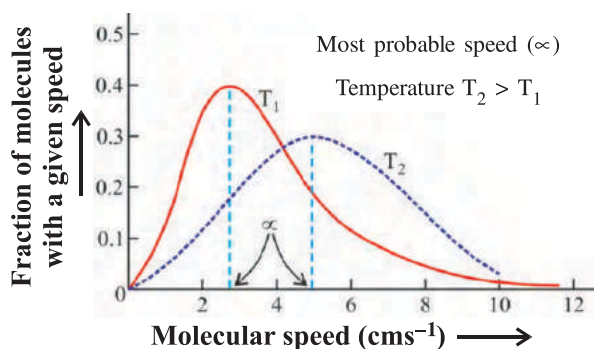
Fig. 2.17 Fraction of Molecules with a given speed → Molecular speed

"The total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of invidual gas."

Partial pressures means pressure of gases that will exert if they are filled separately in the same vessel, under the same conditions.

Suppose, in a vessel mixture of gases A, B, C, D are filled and the partial pressure are p_A, p_B, p_C, p_D respectively, then Dalton's law of partial pressure can be written in mathematical form as follows. Total pressure $(P_{total}) = p_A + p_B + p_C + p_D$

Dalton's law can be explained by the illustration given below :

As shown in Figure 2.18 take three vessels having same volume at constant temperature. Now, fill gas A in the first vessel, fill gas B in the second vessel and note down the pressure of the gases in both the vessels. Suppose the pressure of gas in the first vessel is p_A and that in the second vessel is p_B. There is no chemical reaction between gases A and B on mixing. Now, mix both gases in the third
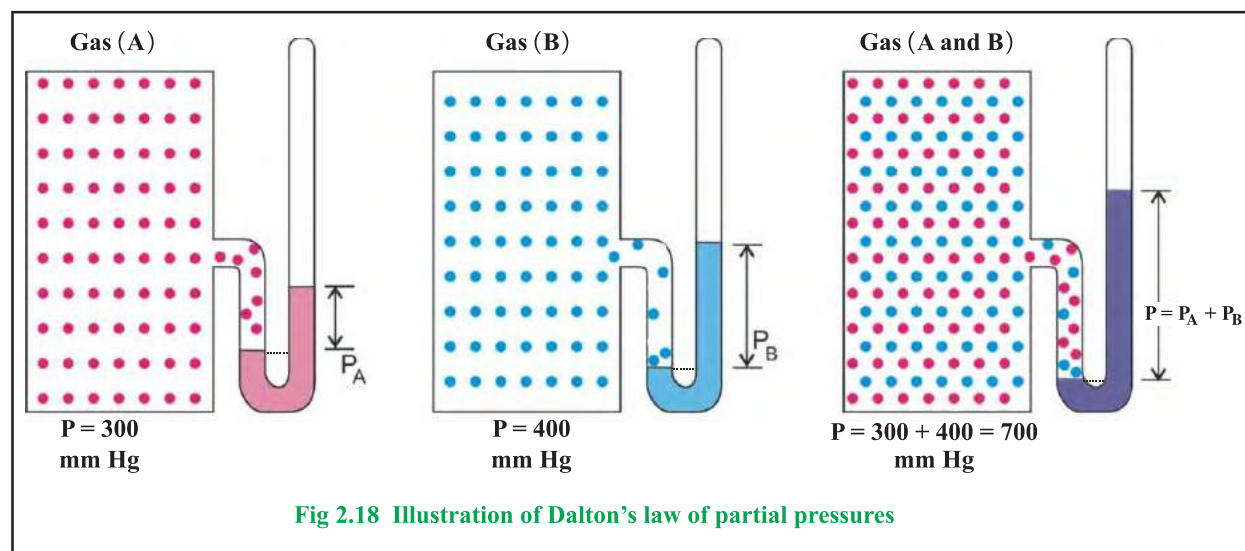
Fig 2.18 Illustration of Dalton's law of partial pressures

2.5   Dalton's Law of Partial Pressure

The component gases in a gaseous mixture behave independently in case of their properties. Moreover, if these gases are in mixture, even then all gases obey this law. Two or more gases which do not undergo chemical reactions are mixed in a closed vessel, the total pressure in a vessel can be obtained by Dalton's law of partial pressure. In 1801, Dalton stated the law of partial pressure which can be written as :

vessel and note down the pressure of a mixture of gases in third vessel which will be the total pressure. From the observation it is proved that total pressure :

$P_{total} = p_A + p_B$.

Sometimes the gases are collected over the water during the prepartion of the gas in laboratory. The gas collected over water is saturated with water vapour at that temperature So the measured pressure is the sum of partial

pressure of a gas collected over water and partial pressure of water vapour at that temperature. So if the measured pressure of gas is to be obtained, then subtract the water vapour pressure at that temperature which gives the partial pressure of dry gas only, e.g. 298 K temperature O_2 gas collected over water having total pressure is P_{total}, subtract the vapour pressure of water (p_{H_2O}) at same temperature, then only the pressure of dry O_2 gas (p_{O_2}) is obtained.

$$p_{O_2} = P_{total} - p_{H_2O}$$

Thus, by using Dalton's law of partial pressure the pressure of gas collected over water can be obtained.

The total pressure (P_{total}) for a mixture of gas collected in a container is obtained by using fomula given below :

Suppose, in V litre container at temperature T, three different gases having number of moles n_1, n_2 and n_3 respectively are filled. The total pressure is P_{total} and the partial pressures of three gases are p_1, p_2 and p_3 respectively in the container, then according to Dalton's law.

$$\text{Total pressure } (P_{total}) = p_1 + p_2 + p_3$$

But $p_1 = \dfrac{n_1RT}{V}$, $p_2 = \dfrac{n_2RT}{V}$ and $p_3 = \dfrac{n_3RT}{V}$

Putting values in above equation

$$\text{Total pressure } (P_{total}) = \dfrac{n_1RT}{V} + \dfrac{n_2RT}{V} + \dfrac{n_3RT}{V}$$

$$= (n_1 + n_2 + n_3)\dfrac{RT}{V}$$

but ($n_1 + n_2 + n_3$) = total number of moles for gaseous mixture.

$$\therefore P_{total} = (\text{total number of moles}) \times \dfrac{RT}{V}$$

Same way from total pressure the values of partial pressure of each gas is obtained by formula given below.

Taking ratio of p_1 and P_{total}

$$\dfrac{p_1}{P_{total}} = \dfrac{n_1RT}{V} \times \dfrac{V}{\text{total mole} \times RT}$$

$$= \dfrac{n_1}{\text{total mole}}$$

but $\dfrac{n_1}{\text{total mole}}$ = mole fraction = X_1

$$\therefore \dfrac{P_1}{P_{total}} = X_1$$

$$\therefore p_1 = X_1 \cdot P_{total}$$

In the same way

$$\therefore p_2 = X_2 \cdot P_{total}$$

$$\therefore p_3 = X_3 \cdot P_{total}$$

So the partial pressure of each gas is obtained from the total pressure and from the mole fraction of each gas. Same way, in a mixture of gases if the % by volume is given for each gas, then the partial pressure of gas is obtained by formula given below.

The partial pressure of gas (p_A) =

$$\dfrac{\% \text{ by volume of gas A} \times \text{total pressure}}{100}$$

Example 15 : At 27^0C temperature in a 2 litre closed vessel, 10 gm H_2 and 22 gm CO_2 gases are filled. Find the partial pressure and total pressure of a mixture.

Solution :

For 10 gm H_2 gas, the mole $= \dfrac{m}{M}$

$$= \dfrac{10}{2} = 5 \text{ mole} = nH_2$$

For 22 gm CO_2 gas, the mole $= \dfrac{m}{M}$

$$= \dfrac{22}{44} = 0.5 \text{ mole} = nCO_2$$

Now, the partial pressure of H_2 gas (pH_2) (27 + 273) = 300 K is

$$p_{H_2} = \dfrac{n_{H_2}RT}{V}$$

$$= \dfrac{5 \times 8.314 \times 10^{-2} \times 300}{2} = 62.355 \text{ bar}$$

$$p_{CO_2} = \dfrac{n_{CO_2}RT}{V}$$

$$= \dfrac{0.5 \times 8.314 \times 10^{-2} \times 300}{2} = 6.236 \text{ bar}$$

According to Dalton's law of partial pressure

$$P_{total} = p_{H_2} + p_{CO_2} = (62.355 + 6.236) \text{ bar}$$

$$= 68.591 \text{ bar}$$

The total pressure will be 68.591 bar.

Example 16 : At 27^0C temperature 4 mole Cl_2, 4 mole N_2 and 2 mole O_2 are filled in a 5 litre closed vessel. Find the total pressure of gaseous mixture.

Solution :

According to Dalton's law of partial pressure

$$= (n_{Cl_2} + n_{N_2} + n_{O_2}) \times \frac{RT}{V}$$

$$= (4 + 4 + 2) \times \frac{RT}{V}$$

$$(T = 27 + 273 = 300 \text{ K})$$

$$= \frac{10 \times 8.314 \times 10^{-2} \times 300}{5} = 49.88 \text{ bar}$$

The total pressure of gaseous mixture will be 49.88 bar.

Example 17 : In a closed vessel, at 25^0C temperature 4 mole O_2, 3 mole Cl_2 and 3 mole N_2 are mixed and the total pressure found is 50 bar. Find the partial pressure of each gas.

Solution : According to Dalton's law of partial pressure

Total number of mole $= n_{O_2} + n_{Cl_2} + n_{N_2}$

$$= 4 + 3 + 3 = 10 \text{ mole}$$

$$p_{O_2} = \left(\frac{n_{O_2}}{\text{total mole}} \right) . P_{total}$$

$$= \frac{4}{10} \times 50 = 20 \text{ bar}$$

$$p_{Cl_2} = \left(\frac{n_{Cl_2}}{\text{total mole}} \right) . P_{total}$$

$$= \frac{3}{10} \times 50 = 15 \text{ bar}$$

$$p_{N_2} = \left(\frac{n_{N_2}}{\text{total mole}} \right) . P_{total}$$

$$= \frac{3}{10} \times 50 = 15 \text{ bar}$$

∴ The partial pressure of O_2, Cl_2 and N_2, are 20 bar, 15 bar and 15 bar respectively.

Example 18 : At 400 K temperature in a closed vessel the % by volume of He, Ne and Ar are 40 %, 40 % and 20 % respectively. If the total pressure is 25 bar, then find the partial pressure of each gas.

Solution :

$$p_{He} = \frac{\text{\% by volume of gas He} \times \text{total pressure}}{100}$$

$$= \frac{40}{100} \times 25 = 10 \text{ bar}$$

$$p_{Ne} = \frac{\text{\% by volume of gas Ne} \times \text{total pressure}}{100}$$

$$= \frac{40}{100} \times 25 = 10 \text{ bar}$$

$$p_{Ar} = \frac{\text{\% by volume of gas Ar} \times \text{total pressure}}{100}$$

$$= \frac{20}{100} \times 25 = 5 \text{ bar}$$

∴ The partial pressures of He, Ne and Ar are 10 bar, 10 bar and 5 bar respectively.

Example 19 : At 500 K temperature in 2 litre vessel 0.32 gm O_2 gas is collected over water. If the vapour pressure of water is 32 bar at 500 K, find the partial pressure of dry O_2 gas.

Solution : The pressure of O_2 gas which is collected over water is

$$P_{O_2} = \frac{mRT}{MV}$$

$$= \frac{0.32 \times 8.314 \times 10^{-2} \times 500}{32 \times 2} = 0.2079 \text{ bar}$$

But, the O_2 gas is collected over water, so this is combined pressure of dry O_2 and water vapour.

The water vapour pressure = 32 milli bar

= 0.032 bar

$$p_{O_2} = p_{O_{2(dry)}} + p_{H_2O}$$

$$p_{O_{2(dry)}} = p_{O_2} - p_{H_2O}$$

$$= (0.2079 - 0.032) = 0.1759 \text{ bar}$$

The partial pressure of dry O_2 gas is 0.1759 bar.

2.6 Graham's Law of Gaseous Diffusion

In laboratory, at one corner, if a bottle of H_2S water is kept open, then within short time the smell of it will spread in the entire laboratory. If a flask filled with brown colour NO_2 gas is attached with flask containing H_2 gas, although the pressure of both flasks are equal, after sometime both the flasks will have same colour intensity (light brown). This happens because the mixture of gaseous molecules have

characteristic to mix uniformly and that results into homogenous system. Such a characteristc of diffusion of gas is called gaseous diffusion. **So the diffusion of gas means, it is a process in which two or more gases mix spontaneously to form homogeneous system.** They mix spontaneously without taking into consideration the density of mixing gases. This happens because in a gaseous state of substances there is a lot of empty space between the molecules. So the molecules of different gases come in contact with each other and the molecules move and diffuse in the empty space. This process continues till the homogeneous system is formed. Thus, the motion of gaseous molecules is called difusion and its rate is called rate of the diffusion.

It is proved by the experiment that all gases possess relation between their diffusion rate and their density; higher the density of gas, lower is the rate of the diffusion. By studying this diffusion of gas, Graham in 1928, presented a relation between diffusion rate of gas and its density which is known Graham's law of diffusion of gases. This can be stated as :

"The rate of diffusion of various gases varies inversely proportional to the square root of their densities."

If the density of gas is (d) and rate of diffusion is (r), then the mathematical form of Graham's law is

$$r \propto \frac{1}{\sqrt{d}}$$

On the basis of measurement of diffusion rate of gas, the molecular mass of the gas can be determined. For this, the diffusion rates of two gases are compared after carrying out the experiment at same temperature and pressure.

Suppose, r_1 and r_2 are the diffusion rates of gas-1 and gas-2 respectively and the densities of these two gases at the same temperature and pressure are d_1 and d_2 respectively, then the following equation can be written from the definition of Graham's law of diffusion of gases.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

Now, at the same temperature and pressure the density of a gas varies directly to its molecular mass.

$$\therefore \ d \propto M$$

Now, $r \propto \dfrac{1}{\sqrt{d}}$ and $d \propto M$, so by combining these two,

$$r \propto \frac{1}{\sqrt{M}}$$

Now, for two different gases, comparing the rates of diffusion,

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

$$\therefore \ \frac{d_2}{d_1} = \frac{M_2}{M_1}$$

Hence, it can be proved that at same temperature and pressure, the ratio of the densities of any two gases is equal to the ratio of their molecular masses.

It can be proved from this equation that if the diffusion rates of two gases are measured and if the molecular mass of one gas is known, then the molecular mass of the other gas can be obtained.

The volume of the diffused gas in a unit time is called rate of diffusion.

$$\therefore \ \text{Rate of diffusion } (r) = \frac{\text{volume of gas diffused (V)}}{\text{time required for diffusion (t)}}$$

$$r = \frac{V}{t}$$

For two gases at the same temperature and pressure the rates of diffusion are $r_1 = \dfrac{V_1}{t_1}$

and $r_2 = \dfrac{V_2}{t_2}$

$$\frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

$$\frac{r_1}{r_2} = \frac{V_1 \cdot t_2}{V_2 \cdot t_1} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

For convenience during the experiment the time taken by two gases for diffusion of equal volumes are measured or the volume of two diffusion gases are measured in equal time. So, during calculation of such experimental observation, the above equation can also be written as below :
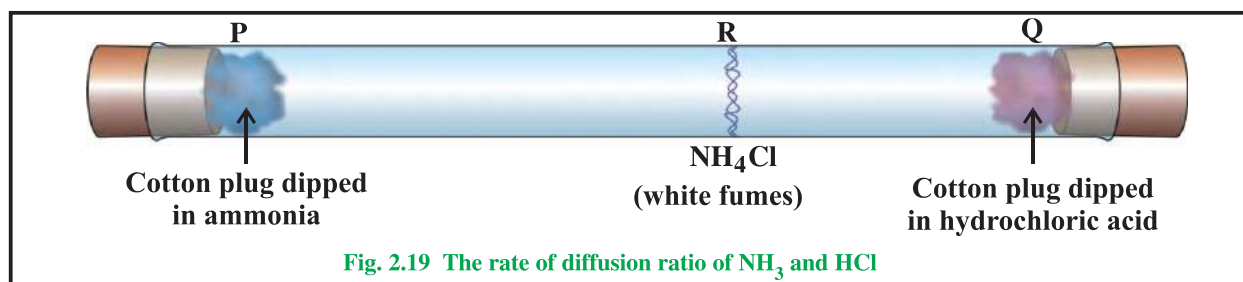
$$\frac{V_1 \cdot t_2}{V_2 \cdot t_1} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

If $t_1 = t_2$ then $\dfrac{V_1}{V_2} = \sqrt{\dfrac{M_2}{M_1}} = \sqrt{\dfrac{d_2}{d_1}}$

If $V_1 = V_2$ then $\dfrac{t_2}{t_1} = \sqrt{\dfrac{M_2}{M_1}} = \sqrt{\dfrac{d_2}{d_1}}$

To determine the ratio of rate of diffusion for two gases, experiment can be carried out in laboratory. For that, at the same temperature and pressure the volume of two gases diffusing at the same time are measured; the experiment performed is as follows :

Experiment : In laboratory to determine the rates of diffusion of NH_3 and HCl gases, the experiment performed is shown in Figure 2.19. A glass tube 100 cm in length and uniform diameter is taken. At the P end of the tube a cotton plug dipped in aqueous ammonia and at the Q end cotton plug dipped in hydrochloric acid are fixed at the same time. As the two gases will diffuse a thin layer of white fumes of ammonium chloride will be formed at the place R as shown in Figure 2.19. Note down this point R and measure the distance PR and QR.

about 1.46 ± 0.01. According to Graham's law of diffusion of gases, it indicates the ratio of diffusion rates for $NH_{3(g)}$ and $HCl_{(g)}$.

Importance of Graham's law of gaseous diffusion : The importance of Graham's law of gaseous diffusion is given below :

(i) To separate the mixture of two isotopes, e.g. Uranium metal has two isotopes ^{235}U and ^{238}U. ^{235}U is more important in production of nuclear energy. The proportion of ^{235}U in uranium metal is only 0.7 %.

The uranium hexafluoride (UF_6) is a volatile compound. Uranium hexafluoride is prepared from uranium metal. The difference between the molecular masses of $^{235}UF_6$ and $^{238}UF_6$ is very less. Hence, the ratio of rate of diffusion of these gases is 1.0047.

Now, if the mixture of $^{235}UF_6$ and $^{238}UF_6$ gas filled in a porous vessel and allowed to have the diffusion the amount of $^{235}UF_6$ of less molecular mass will be somewhat faster in diffusion rate than $^{235}UF_6$. A series of experiments were carried out. This type of work is carried out in a laboratory extented to a kilometer distance at OaK Ridge in Tenessey

Fig. 2.19 The rate of diffusion ratio of NH_3 and HCl

P   R   Q

Cotton plug dipped in ammonia

NH_4Cl (white fumes)

Cotton plug dipped in hydrochloric acid

Reaction :

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(g)} \quad \text{White fumes}$$

The white fumes of ammonium chloride is seen, there is a diffusion of ammonia gas which occupies distance PR and the diffusion of hydrochloric acid gas occupies distance QR. As the diameter of the tube is uniform,

$$\frac{V_{NH_3}}{V_{HCl}} = \frac{\text{Distance PR}}{\text{Distance QR}}$$

After doing the experiment three times the average ratio of distances $\dfrac{PR}{QR}$ comes out to be

State of U.S.A. The experiment of diffusion of this gas through porous membrane is distributed (extended) to about a kilometer. After a long time pure $^{235}UF_6$ is obtained which is decomposed to get pure ^{235}U. Thus, the isotopes of uranium are separated by gaseous diffusion.

(ii) Graham's law of gaseous diffusion is used in finding out the molecular masses of gases and the density of gases.

(iii) Graham's law of gaseous diffussion is used in determining the rate of diffusion ratio for any two gases.

Example 20 : Under the uniform experimental conditions, find the rate of diffusion ratio for O_3 and SO_2 gases.

Solution : The molecular masses of O_3 and SO_2 are 48 and 64 gram mol^{-1} respectively. So according to Graham's law of gaseous diffuion.

$$\frac{r_{O_3}}{r_{SO_2}} = \sqrt{\frac{M_{SO_2}}{M_{O_3}}}$$

$$= \sqrt{\frac{64}{48}} = 1.1547$$

∴ The ratio of rate of diffusion of O_3 and SO_2 is 1.1547.

Example 21 : The time taken by O_2 gas to travel from sun to earth is 80 seconds. Find the time taken by helium gas from the same source.

Solution : Here, the distance for diffusion of both the gases is equal. So, according to Graham' law of diffusion,

$$\frac{t_{O_2}}{t_{He}} = \sqrt{\frac{M_{O_2}}{M_{He}}}$$

$$\frac{80}{t_{He}} = \sqrt{\frac{32}{4}} = \sqrt{8}$$

(As the molecular mass of O_2 and He are 32 and 4 $gmol^{-1}$ respectively)

$$\therefore t_{He} = \frac{80}{\sqrt{8}}$$

$$= 28.288 \text{ second} \cong 28.29 \text{ second}$$

∴ The time taken by helium gas is 28.29 second.

Example 22 : The volumes occupied by N_2 and unknown gas in same time are 50 ml and 70 ml respectively. Find the molecular mass of unknown gas.

Solution : According to Graham's law of gaseous diffuson :

$$\frac{r_{N_2}}{r_{unknown\ gas}} = \frac{v_{N_2}}{V_{unknown\ gas}} = \sqrt{\frac{M_{unknown\ gas}}{M_{N_2}}}$$

$$\therefore \frac{50}{70} = \sqrt{\frac{M_{unknown\ gas}}{28}}$$

$$\therefore M_{unknown\ gas} = \frac{2500 \times 28}{4900}$$

$$= 14.29 \text{ gmol}^{-1}$$

∴ The molecular mass of unknown gas is 14.29 $gmol^{-1}$.

2.7 Avogadro's Hypothesis

Avogadro proposed a hypothesis, in 1811. It can be expressed as "The number of molecules of any gas in same volume at standard temperature and pressure is same."

Simple gas equation is one of the methods to present the Avogadro's hypothesis. All the relations derived from Avogadro's hypothesis are included in this equation. This gas equation is applicable to all the gases in favourable conditions. The presentation of this equation in the form of symbol can be made as follows.

In a V litre volume of any gas at P bar pressure and T Kelvin temperature, n moles of molecules = n × N (where N = 6.02×10^{23} is known as Avogadro's number or Avogadro's constant).

One important dimension resulting from Avogadro's hypothesis is molar volume. Molar volume can be explained by using simple gas equation. **Molar volume means the volume occupied by the molar mass expressed in gram of a gas.** The volume of 1 mole at 273 K temperature and 1 bar pressure can be found by general gas equation and is called molar volume. The 22.4 litre value is accepted as a standard value. **The molar volume is also known as gram molar volume.** The presentaion of Avogadro's hypothesis on the basis of molar volume can be made as follows.

"In 22.4 litre of any gas at 273 K temperature and 1 bar pressure (STP) contain 1 mole molecules." This statment can be given alternatively as the mass of 22.4 litre of any gas at 273 K temperature and one bar pressure is its molecular mass. According to Avogadro's hypothesis, **"The number of molecules in one molar volume of any gas is 6.022×10^{23}."**

"The mass in gram of one mole of any subtance is its molar mass."

The relations among mole number(n), number of particle (N), Volume (V) of STP and molecular mass (M) are given in Figure 2.20.

Fig. 2.20 Inter relation between mole (n), no. of particles (N), volume of gas (STP) and Gram molar mass
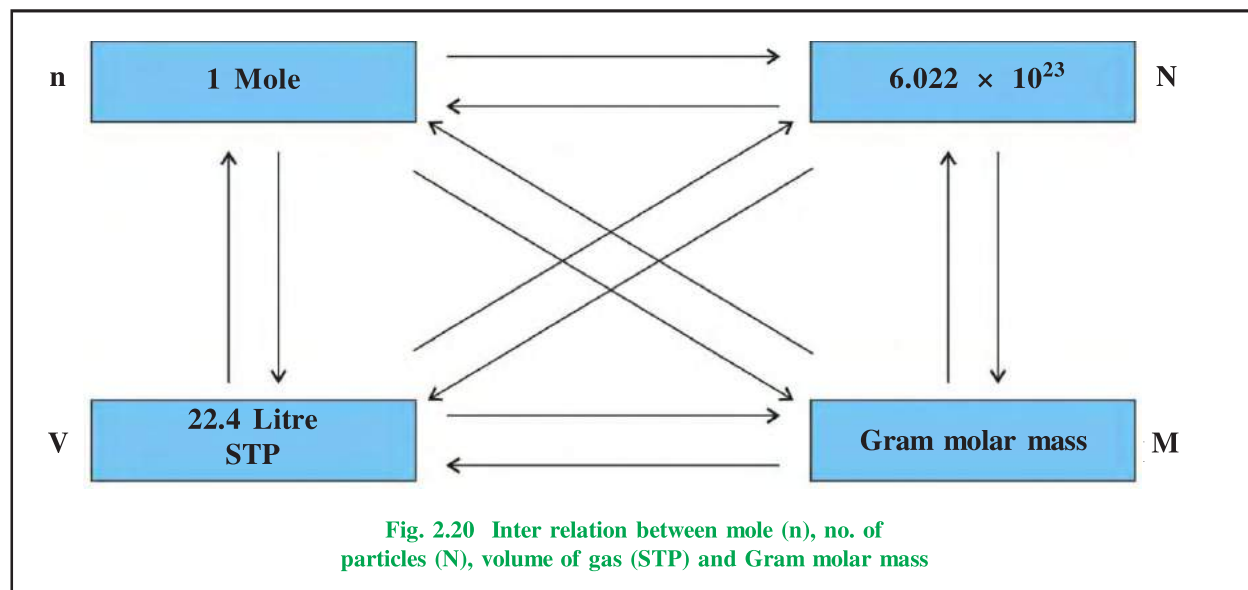
Example 23 : Find the number of molecules, atoms and total number of atoms in 20 gram $CaCO_3$.

Solution : The molecular mass of $CaCO_3$ is 100 g mol^{-1}

$$\therefore \text{Mole of } CaCO_3 = \frac{m}{M} = \frac{20}{100}$$
$$= 0.2 \text{ mole}$$

Now, the number of $CaCO_3$ molecules

= mole × Avogadro's number

= 0.2 × 6.022 × 10^{23}

= 1.2044 × 10^{23} molecules

One molecule of $CaCO_3$ is having one atom Ca, one atom C and three atoms of oxygen and total number of atoms is 5.

So the number of Ca atoms =

molecules 1.2044 × 10^{23} × 1

= 1.2044 × 10^{23}

The number of C atoms =

molecules 1.2044 × 10^{23} × 1

= 1.2044 × 10^{23}

The number of O atoms =

molecules 1.2044 × 10^{23} × 3

= 3.6132 × 10^{23}

Total number of atoms in $CaCO_3$

= no. of molecules × 5

= 1.2044 × 10^{23} × 5

= 6.022 × 10^{23}

Example 24 : Find the number of molecules, number of atoms and total number of atoms in 5.6 litre of CH_4 at STP.

Solution :

$$\text{Mole of } CH_4 = n = \frac{V}{22.4} = \frac{5.6}{22.4} = 0.25$$

The number of molecules in CH_4

= mole × Avogadro's number

= 0.25 × 6.022 × 10^{23}

= 1.5055 × 10^{23} molecules

Now, one molecule of CH_4 has one carbon atom and four hydrogen atoms and total number of atoms are five.

The number of C atoms = 1.5055 × 10^{23} × 1

= 1.5055 × 10^{23}

The number of H atoms = 1.5055 × 10^{23} × 4

= 1.5055 × 10^{23} × 4

= 6.022 × 10^{23}

Total number of atoms = 1.5055 × 10^{23} × 5

= 7.5275 × 10^{23}

Example 25 : Find the volume at STP and mass of 6.022×10^{22} molecules of O_2.

Solution :

$$\text{mole of } O_2 = \frac{\text{No. of molecules of } O_2}{\text{Avogadro's number}}$$

$$= \frac{6.022 \times 10^{22}}{6.022 \times 10^{23}} = 0.1 \text{ mole}$$

$$\text{Volume of } O_2 \text{ at STP} = \text{mole} \times 22.4 \text{ ltr.}$$

$$= 0.1 \times 22.4$$

$$= 2.24 \text{ litre}$$

$$\text{Mass of } O_2 = \text{mole} \times \text{molecular mass}$$

$$= 0.1 \times 32 = 3.2 \text{ grams.}$$

2.8   Liquid State and its Physical Properties

The liquid has a fixed volume but not a definite shape. It takes the shape of container in which it is poured. As compared to the gaseous state the molecules are arranged near each other in the liquid state. In the liquid state the intermolecular distance between two molecules is less compared to the gaseous state. So the force of attraction is more compared to the gaseous state, but less compared to the solid state and as a result the liquid has fixed volume but not a definite shape. In the liquid state the arrangment of molecules is more in order compared to the gaseous state, but less in order compared to the solid state. Thus, the liquid state is the linking middle state between the solid and the gaseous states. Each liquid state has measurable characteristics of physical properties as mentioned below :

(i) Fixed volume : Liquid has fixed volume. It never expands like gas when it is filled in a vessel. In liquid one surface is free while the remaining surfaces depend on the vessel. As the liquid has fixed volume, the volume will not change by changing the vessels. e.g. 500 ml water poured in beaker, conical flask, bowl bucket, its volume remains only 500 ml. There is no change in volume but it assumes the shape of vessels in which it is poured.

(ii) Fluidity : Liquid can flow and can be poured from one container to another. It assumes the shape of the container because liquid possesses the properties of fluidity.

(iii) Non-compressibility : Compared to gas, the compressive character is very less in liquid. For example at 298 K temperature, if double pressure is exerted on gaseous state the volume becomes half, while in liquid if the pressure is doubled, the volume decreases by 0.0045 % only. If 1000 bar pressure is applied on water at 293 K temperature, then its volume decreases by only 4 %. Thus, compared to gas the liquid has property of non-compressibility.

(iv) Diffusion : If a cylindrical vessel is half filled with water and ethyl alcohal is added carefully from the inner side of the cylinder, the ethyl alcohol keeps floating on the surface of water and a separate surface between the two can be clearly observed. If this system is kept for sometime, gradually the separate surface will become invisible and ultimately it will disappear. Hence, it can be said that ethyl alcohol diffuses in water. If this system is kept for longer time, then both the liquids form homogeneous mixture. The diffusion is shown in liquid compared to gas, because in liquid the molecules are arranged close to each other, so when they diffuse, they undergo collision with the neighbouring molecules which are obstructive in diffusion. Moreover, the intermolecular attractive forces are more in liquid compared to gas which also restricts the molecules in fast diffusion, so the diffusion becomes slow. Moreover, in liquid the rate of diffusion increases with increasing temperature because the kinetic energy of molecules increases due to increase in temperature, so the molecules move faster. The diffusion character is observed in molecules of liquid having same polarity like polar liquid cohesion contact with another polar liquid. Then diffusion takes place, but when comes in contact with non-polar liquid then diffusion will not take place and vice versa is also true.

(v) Evaporation : If the liquid is poured on an open surface it will evaporate as the time passes. The reason is that certain liquid gets converted on its own into gaseous state at normal temperature. This phenomenon is called evaporation. More or less evaporation is there at all temperatures. Like gaseous molecules, the speed of all liquid molecules are not the same as some molecules have maximum speed; some

have medium speed and some have minimum. Now, those molecules with maximum speed have also the maximum kinetic energy and such molecules undergo evaporation and they escape from the liquid surface (into vapour) and as a result the speed of remaining molecules become less so the kinetic energy also becomes less and hence, the temperature decreases. Due to evaporation of liquid the temperature decreases and hence it creates cooling. The evaporation depends upon temperature, strength of intermolecular attractive forces and exposed surface area of liquid.

(vi) Vapour presssure : As the gas in closed container shows pressure, similarly the liquid also shows pressure in a closed container. Due to evaporation the molecules escape from liquid surface but do not leave the container and they are collected in the vapour state above the surface of the liquid. The vapour state molecules move randomly in all directions and collide with one another, with wall of the container and also with the liquid surface. During this, some slow moving molecules when collide with surface of liquid may be recaptured by the intermolecular attraction get and converted into liquid known as condensation. Initially the rate of evaporation and condensation are not equal, but after sometime the rates become equal and this stage is known as dynamic equilbrium and now, the concentration of the molecules in vapour state becomes constant and the pressure exerted by the vapour molecules is in equllibrium with its liquid called vapour pressure. The vapour pressure depends on the nature of liquid. This means that it depends upon the intermolecular attraction forces of the liquid molecules. Weaker the intermolecular attractive forces, higher is the vapour pressure. Higher the temperature of liquid more is the vapour pressure.

(vii) Surface tension : The molecules of a liquid on one side of hypothetical unit length line on free surface of liquid exerts the force parallel to the surface and perpendicular to the molecules, on the other side of the line is called surface tension of liquid. Due to surface tension the drop is always spherical and the water (liquid) rises in a capillary tube upto certain level (height).

(viii) Viscosity : There is a viscosity between any two successive layers in a movement (conduction) as a result there exists a touching friction resistance force on the contact surface. Such internal resistance force is called viscosity force. **The property of having such a force existing in the liquid is called viscosity.** The viscosity depends on intermoleculer forces. As the intermolecular forces increase the viscosity also increases. Viscosity decreases with increase in the temperature.

SUMMARY

The group of molecules is called matter. Matter is made up of small particles. Matter is in three states, Solid, liquid and gas. The other two states are known as Plasma and Bose-Einstein condensate. The physical state of the matter changes by changing temperature. The physical properties of a subtance are changed by changing its physical state but the chemical properties do not change, sometimes the rate of chemical reaction changes by changing the physical state. During the chemical calculation, it is most essential to have the information about the physical state of substances (reactant or product) and hence it is essential to study the physical state of matter, factors affecting and related some important laws. The deciding factors of the physical state of matter are intermolecular forces, molecular interaction and the effect of thermal energy on the motion of particles.

The Dutch scientist van der Waals suggested that the weak forces of attraction exist between the molecules, which cannot be explained by any other chemical attraction forces is known as van der Waals attractive forces. This force is universal. This force of attraction is exerted upto $4.5 \, \overset{0}{A}$ distance in substance. van der Waals forces depend upon the shape of molecules, number of electrons present in molecules, contact surface of molecules and

average intermoleculer distance. The van der Waals forces of attraction are different like (i) Dispersion forces or London forces. (2) Dipole-dipole forces and (3) Dipole-induced dipole forces.

Dispersion forces of attraction was first of all proposed by the German scientist Fritz London so it is known as London forces. This type of force of attraction is observed in atoms or molecules, there is a temporary dispersion in electron density that affect the electron density of nearby atom or molecule so the force of attraction is developed and so such effect is called dispersion force. The dipole-dipole forces are observed in permantently dipolar molecules. Such dipolar molecules also have interactive London forces so the cummulative effect of both forces are observed. The dipole-dipole force is stronger than London forces. The dipole-induced dipole forces are observed when dipolar molecules come near to non-polar molecules. This type of molecules also have London forces and hence the cumulative effect of both forces are observed. The hydrogen bonding is an important intermolecular force. The first elements of groups 5, 6 and 7 due to their high electronegativity combine with hydrogen to form hydride compounds, in which hydrogen bond is observed. There also exists an intermolecular repulsive forces; and based on that the effect of pressure on solid, liquid and gaseous state are explained very easily. The most important factor which decides the physical, state of matter is the effect of thermal energy, on motion of molecules due to this motion of molecules or atoms the energy produced is called thermal energy to keep the molecules near to each other while the thermal energy has tendency to keep the molecules away from each other. By balancing combination of the two opposite factors, the physical state of matter as solid, liquid or gas is decided. Due to weak forces of attraction between molecules of gaseous state have some characteristics. The behaviour of gas is described by the quantitative relation between mass, volume, temperature and pressure and these relations are discovered by experimental observations and such relations are called laws of gases. The relation between pressure and volume of a gas was studied and it is known as Boyle's law. At constant temperature for a fixed amount gas, pressure (P) varies inversely with its volume (V). Mathematically the Boyle's law is written as $PV = K$ or $P_1V_1 = P_2V_2$. The equation $d/P = K$ derived from Boyle's law where d is the density. The Kelvin temparature is accepted as an SI unit. The relation $T = (t + 273.15)$ K is obtained. On the basis of experimental observations a relation between absolute temperature and volume is obtained,

which is known as Charles' law. Mathematically it is written as $\dfrac{V}{T} = K$ or $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$. The relation between pressure and absoulte temperature (T) is obtained on the basis of experimental orbservations by scientist Gay Lussac and is known as Gay Lussac's law. Mathematically it is written as $\dfrac{P}{T} = K$ or $\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$. The relation between volume of a gas and number of molecules was given by Avogadro, which is known as Avogadro's law. The mathematical form of it is $V = K \cdot n$. The 0^0C or 273 K temperature and 1 bar pressure is accepted as a standard value by SI system and hence these values are known as standard temperature and pressure (STP). 1 mole of gas at STP is having volume 22.4 litre and number of molecules equal to 6.022×10^{23} known as molar volume and Avogadro's number respectively. Combining Boyle's law and Charles' law, the relation obtained $\dfrac{PV}{T} = K$ or $\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2}$ is known as combined gas equation. The ideal gas equation, $PV = nRT$ is also known as equation of state and R is called universal gas constant which has different values in different units. The real gas behaves as ideal gas

at high temperature and low pressure and are called ideal gases. The behaviour of real gas is deviated from that of ideal gas and its study came from the study of effect of pressure and temperature and so the ideal gas equation is written as $\left(P + \dfrac{an^2}{V^2} \right)$ $(V - nb) = nRT$ and this equation is also known as van der Waal's equation. The gas can be liquefied by lowering the temperature and increasing pressure at which gas get liquified is known as critical temperature (T_C) and critical pressure (P_C) respectively and at critical temperature and critical pressure the volume occupied by 1 mole of gas is called critical volume (V_C) and this state is called critical state. The P_C, T_C and V_C values are constant so they are known as critical constants. The liquefication of gas is explained by isotherm. Maxwell and Boltzmann had studied the distriubution of molecules between different possible velocities and plotted graph which is known as Maxwell's distribution curve.

The total pressure of the mixture of two or more than two gases is obtained by the Dalton's partial pressure law. Total pressure $(P) = p_A + p_B + p_C + p_D$ .... and the partial pressure (p) is calculated from total pressure by equation $p_1 = X_1 \times P_{total}$. If the % by volume is given then the partial pressure of gas is caculated using equation.

Partial pressure $p_A = \dfrac{\% \text{ by volume of gas A} \times \text{total pressure}}{100}$. The Graham's law of gaseous diffusion is $r \propto \dfrac{1}{\sqrt{d}}$ and using formula the ratio of rate of diffuson of NH_3 and HCl gas was obtained practically as 1.46 ± 0.01. The application of Graham's law of gaseous diffusion are as given in the text. The Avogadro's hypothesis is useful to calculate the number of molecules, atoms and total number of atoms in given amount of gas.

The liquid state has its physical properties like fixed volume, fluidity, non-compressibility, diffusion, evaporation, vapour pressure, surface tension and viseosity.

EXERCISE

1. **Select the proper choice from the given multiple choices :**

    (1) Which type of forces are known as the London forces of attraction ?

    (A) Ionic   (B) Covalant   (C) van der Waals   (D) H-bonding

    (2) State the type of force of van der Waals attraction between HCl and O_2 molecules.

    (A) London   (B) Dipole-dipole

    (C) Dipole-induced dipole   (D) Polar-polar

    (3) The value of energy for 1 mole hydrogen bond is .....

    (A) 10 kcal   (B) 10 kJ   (C) 100 kcal   (D) 10-100 kJ

    (4) Which of the following substances has the lowest density under normal condition ?

    (A) Ice   (B) Water   (C) Copper   (D) Bronze

    (5) The relation between density and pressure is given by ....

    (A) Boyle's law   (B) Charles' law

    (C) Gay-Lussac's law   (D) Avogadro's law

(6)   The temperature of O_2 gas is changed from 25 ^{0}C to 50 ^{0}C, then the change in volume is...

(A) twice   (B) less than twice (C) half   (D) more than twice

(7)   What is the value of compression factor Z for helium gas ?

(A) 1   (B) >1   (C) <1   (D) Zero

(8)   At what temperature does the gas start liquefying ?

(A) T_C (B) > T_C (C) < T_C (D) T_C or < T_C

(9)   Which change is observed during evaporation of liquid in atmosphere ?

(A) heat increases   (B) cooling starts

(C) heat becomes zero   (D) all of above

(10) How many number of hydrogen atoms are in 1 gram H_2 ?

(A) 6.022×10^{23} (B) 3.011×10^{23} (C) 6.022×10^{-23} (D) 6.022×10^{24}

(11) Higher the critical temperature ...... is liquefaction.

(A) slow   (B) fast   (C) slow or fast (D) all the above

(12) Which relation is true for 4 gms of He gas ?

(A) the number of atoms are double than molecules

(B) the number of atoms are four times that of molecules

(C) the number of atoms are sixteen times that of molecules

(D) the number of atoms and molecules are same

(13) If the temperature is increased the viscosity is ......

(A) increased   (B) decreased   (C) not changed   (D) becomes zero

(14) Which two liquids on mixing starts diffusion ?

(A) water-kerosene   (B) water-benzene

(C) water-petrol   (D) water-alcohol

2.   Write answers to the following questions :

(1)   Write types of van der Waals' forces.

(2)   In which type of atoms or molecules London forces are observed ?

(3)   Which type of molecules possess hydrogen bonding ?

(4) Which combined forces decide the physical state of subtances ?

(5) Write Boyle's law.

(6) What is the absolute temperature ?

(7) Give value of standard temperature and pressure.

(8) Write Charles' law.

(9) Write Avogadro's law.

(10) State Gay-Lussac's law.

(11) Write combined gas equation.

(12) State the variables in ideal gas equation.

(13) What is a real gas ?

(14) In which condition the real gas behaves as an ideal gas ?

(15) What is an ideal gas ?

(16) State the equation of compression constant Z.

(17) Write van der Waals' equation.

(18) What is critical temperature ?

(19) What is critical mass ?

(20) Write Graham's law.

(21) Write Avogadro's hypothesis.

(22) Define viscosity, diffusion, vapour pressure.

(23) State different critical constants.

(24) State the factors affecting vapour pressure.

3. Write answers to the following questions :

(1) Give the different types of van der Waals' forces.

(2) Explain dipole-dipole forces.

(3) Explain London forces.

(4) Explain dipole-induced dipole forces.

(5) What is Kelvin scale ?

(6) Write Avogadro's law and explain.

(7)   Derive combined gas equation.

(8)   Derive unit of R from ideal gas equation.

(9)   Explain liquid state and write its properties.

(10)   Explain kinetic energy of molecules.

(11)   Explain positive and negative deviation for real gas.

4.   Write answers to the following questions :

(1)   Write a short note on hydrogen bonding.

(2)   Explain characteristics of gaseous state.

(3)   State gas laws and derive ideal gas equation.

(4)   Obtain values of R from different unit systems

(5)   Explain deviation from ideal gas.

(6)   Explain liquefaction of gas.

(7)   Explain isotherm curve for liquefaction of gas.

(8)   Explain Graham's law of gaseous difussion.

(9)   Explain Dalton's law of partial pressures.

(10)   Describe the experiment of diffusion of NH_3 and HCl.

5.   Solve the following examples :

(1)   Find the volume of 6.022×10^{21} molecules of CO_2 gas at 27^0 C temperature and 2 bar pressure.

(2)   Find the number of molecules, atoms and total number of molecules, of 4 litre SO_2 gas atoms at 350 K temperature and 10^3 Pa pressure.

(3) 2×10^6 molecules of N_2 gas enter into the vessel having volume 400 ml at 127^0 C temperature. Find the pressure of N_2 gas.

(4)   The % composition by volume of Cl_2, H_2 and N_2 are in 1:2:7 by proportion. If the total pressure is 40 bar, find the partial pressures of each gas.

(5)   At 25^0 C temperature 4 gram H_2 is filled in 500 ml vessel. Due to small hole in vessel, after sometime, the pressure in vessel became 50 bar. Find the number of molecules which have escaped from the vessel.

(6)   Two moles of O_2 gas is collected over water at 400 K temperature in 2 litre vessel. If the pressure of dry O_2 gas is 32.20 bar then find the vapour pressure of water under the same conditions.

(7)   A square has length 50 feet. At the ends of diagonal NH_3 and HCl are kept. Find the point where the white fumes will appear.

(8)   At 27^0 C temperature 20 gm. H_2, 220 gm CO_2 and 140 gm N_2 are filled in a vessel having volume 2 litre. Find the total pressure in bar unit and which gas is removed from the vessel so that pressure can be reduced by 50 %.

(9)   Time taken by CO_2 gas to diffuse 5000 km distance is 2 seconds. Find the time taken by Cl_2 gas to diffuse the same distance.

(10)   Air contains 79 % N_2, 20 % O_2 and 1 % CO_2 by volume. If the total pressure of air is 1 bar, find the partial pressures of N_2, O_2, CO_2.

●

Prof. Tribhuvandas Gajjar

Prof Tribhuvandas Gajjar was born on August 1863 in Surat city of Gujarat State. His father Kalyandas was a great architect. He had gone to Bombay to obtain the college education and he got admission in Elphiston College. After obtaining B.Sc. with first calss, he did M.Sc. After his study, he had joined as Lecturer in Chemistry at Kala Bhavan, Baroda, He had started the laboratory of printing and dyeing work. He then went to Bombay and settled there.

In 1898, somebody had coloured the statue of Queen Victoria on Esplanade Road, Fort Area of Bombay, by throwing black colour on its face. The colour was so fast that it could not be removed even after many efforts. To remove this colour, many chemists were called by the Government. Many attempts have been tried on the statue but the colour could not be removed. Finally, the European scientists were also called but they also could not be successful. This matter was discussed in the country and outside the country. At that time, Professor Tribhuvandas Gajjar, Lecturer in Chemistry, Wilson College wrote a letter to the Municipal Corporation of Bombay for handling this work to him. But the government did not like it proper to give this work to Tribhuvandas because of the experience from the earlier scientists. Hence, Tribhuvandas again sent an application. Afterwards, he was given permission to remove the colour from some part of the statue. Tribhuvandas started his work according to his understanding. In short time all the colour from the face of the statue of Queen Victoria was completely removed. As a result, the people of the country started to look at him with honour.

Tribhuvandas found out by rasearch the medicine 'iodine terchoride' for iradication of Plague that had spread in Bombay. It was proved to be very effective. The society appraised his work. Some of his friends advised him to get patent for this medicine and earn fame and money but patriot Tribhuvandas did not agree to this. He placed this medicine for plague before the whole world. He expired on July, 16, 1920.

Thermodynamics

"It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown."

- Albert Einstein

3.1 Introduction

If we observe all the chemical reactions from microscopic point of view, same reactions occur. (i) The reaction of breaking of some of the bonds present in molecules of reactants experiencing chemical reaction. (ii) Reaction of formation of bonds of some new products. Energy is to be supplied to the reactant for breaking of any chemical bond, i.e. breaking of chemical bond is endothermic reaction. e.g.

$$H_{2(g)} + Energy \rightarrow 2\overset{\bullet}{H}$$

$$Cl_{2(g)} + Energy \rightarrow 2\overset{\bullet}{Cl}$$

Opposite to this, the energy is evolved when bond formation takes place, i.e. the bond formation reaction is exothermic reation.

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)} + Energy$$
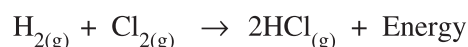
As the values of energy required to break the chemical bonds and the energy evolved in the chemical bond formation during the above reactions are not the same, either the energy is absorbed or the energy is evolved.

When fuel like methane is combusted, then, at the end of certain chemical reactions the energy stored by its molecule is liberated as chemical energy. Like combustion of cooking gas and coal energy liberated in the air, when fuel is combusted in engine, the use of chemical energy is made in mechanical work; in a galvanic cell like dry cell energy is obtained in the same way. In the similar way, energy can be obtained with the help of intereactions under certain conditions, from the different forms of energy. They can be transformed from one form to the other. The study of all these forms of energy is called thermodynamics. The laws of thermodynamics are concerned with the transformations of energy. They are associated with molecules in large proportion associated with macroscopic systems and a few molecules present in microscopic systems are not related to how the reaction occurs and with what rate. Thus, thermodynamics is independent of study of chemical kinetics. It depends on the energy transformation between initial state and final state. Laws of thermodynamics apply only when a system is in equilibrium or move from one equilibrium state to another equilibrium state. The macro factors like temperature, pressure etc. are unable to change the system in equilibrium with time. We shall try to obtain answers for some of the important questions with the help of thermodynamics.

It is important in chemistry to get answers to the following questions :

(i) Will the reaction occur between certain substances in definite conditions ?

(ii) If the reaction between these substances is possible, to what extent (proportion) will it occur ?

If the answers to these two questions can be obtained theoretically, the work of the chemist will be easier. We know that both graphite and diamond are the allotropes of carbon. Can graphite be transformed into diamond ? The answer to this question, when examined from theoretical point of view is found to be positive. So the scientists got inspiration to transform graphite into diamond and now-a-days artificial diamonds are prepared and produced in a similar way. The science which can answer the chemical problems is called chemical thermodynamics.

In chemical thermodynamics, the changes in energy associated with physical and chemical reactions have been studied. This whole study is based on four basic laws. These four laws are known as the zeroth, the first, the second and the third law of thermodynamics. These laws are the conclusions obtained from the available experimental results. Not a single chemical reaction till present time is found to be the exception to these laws. Here, before we study the laws of thermodynamics, it is necessary to understand its background.

3.2 Basic Concepts of Thermodynamics

We are interested in the chemical reactions and energy exchange. For this, we shall discuss the basic concepts of thermodynamics.

3.2.1 System and Surrounding :
An exteremely small part of the universe which is separated from the remaining part of universe by a definite boundary and on which we note the observations of the experiments carried out by external changes is called system. The remaining part of the universe excluding the system is called surrounding. Surrounding means the part of the universe except the system. The system and the surrounding together makes the formation of universe viz. whether there is any reaction of hydrochloric acid (HCl) with washing soda (Na_2CO_3) ? We add few drops of hydrochloric acid on washing soda by taking it into a testtube and observe whether the reaction occurs or not. Here, the mixture of washing soda and hydrochloric acid is a system. Testtube is not included in the system. Testtube is the borderline of the system while the remaining universe which is in contact with system is surrounding of the system.

Types of the system : There are three types of systems depending on the exchange of energy and matter between system and surrounding. (i) Open system (ii) Closed system (iii) Isolated system.
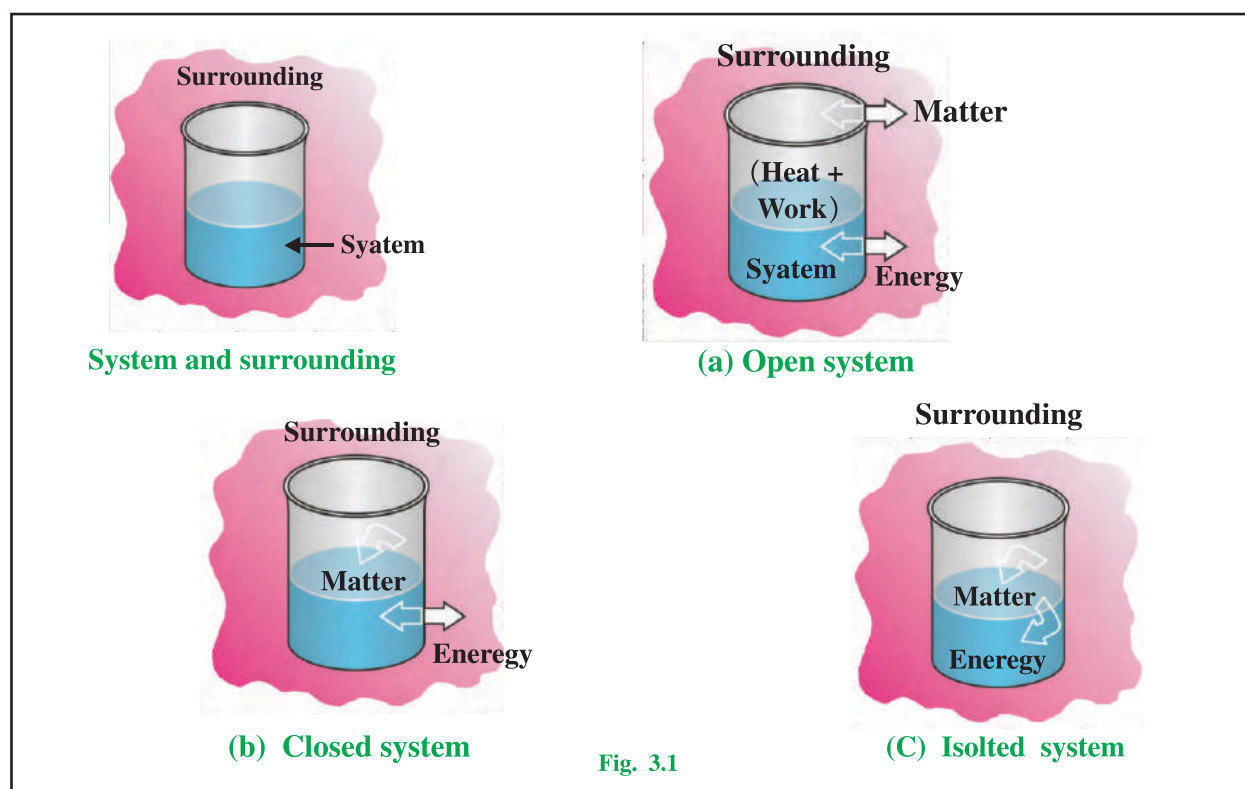
(i) Open system : The system in which the energy and the matter can go on its own from system to the surrounding or enter from surrounding to the system is called open system viz. If we place an ice cube in a saucer, it melts on its own absorbing heat from atmosphere and the water from saucer enters the atmosphere through evaporation. Hence, the ice cube placed in the open vessel saucer and the water in the saucer is an open system. Similarly a flame of the burner is also an open system.

(ii) Closed system : The system which can exchange energy on its own with surrounding but the exchange of matter on its own is not possible, is called a closed system.

of good quality provides its example at a particular moment, but after sometime, it   provides the example of the colsed system. Hence, it is difficult to find an example of an absolute isolated system.

3.2.2 Process : The conversion of state of system from one to another is called a process. During this conversion, if the temperature of the system does not change that is temperature remains constant, then, the process is called Isothermal process that is the system gain energy from the surrounding or releare the energy to the surrounding.

During the change in the system, **if the system does not lose heat or does not**

System and surrounding

(a) Open system

(b) Closed system   Fig. 3.1   (C) Isolted system

viz. The cold or hot water poured in the bottle and closed with a cork. The vessel in which this system is present must be energy conductor. The cooker used in household purposes is the closed system.

(iii) Isolated system : The system which is not able to exchange energy and matter on its own with surrounding is called an isolated system. In fact, formation of isolated system is not possible but the thermos flask of very good quality is the example of isolated system. The hot tea poured in a thermos flask

receive heat, then the process is called Adiabatic process.

If the system contains gaseous materials and the pressure of the system remains constant during the change, then that process is called Isobaric process.

3.2.3 Extensive and Intensive properties : Some properties of the substance depend on the quantity of the matter. These properties are known as **Extensive properties.** The mass of a substance, volume, enthalpy of formation, entropy, free energy, elevation in boiling point, depression in freezing point etc. are such

type of properties. Generally, these properties are expressed in the unit of per mole or mole^{-1}.

The properties of the substances which do not depend upon the mass of the substance but depend upon the structure of the compounds are known as **intensive properties.** The melting point of solid substance, density, boiling point of liquid, conductivity, refraction etc. are such type of properties. Thus, the boiling point of liquid is an intensive property while elevation in boiling point is an extensive property. Similarly, the freezing point of a substance is an intensive property but depression in freezing point is an extensive property.

3.2.4 State Function : The values of the properties of the system which depend on the state of the system but do not depend on the method how the state can be obtained is called the state function. viz. There can be different methods to take a substance having mass (m) to a height (h) but the value of its potential energy *mgh* at that height is constant. Thus, potential energy of a substance is its state function.

In the same way, 1 mole of any ideal gas possesses 22.4 litre volume at 273 K temperature and 1 atmosphere (bar) pressure but the volume does not depend on; in which state the substance was before bringing to 1 atmosphere and 273 K. Thus, the definite volume of a definite quantity of a gas at constant temperature and pressure is the state function of the gas. The other state functions of this type are (i) Internal energy (U) of a substance (ii) Enthalpy (H) a substance (iii) Entropy (S) of a substance (iv) Free energy (G) of a substance etc.

3.2.5 Thermodynamically Reversible Process : If the state of a system changing with infinitesimal rate, then the difference in state function values of system are very small. This type of process is known as thermodynamically reversible process. In this type of process, the equilibrilum is established between system and surrounding at each microscopic level.

3.2.6 Internal Energy (U) : In every substance definite energy is stored in it on the basis of its mass and characteristic structure, which is called internal energy (U). This energy is stored in the form of kinetic

energy and potential energy. The component particles of a substance have their linear rotation and vibration energy. In addition, their electron and nucleus also possess different types of motion. Hence, substance possesses kinetic energy. Also the attractive and repulsive forces between component particles of the substance are operative. In the same way, substance possesses potential energy due to repulsion between electron-electron and repulsive forces between nucleus-nucleus as well as attractive forces between electron and nucleus. In addition, the proton and neutron in the nucleus experience attractive forces. Also, according to the equation $E = mc^2$ (where m = decrease in the quantity of matter and c = velocity of light) the matter itself is one form of its energy. Hence, if the energy of the matter is changed into heat, large amount of heat will be obtained. Thus, the total energy available from a substance is called internal energy (U) of the substance.

The value of iternal energy of any matter depends on temperature. If the physical state of substance changes, the internal energy present in it also changes. As the absolute value of internal energy cannot be measured the change in internal energy can be measured accurately by experiment.

During any chemical reaction the quantity of matter remains constant, though there is change in their characteristcs due to change in the states of the substance. As a result, the internal energy of products (U_p) is different from internal energy of reactants (U_r). The energy difference is equal to internal energy of products and internal energy of reactant. This energy is liberated or absorbed in form of heat. This is expressed as change in internal energy (ΔU).

During any reaction, if there is change in the volume of the matter, there will be change in its work. Hence, heat produced by the change in internal energy in chemical reaction is to be kept constant and the reaction is to be carried out. When any chemical reaction is carried out at constant volume, the change in heat (q_v) is equal to the difference between internal energy of the reactant and the internal energy of the product.

$$q_v = U_p - U_r = \Delta U$$

Thus, internal energy difference at constant volume is the change of heat energy.

3.2.7 Enthalpy (H) : The total amount of energy obtained from internal energy (U) of substance and energy obtained by product of pressure (P) and volume (V) is called enthalpy (H).

$$H = U + PV$$

If any reaction is carried out in an open vessel, then the reaction system is in direct contact with the atmosphere and so the pressure of constant atmosphere applies. Thus, any chemical reaction, when carried out at constant pressure, then the change in its energy is called enthalpy change (ΔH)

$$q_p = H_p - H_r = \Delta H$$

when H_p is enthalpy of products and H_r is enthalpy of reactants.

Thus, enthalpy is the change in heat at constant pressure.

3.3   Zeroth Law of Thermodynamics

When two diathermic (thermal conductor) substances at different temperatures come in contact with each other, then heat conducts on its own from the substance having higher temperature to substance having lower temperature. This conduction of heat continues till the temperatures of both the substances do not remain the same. When the temperatures of the two substances become the same, the conduction of heat does not take place in them. This condition (state) is called **thermal equilibrium.** Thus the procedure to obtain thermal equilibrium of any two diathermic substances is called **zeroth law of themodynamics.**

When any person suffers from fever, the temperature of his body is measured by a thermometer. The thermometer comes in contact with the body of that person, the heat from human body enters into the mercury of the thermometer and the volume of the mercury increases. When the temperature of the body and the temperature of mercury become equal, the increase in the volume of mercury stops. Hence, it can be said that the temperature of the body and that of the mercury in the thermometer is the same. This condition (state) is known as thermal equilibrium. From the reading on the thermometer, fever can be measured.

3.4   First Law of Thermodynamics

The first law of thermodynamics, in fact, is the law of conservation of energy. This law can be expressed in different forms. **(i) The total quantity of energy in the universe is constant. (ii) Energy can neither be created nor can be destroyed but transformation of one form into another form can be possible.**

The change in internal energy of the system can be brought by two methods. (i) By adding heat to the system or removing the heat from the system. (ii) By working on the system or working by the system.

Here, heat and work are on one side while energy on the other. It is necessary to understand the important difference between these two.

The heat and work indicate the process, which is not a state function, while energy is the property associated with any equilibrium and it is state function.

3.4.1 Symbolic equation of the First law of thermodynamics : Suppose, the internal energy of any system, at a definite equilibrium state is U_1. If this system after undergoing a reaction attains a new equilibrum state having internal energy U_2, then, the heat absorbed by the system or heat lost by the system during this reaction is q. Now, if the work done (W) is on the system or the work done by the system is W, then according to First law of themodynamics :

$$U_2 = U_1 + q + W \qquad OR$$
$$U_2 - U_1 = q + W$$

Now, writing change in energy

$$U_2 - U_1 = \Delta U$$
$$\Delta U = q + W$$

This equation is the symbolic form of the First law of thermodynamics.

3.4.2 Mathematical form of the First law of thermodynamics : In the symbolic equation of the First law of thermodynamics, when it is used for the calculation, then, generally, (+) positive and (−) negative signs are connected with q and W.

(i) If heat is lost during process in the system, the value of q is negative (−) or the value of exothermic reaction is always negative (−).

(ii) If heat is added during the process in the system, the value of q is positive (+) or the value of q for endothermic reaction is always positive (+).

(iii) If the work is done on the system, then the value of W is always posititve (+).

(iv) If the work is done by the system, then the value of W is always taken negative (−).

If the internal energy of the system during any process remains constant then $\Delta U = 0$. i.e., $q + W = 0$ or $q = -W$. This indicates that the total heat absorbed by system during the process is completely used up in the work.

Internal energy is the state function. If the system follows any path during change from one state to another, even then the value of ΔU does not change, but q and W are not being state functions, their values do not depend upon how one form of the system changes into the other.

Example 1 : A system receives 224 joule heat and does work of 156 joule. Calculate the change in the internal energy.

Solution : System receives the heat

$\therefore$ q = 224 joule

Work done by the system

$\therefore$ W = −156

According to First law of thermodynamics

$\Delta U = q + W$

$\Delta U = 224 - 156 = 68$ joule

3.4.3 Work and the First law of thermodynamics : It is necessary to have information about work before we understand the applications of the First law thermodynamics. When can we say that work is done ? When on any substance, force is applied at a point where it is applicable and the point moves in the direction of the force applied, then it is said that work is done.

In chemistry mainly two types of works are observed :

(i) Electrical work and (ii) Mechanical work.

Electrical work is important in the reaction between ions in the system. The mechanical work is important in which, during the reactions there is change in volume in presence of external pressure. The systems which possess gaseous state, for them, mainly, mechanical work is more important. If gaseous substances are associated with the chemical reaction, then there is change in volumes in most of the reactions under constant external pressure. If the volume of this type of system increases during reaction, then work is done by the system and if the volume decreases, then work is done on the system.

If the initial volume of the system is V_1 and the final volume is V_2 and the external pressure P applied on the system is constant, then, the work done by the system due to change in volume can be shown by the following equation :

$W = P(V_2 - V_1)$

$\quad = P\Delta V$

Hence, if the work done during the reaction is only of PV type $q = q_p$ and if the work is done by the system, then $W = -P\Delta V$.

According to symbolic equation of First law of thermodynamics,

$\Delta U = q + W$

$\Delta U = q - P\Delta V$

But, if there is no change in the volume of the system during chemical reaction, $\Delta V = 0$. Hence, $\Delta U = q_v$. Thus, in the reactions occurring at constant volume, the value of change in internal energy of the system is equal to the heat received by the system or heat lost by the system at constant volume.

Example 2 : At one bar pressure, the volume of a gas is 0.6 litre. If the gas receives 122 Joules of heat at one atmosphere pressure, the volume becomes 2 litres, then calculate its internal energy. (1 litre bar = 101.32 Joule)

Solution : Pressure P = 1 bar

Initial volume of gas V_1 = 0.6 litre

Final volume of gas V_2 = 2 litre

$\Delta V = V_2 - V_1$

$\quad = 2.0 - 0.6 = 1.4$ litre

Now, $W = P \Delta V$

$W = 1 \times 1.4 = 1.4$ litre bar

But 1 litre bar = 101.32 joule

$\therefore$ W = 1.4 × 101.32 = 141.85 joule

Here, the work is done by the system

$\therefore$ W = − 141.85 joule

The heat obtained by the system

q = 122 joule

According to First law of thermodynamics

$\Delta U = q + W$

$= 122 - 141.85 = -19.85$ joule

3.4.4 Enthalpy and First Law of Thermodynamics :

Generally, the chemical reactions occur in open vessels at constant pressure. A new state function has to be defined for change in energy occurring in this type of process. This new state function is called enthalpy (H). The relation between enthalpy (H) and internal energy (U) is shown by the following equation :

$$H = U + PV$$

Hence, if there is a change in state of a system, the change in its enthalpy can be shown by the following equation.

$$\Delta H = \Delta U + \Delta(PV)$$
$$= \Delta U + P\Delta V + V\Delta P$$

If the reaction occurs at constant pressure, then $\Delta P = 0$. Hence

$$\Delta H = \Delta U + P\Delta V$$

But, according to symbolic equation of the First law of thermodynamics, if the reaction occurs at constant pressure, then work done by the system is only of PV type and so $q = q_p$ and $W = -P\Delta V$.

$$\therefore \Delta U = q_p - P\Delta V$$

Hence, the equation,

$\Delta H = \Delta U + P\Delta V$ will be as follows.

$$\Delta H = (q_p - P\Delta V) + P\Delta V$$

$$\therefore \Delta H = q_p$$

Thus, the change in enthalpy of the system in which chemical reactions occur, at constant pressure is equal to the value of the heat gained or lost by the system.

Hence, it is apparent that at constant temperature and constant pressure, the enthalpy of the substance is constant.

Reaction	Change in internal energy	Change in enthalpy
Exothermic	$\Delta U = -Ve$	$\Delta H = -Ve$
Endothermic	$\Delta U = +Ve$	$\Delta H = +Ve$

3.4.5 Mole and First Law of Thermodynamics :

If the number of gaseous molecules of the reactants is changing because of chemical reaction and the reaction is occurring at constant pressure, then the volume of the system changes.

Suppose, the volume of the system has n_1 moles of gaseous reactants at constant pressure P and constant temperature T. Now, if under constant pressure and constant temperature the volume of n_2 moles of gaseous products, becomes V_2, then according to ideal gas equation,

$$PV = nRT$$
$$PV_1 = n_1RT \text{ and } PV_2 = n_2RT$$
$$PV_2 - PV_1 = n_2RT - n_1RT$$
$$P(V_2 - V_1) = (n_2 - n_1)RT$$
$$P\Delta V = \Delta n_g RT$$

Here, Δn_g shows the difference between total number of moles of gaseous products and the total number of moles of gaseous reactants. Now, according to the equation showing relation between change in internal energy and change in enthalpy,

$$\Delta H = \Delta U + P\Delta V$$
$$\Delta H = \Delta U + \Delta n_g RT \qquad OR$$
$$\Delta U = \Delta H - \Delta n_g RT$$

If the total number of moles of gaseous reactants and gaseous products is same, then the difference will be zero;

$\Delta n_g = 0$ and so $\Delta H = \Delta U$

If the total number of moles of gaseous reactants is more than the total number of moles of gaseous products;

$\Delta n_g < 0$, and hence, $\Delta H < \Delta U$

If the total number of moles of gaseous products is less than the total number of moles of gaseous reagents $\Delta n_g > 0$, and hence, $\Delta H > \Delta U$

If, $\Delta n_g \neq 0$, then $\Delta H \neq \Delta U$

Example 3 : The specific volumes of ice and water are 1.089 and 1.0 ml gm^{-1} at 273 K temperature. The molar heat of fusion (melting) of ice is 6.025 kJ mole^{-1} at 273 K temperature and 1 bar pressure. If 90 gram ice melts at 273 K temperature and 1 bar pressure, water is produced at that temperature, then, calculate the values of ΔH and ΔU for the process. (1 litre bar = 101.32 joule)

Solution :

$$\therefore \text{ Moles of ice} = \frac{\text{Weight of ice}}{\text{Molecular mass of ice}}$$

$$= \frac{90 \text{ gram}}{18 \text{ gram mole}^{-1}}$$

$$= 5 \text{ moles}$$

When 1 mole of ice melts at standard pressure 6.025 kilojoule heat is absorbed.

$\therefore$ When 5 moles of ice melts

$$= 5 \text{ mole} \times 6.025 \text{ kilojoule mole}^{-1}$$

$$= 30.125 \text{ kilojoule}$$

$$= 30125 \text{ joule heat will be absorbed.}$$

At, constant pressure,

$$\therefore \Delta H = q_p = 30125 \text{ joule}$$

Now, $\Delta H = \Delta U + P\Delta V$

$$= \Delta U + P(V_2 - V_1)$$

$$\therefore \Delta U = \Delta H - P(V_2 - V_1) = q_v$$

Here, V_1 = Volume of ice;

V_2 = Volume of water

Volume of 1 gram ice = 1.089 mililitre

$\therefore$ Volume of 90 gram ice (V_1)

$$= 90 \times 1.089 = 98 \text{ mililitre}$$

Volume of 1 gram water = 1 mililitre

$\therefore$ Volume of 90 gram water (V_2)

$$= 90 \times 1 = 90 \text{ mililitre}$$

Here the change in volume of the system

$$\Delta V = V_2 - V_1$$

$$= 90 - 98 = -8 \text{ mililitre}$$

$$= -0.008 \text{ litre}$$

$$P(V_2 - V_1) = 1 \times -0.008$$

$$= -0.008 \text{ litre bar}$$

Now, 1 litre bar = 101.32 joule

$$\therefore -0.008 \text{ litre bar}$$

$$= 101.32 \text{ joule} \times (-0.008) = (-0.81) \text{ joule}$$

According to the above equation

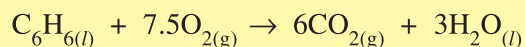$$\Delta U = q_v = \Delta H - P(V_2 - V_1)$$

$$= 30125 - (-0.81)$$

$$= 30125 + 0.81 \text{ joule } (0.81 \text{ joule is negligible in comparison to } 30125)$$

$$\therefore \Delta U = 30125 \text{ joule}$$

Example 4 : The heat associated with combustion of liquid benzene, at constant volume is -3268 kilojoule mole^{-1}. Calculate the change in enthalpy, when this reaction occurs at 300 K temperature (R = 8.314 joule mole^{-1} kelvin^{-1})

Equation :

$$C_6H_{6(l)} + 7.5O_{2(g)} \rightarrow 6CO_{2(g)} + 3H_2O_{(l)}$$

Solution : Here, the change in heat at constant volume,

$$q_v = \Delta U = -3268 \text{ kilojoule mole}^{-1}$$

Δn_g = (Total number of moles of gaseous products) $-$ (Total number of moles of gaseous reactants)

$$= 6 - 7.5 = -1.5 \text{ mole}$$

T = 300 K, R = 8.314 joule

$$= 8.314 \times 10^{-3} \text{ kilo joule mole}^{-1} \text{ kelvin}^{-1}$$

Now, according to the equation

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\therefore \Delta H = -3268 + (-1.5 \times 8.314 \times 10^{-3} \times 300)$$

$$= -3268 - 3.74 = -3271.74 \text{ kJmole}^{-1}$$

Example 5 : 1 mole of an ideal gas is filled in a cylinder at 300 K temperature and 10 bar pressure. This gas leaks in atmosphere due to leakage in the valve of the cylinder, then (What work should be done in the diffusion of gas under this condition ?) calculate the values of ΔH and ΔU for this process. (1 litre bar = 101.32 joule) (Take R = 0.082)

Solution : If expansion or contraction of any ideal gas at constant temperature takes place, then the internal energy and the enthalpy of the gas do not change.

Gas is ideal and so $\Delta U = 0$ and $\Delta H = 0$. Now, the work is done by the gas $W = P\,\Delta V$ where $P = 1$ bar and ΔV = change in volume of gas. Here, the volume of 1 mole of gas before expansion and after expansion will have to be found out.

Now, $PV_1 = nRT$

$\therefore\ 10 \times V_1 = 1 \times 0.082 \times 300$

$\therefore$ Volume before expansion $V_1 = 2.46$ litre

For, volume after expansion $V_2 = ?$

$PV_2 = nRT$

$\therefore\ 1.0 \times V_2 = 1 \times 0.082 \times 300$

$\therefore$ Volume after expansion $V_2 = 24.60$ litre

$\Delta V = (V_2 - V_1)$

$\qquad = 24.60 - 2.46\ = 22.14$ litre

Work done by the gas $W = P\Delta V$

$\qquad = 1 \times 22.14 = 22.14$ litre bar

Now 1 litre bar $= 101.32$ joule

$\therefore\ 101.32 \times 22.14 = 2243.23$ joule

Here, the work is done by the gas $W = -2243.23$ joule.

Example 6 : Calculate the change in internal energy of the following reaction at 300 K temperature (R = 8.314 Joule)

Equation :

$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}$ $\Delta H = -110.53$ kilojoule
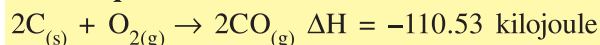
Solution :

$\Delta n_g = n_p - n_r = 2 - 1 = 1$

$\qquad\qquad T = 300\ K,$

$\qquad\qquad R = 8.314$ joule

$\qquad\qquad = 8.314 \times 10^{-3}$ kilojoule

Now, $\Delta H = \Delta U + \Delta n_g RT$

$\Delta U = \Delta H - \Delta n_g RT$

$\therefore\ \Delta U = -110.53 - (1 \times 8.314 \times 10^{-3} \times 300)$

$\qquad = -110.53 - 2.494$

$\Delta U = -113.024$ kilojoule

3.4.6 Applications of First Law of Thermodynamics :

The basis of thermochemistry is on the First law of thermodynamics. Hence, by using the First law, bond enthalpy, enthalpy of formation of compound, enthalpy of combustion, change in internal energies (ΔU) in reaction, change in enthalpy (ΔH) etc. can be obtained. The first law is associated with thermochemistry of chemical reaction. Hence, the study of thermochemistry is carried out on the basis of the First law. The values of standard enthalpy of formation and standard enthalpy of combustion of some compounds are given in Table 3.1 and Table 3.2

Table 3.1 Standard Enthalpy of formation of some compounds at 298 K temperature

Compound	$\Delta_f H^0$ kilojoule mole^{-1}	Compound	$\Delta_f H^0$ kilojoule mole^{-1}
$H_2O_{(g)}$	-241.82	$CH_{4(g)}$	-74.81
$H_2O_{(l)}$	-285.83	$C_2H_{6(g)}$	-84.68
$HCl_{(g)}$	-92.31	$C_2H_{4(g)}$	52.26
$SO_{2(g)}$	-296.83	$CH_3OH_{(l)}$	-238.86
$SO_{3(g)}$	-395.72	$C_2H_5OH_{(l)}$	-277.69
$NO_{(g)}$	$+90.25$	$CH_3COOH_{(l)}$	-484.5
$NO_{2(g)}$	$+33.18$	$C_6H_{6(l)}$	49.0
$CO_{(g)}$	-110.53	$Fe_2O_{3(s)}$	-1118.4
$CO_{2(g)}$	-393.51	$Al_2O_{3(s)}$	-1675.7

Table 3.2 Standard Enthalpy of combustion of some compounds at 298 K temperature

| Compound	$\Delta_c H^0$ kilojoule mole^{-1}	Compound	$\Delta_c H^0$ kilojoule mole^{-1}
$CH_{4(g)}$	-890	$C_4H_{10(g)}$	-2878
$C_2H_{6(g)}$	-1560	$CH_3OH_{(l)}$	-726
$C_2H_{4(g)}$	-1411	$C_2H_5OH_{(l)}$	-1368
$C_2H_{2(g)}$	-1300	$CH_3COOH_{(l)}$	-875
$C_2H_{6(g)}$	-1560	$C_6H_{6(l)}$	-3268
$C_3H_{8(g)}$	-2220		

3.4.7 Limitations of First Law of Thermodynamics :

On the basis of the First law of thermodynamics, it is not possible to know whether any chemical reaction will occur on its own (Spontaneous). In addition, the reactants will be transformed to what proportion of products

also cannot be obtained from the First law of thermodynamics. This point can become clear from the following examples of physical change.

(i) If an ice-cube is kept in a saucer, at room temperature, it melts by absorbing heat from atmosphere and the heat absorbed by the ice becomes equal to the heat lost by the atmosphere. This process occurs on its own and obeys the first law. In the reaction opposite to this, if the water in the saucer loses heat and changes into ice, then again the First law of thermodynamics will be obeyed, but this does not occur on its own.

sodium hydroxide (NaOH), neutralisation reaction will occur on its own and sodium chloride and water will be produced. 56 kilojoule mole^{-1} energy is released in this exothermic reaction. This reaction occurs on its own, but by dissolving sodium chloride in water and supplying 56 k Joule mole^{-1} heat to it, sodium hydroxide (NaOH) and hydrochloric acid (HCl) cannot be obtained by reverse reaction on its own. Thus, in this chemical reaction, the First law is obeyed but reverse reaction does not occur on its own.

Thus, the prediction for any reaction to occur on its own cannot be done on the basis of the

Closed valve   **Open valve**

(a)   (b)

Fig. 3.2
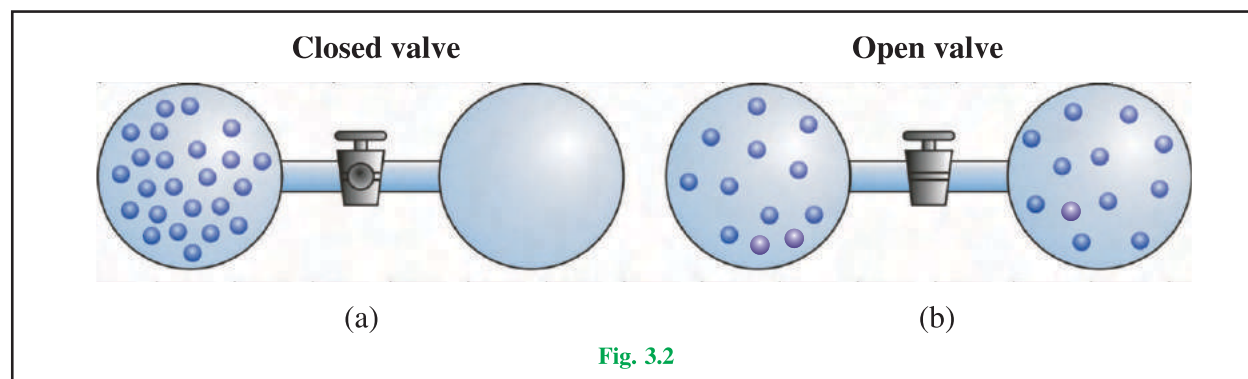
Similarly, the hot tea kept in saucer gets cold on its own, but if the cold tea becomes hot on its own, then the First law is obeyed. But, here also, this reaction is not possible on its own.

(ii) As shown in the Figure 3.2, if one bulb filled with gas is connected with an evacuated bulb and on opening the valve in the tube connecting the two bulbs, the gas from one bulb will diffuse into the second bulb till the pressure of both the bulbs is not same. This reaction occurs on its own. This system also follows the First law of thermodynamics. Now, if the gas in one of the bulbs diffuses into the second bulb and attains its original state, then prodction of vacuum in the other bulb can be imagined. In this also, the First law is obeyed but this does not occur on its own.

(iii) If a drop of ink is dropped in a beaker containing water, the drop of the ink diffuses on its own throughout the water in the beaker and the solution becomes coloured. Is it possible to have reaction opposite to this ? Is the first law obeyed ?

Now, for the experience of chemical change we take the following example :

On mixing equal volumes and equal concentrations of hydrochloric acid (HCl) and

First law of thermodynamics. To get this information, the Second law of thermodynamics is useful.

3.5 Heat Capacity

Enthalpy is the state function only for measuring the changes in heat of the system at constant pressure. This state is not useful for determining changes in energy at constant volume. Hence, a new function becomes necessary to explain the relation between temperature and changes in heat at constant pressure or at constant volume. This new function is called heat capacity. It is not a state function.

The quantity of heat required for increase in temperature by 1 ^{0}C of any substance is called heat capacity (C) of that substance.

If the temperature of the substance is increased by 1 ^{0}C at constant volume, the heat capacity is expressed as C_v, and if the temperature of the substance is increased by 1 ^{0}C at constant pressure, the heat capacity can be expressed as C_p. There is not much difference in heat capacities C_p and C_v of liquid and solid substances, but in gaseous substances, this difference is observed to a greater extent.

When the initial temperature T_1 of a sample of gaseous substance is changed to temperature T_2, then the relation between heat (q), heat capacity (C) and difference in temperature $(T_2 - T_1)$ is shown by the following equation.

$$q = C \times (T_2 - T_1)$$

$$(T_2 - T_1) = \Delta T$$

$$C = \frac{q}{\Delta T}$$

$$\therefore \text{ Heat Capacity} = \frac{\text{Absorbed heat}}{\text{Difference in temperature}}$$

The unit of heat capacity is joule kelvin^{-1}.

The heat capacity is proportional to the quantity of the substance and so it is an extensive property. Hence, sometimes specific heat capacity and molar heat capacity are used in chemistry.

Specific Heat Capacity : The quantity of heat required for increase of temperature of 1 gram substance by 1^0C is called specific heat capacity.

$\therefore$ Specific heat capacity =

$$\frac{\text{Absorbed heat}}{\left(\begin{array}{c}\text{Difference in}\\\text{temperature}\end{array}\right) \times \left(\begin{array}{c}\text{Weight of}\\\text{substance in gram}\end{array}\right)}$$

The unit of specific heat capacity is joule kelvin^{-1} gram^{-1}.

Molar Heat Capacity : The quantity of heat required for increase of temperature of 1 mole substance by 1^0C is called molar heat capacity.

$\therefore$ Molar heat capacity =

$$\frac{\text{Absorbed heat}}{\left(\begin{array}{c}\text{Difference in}\\\text{temperature}\end{array}\right) \times \left(\text{mole}\right)}$$

The unit of molar heat capacity is joule kelvin^{-1} mole^{-1}.

3.5.1 Relation between C_p and C_v : The heat capacity (C_p) for the temperature change at constant pressure.

$$C_p = \frac{q_p}{\Delta T} \text{ and } q_p = C_p \times \Delta T = \Delta H$$

The heat capacity (C_v) for temperature change at constant volume

$$C_v = \frac{q_v}{\Delta T} \text{ and } q_v = C_v \times \Delta T = \Delta U$$

As studied earlier, for 1 mole ideal gas,

$$\Delta H = \Delta U + \Delta(PV)$$

$$PV = nRT$$

Hence, for 1 mole PV = RT

$$\Delta H = \Delta U + \Delta(RT)$$

$$\Delta H = \Delta U + R\Delta T$$

Putting the value of ΔH nad ΔU

$$C_p\Delta T = C_v\Delta T + R\Delta T$$

$$\therefore C_p = \frac{(C_v + R)\Delta T}{\Delta T}$$

$$\therefore C_p = C_v + R$$

$$\therefore C_p - C_v = R$$

Similarly the ratio of C_p and C_v i.e. C_p/C_v will be constant which can be expressed as γ (gamma).

$$\therefore C_p / C_v = \gamma \text{ (gamma)}$$

where γ is a constant. The value of γ for ideal gas is 1.4.

3.5.2 Enthalpy of reaction : When a chemical reaction occurs at constant pressure and constant temperature, the change in heat is called enthalpy change ΔH or heat of reaction.

To understand the characteristics of the reaction, scientist in practice express heat as standard enthalpy change (ΔH^0). For this, it is necessary to know the standard enthalpy of the elements and compounds. In scientific practice, 1 bar pressure and 298 K temperature are considered as standard states. The element or compound whose solid, liquid or gaseous form is stable at 1 bar pressure and 298 K temperature, it is called a standard state.

Solid elements sodium, copper, silver etc. are accepted as standard states. The gaseous elements like H, N, O and Cl are taken in the form of their diatomic molecules H_2, N_2, O_2 and Cl_2 respectively as standard state. The elements which are available in allotropic forms, their most stable allotrope is considered as standard state, viz., graphite allotrope for carbon and rhombic sulphur allotrope in standard state. The enthalpy of the compound in standard state is mentioned as standard enthalpy H^0.

The value of standard enthalpy (H^0) of any element is considered as zero. Starting from the standard forms of the reactants and bringing the

products obtained at the end of chemical reaction in standard state, the value of total change in the enthalpy during the reaction is called standard enthalpy change of the reaction (ΔH^0). This standard enthalpy change is called "Heat of reaction". Its value is expressed in kilojoule.

Example 7 : In the following reaction, the standard enthalpies of $Al_2O_{3(s)}$ and $Fe_3O_{4(s)}$ are -1669.4 kilojoule mole^{-1} and -1117 kilojoule mole^{-1} respectively. What is the enthalpy change of the reaction ?

Reaction :

$$8Al_{(s)} + 3Fe_3O_{4(s)} \rightarrow 4Al_2O_{3(s)} + 9Fe_{(s)}$$
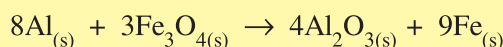
Solution :

ΔH^0 = (Total enthalpy of products) −
$\qquad$ (Total enthalpy of reactants)

$\Delta H^0 = (4 \times \Delta H^0_{Al_2O_3} + 9 \times \Delta H^0_{Fe}) -$
$\qquad (8 \times \Delta H^0_{Al} + 3 \times \Delta H^0_{Fe_3O_4})$

$\therefore \Delta H^0 = [4 (- 1669.4) + 9(0)] -$
$\qquad [8 (0) + 3(- 1117)]$

The enthalpy of elements Al and Fe are taken to be equal to zero as they are in elemental forms.

$\therefore \Delta H^0 = - 6677.6 - (- 3351)$

$\qquad = - 6677.6 + 3351$

$\qquad = - 3326.6$ kilojoule

$\therefore$ Enthalpy of reaction $= - 3326.6$ kilojoule

Enthalpy of Neutralisation : The experimental results show that when 1 mole dilute aqueous solutions of strong acids HCl, H_2SO_4 or HNO_3 are neutralised by 1 mole dilute aqueous solutions of strong bases like NaOH or KOH one mole of salt and one mole water are formed, with 56 kilojoule heat is produced which is known as enthalpy of neutralisation. In short, when one equivalent weight of any strong base in its dilute solution neutralises one equivalent weight of any strong acid in its dilute solution, the heat produced is called enthalpy of neutralisation. The standard enthalpy of neutralisation is constant equal to 56 kilojoule mole^{-1}.

In neutralisation experiment dilute solutions are used so that acid and base are completely dissociated. In neutralisation reaction between acid and base the net reaction is the formation of $H_2O_{(l)}$ by reaction of $H^+_{(aq)}$ of the acid and $OH^-_{(aq)}$ of the base. Hence, standard enthalpy change in the reaction between these two ions is called standard enthalpy of neutralisation. Thus,

in neutralisation of any strong acid with any strong base, the net reaction being same, the value of enthalpy of neutralisation remains constant.

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \quad \Delta H = -56 \text{ kJmole}^{-1}$$
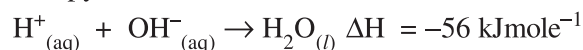
Enthalpy of Formation $\Delta_f H^0$: When one mole of compound is formed under standard conditions from elemental state of constituent elements, thermal changes is called standard enthalpy of formation $\Delta_f H^0$.

Generally, the value of enthalpy of formation of stable compounds is negative (−ve) but in certain stable compounds the value of heat of formation is positive (+ve).
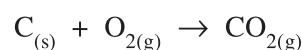
$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$
$$\Delta_f H^0 = - 393.5 \text{ kilojoulemole}^{-1}$$

In the formation of carbon dioxide (CO_2) by combustion of carbon, the standard enthalpy change will be

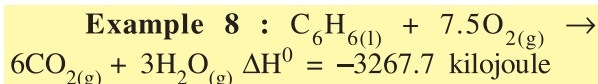$\Delta_f H^0 = - 393.5$ kilojoulemole^{-1}

$\Delta_f H^0 = H_p^0 - H_r^0$

$\Delta_f H^0$ = (Total standard enthalpy of products)
$\qquad$ − (Total standard enthalpy of reactants.)

$\qquad$ = (standard enthalpy of $CO_{2(g)}$) −

$\qquad$ (standard enthalpy of $C_{(s)}$ and $O_{2(g)}$)

Here, $C_{(s)}$ and $O_{2(g)}$, elements are in standard state and so their enthalpies are cosidered as zero.

$\therefore \Delta_f H^0$ = (standard enthalpy of $CO_{2(g)}$)

$\qquad = \Delta_f H^0_{CO_2}$ = enthalpy of formation

$\therefore$ enthalpy of formation $\Delta_f H_{CO_2} = - 339.5$ kilojoulemole^{-1}

In this reaction the value ΔH^0 is negative (−ve) and so the reaction is exothermic. Thus, the total enthalpy of the products, is less than the total enthalpy of the reactants.

Example 8 : $C_6H_{6(l)} + 7.5O_{2(g)} \rightarrow 6CO_{2(g)} + 3H_2O_{(g)} \quad \Delta H^0 = -3267.7$ kilojoule

In this reaction, the standard enthalpy of formation of $CO_{2(g)}$ and $H_2O_{(l)}$ are -393.5 and -285.85 kilojoule mole^{-1} respectively. Calculate the standard enthalpy of formation of benzene.

Solution :

$\Delta H^0 = (\Sigma$ enthalpy of formation of products)−
$\qquad (\Sigma$ enthalpy of formation of reactants.)

$\therefore \Delta H^0 = (6 \times \Delta_f H^0_{CO_2} + 3 \times \Delta_f H^0_{H_2O}) -$
$\qquad (\Delta_f H^0_{C_6H_6} + 7.5\Delta_f H^0_{O_2})$

$-3267.7 = [6(-393.5) + 3(-285.85)] - [(\Delta_f H^0_{C_6H_6} + 7.5 \Delta_f H^0_{O_2})]$

The standard enthalpy of formation of element O_2 is zero

$-3267.7 = [-2361 + (-857.55)] - [\Delta_f H^0_{C_6H_6}]$
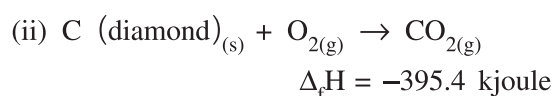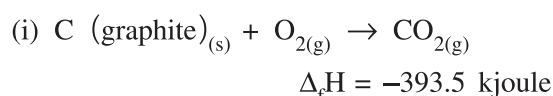
$-3267.7 = -3218.55 - \Delta_f H^0_{C_6H_6}$

$\Delta_f H^0_{C_6H_6} = 49.15$ kilojoule mole^{-1}

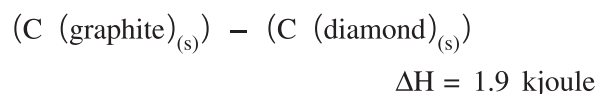The standard enthalpy of formation of benzene = 49.15 kilojoule mole^{-1}

Enthalpy of Combustion : The heat evolved during the complete combustion of one mole of organic compound at constant pressure in presence of oxygen is called the enthalpy of combustion.

Mostly by the combustion of organic compounds carbon dioxide and water are obtained as products. So, if its enthalpy and the enthalpy of combustion are known, the enthalpy of organic compound can be calculated. In fact, enthalpy of combustion is one type of enthalpy of reaction.

Thus, on the basis of the enthalpy of combustion, change in enthalpy between different allotropes of some elements can be calculated. The value of enthalpy between two allotropes of carbon graphite and diamond can be calculated from the values of this enthalpy of combustion.

(i) $C\ (graphite)_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

$\Delta_f H = -393.5$ kjoule

(ii) $C\ (diamond)_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

$\Delta_f H = -395.4$ kjoule

subtracting reaction (ii) from reaction (i)

$(C\ (graphite)_{(s)}) - (C\ (diamond)_{(s)})$

$\Delta H = 1.9$ kjoule

Hence, it can be said that the conversion of graphite to diamond is an endothermic reaction. 1.9 kjoule mole^{-1} heat is absorbed during this conversion.

Activity : Do you think it is possible to prepare a diamond by supplying 1.9 kjoulemole^{-1} heat to graphite ? Why ?

Example 9 : $C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ In this reaction, the standard enthalpies of ethanol$_{(g)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ are −183.35, −393.5 and −285.85 kjmole^{-1} respectively. Find the enthalpy of combustion of ethanol.

Solution :

$\Delta_f H^0 = $ (enthalpy of formation of products) − (enthalpy of formation of reactants)

$\therefore \Delta_f H^0 = (2\Delta H^0_{CO_2} + 3\Delta H^0_{H_2O}) - (\Delta H^0_{C_2H_5OH} + 3\Delta H^0_{O_2})$

$= [2(-393.5) + 3(-285.85)] - [(-185.35) + 3(0)]$

$= [-787 + (-857.55)] + 185.35$

$= -1644.55 + 185.35$

$\therefore \Delta_f H^0 = -1459.20$ kilojoule mole^{-1}

The enthalpy of combustion of ethanol is −1459.20 kilojoule.

3.5.8 Hess's Law of Constant Heat Summation : In 1840, Russian scientist Hess studied the changes in heat (enthalpy) occurring in chemical reactions and deduced the law as follows;

"The total change in enthalpy in a chemical reaction is equal to the algebraic sum of the changes in enthalpy occurring during different steps."

Thus, if a reaction takes place in one step or more than one steps, the total heat of the reaction remains constant. This law is called Hess's law of constant heat summation. This law can be explained on the basis of the first law of thermodynamics.
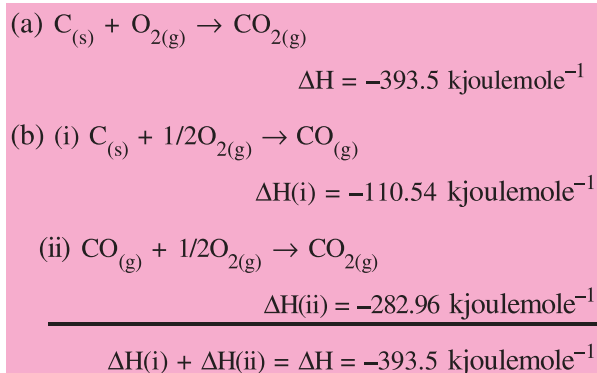
The change in enthalpy at constant pressure and constant temperature (q_p) in a chemical reaction is equal to the change in enthalpy ΔH of that reaction. The enthalpy of reactants and products are constant at constant pressure and constant temperature. Hence, if the reaction occurs in one step or more steps even then the value of enthalpy change remains constant.

It is apparent from this, that if a chemical reaction occurs in different steps, the total change in enthalpy is equal to the algebraic summation of the enthalpy changes of different steps.

The important outcome of Hess's law is that of the addition or subtraction of thermo-chemical equations can be carried out followed by addition or subtraction of corresponding changes. As a result, the enthalpy changes, which cannot be measured experimentally, can be made possible on the basis of calculating the enthalpy changes

according to Hess's law. The enthalpy evolved or absorbed during different chemical reactions like enthalpy of formation, enthalpy of combustion, enthalpy of neutralisation etc. can be determined on the basis of Hess's law. The utility of Hess's law can be understood from the following example :
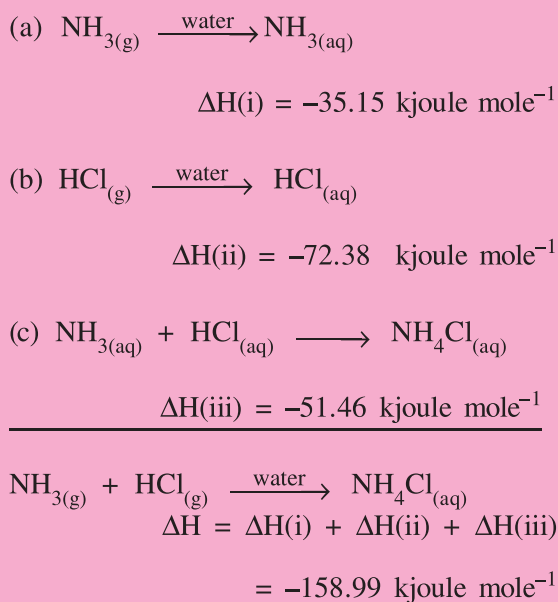
Illustration (a) : Carbon dioxide is formed by chemical reaction between carbon and oxygen. This reaction can occur in the following two steps.
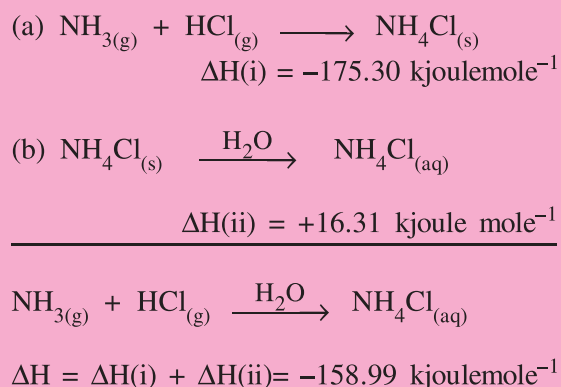
(a) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

$$\Delta H = -393.5 \text{ kjoulemole}^{-1}$$

(b) (i) $C_{(s)} + 1/2 O_{2(g)} \rightarrow CO_{(g)}$

$$\Delta H(i) = -110.54 \text{ kjoulemole}^{-1}$$

(ii) $CO_{(g)} + 1/2 O_{2(g)} \rightarrow CO_{2(g)}$

$$\Delta H(ii) = -282.96 \text{ kjoulemole}^{-1}$$

$$\overline{\Delta H(i) + \Delta H(ii) = \Delta H = -393.5 \text{ kjoulemole}^{-1}}$$

In reaction (a) direct combustion of carbon takes place in one step. While reaction (b) takes place in two steps, when first step (i) and second step (ii) are added, the value of ΔH will be equal to the value of ΔH in reaction (a)

Illustration (b) : Aqueous solution of ammonium chloride from gaseous ammonia can be obtained by two different methods. The different reactions and the different enthalpy changes during these two methods are as follows.

First Method :

(a) $NH_{3(g)} \xrightarrow{\text{water}} NH_{3(aq)}$

$$\Delta H(i) = -35.15 \text{ kjoule mole}^{-1}$$

(b) $HCl_{(g)} \xrightarrow{\text{water}} HCl_{(aq)}$

$$\Delta H(ii) = -72.38 \text{ kjoule mole}^{-1}$$

(c) $NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$

$$\Delta H(iii) = -51.46 \text{ kjoule mole}^{-1}$$

$$\overline{NH_{3(g)} + HCl_{(g)} \xrightarrow{\text{water}} NH_4Cl_{(aq)}}$$
$$\Delta H = \Delta H(i) + \Delta H(ii) + \Delta H(iii)$$
$$= -158.99 \text{ kjoule mole}^{-1}$$

Second Method :

(a) $NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$

$$\Delta H(i) = -175.30 \text{ kjoulemole}^{-1}$$

(b) $NH_4Cl_{(s)} \xrightarrow{H_2O} NH_4Cl_{(aq)}$

$$\Delta H(ii) = +16.31 \text{ kjoule mole}^{-1}$$

$$\overline{NH_{3(g)} + HCl_{(g)} \xrightarrow{H_2O} NH_4Cl_{(aq)}}$$

$$\Delta H = \Delta H(i) + \Delta H(ii) = -158.99 \text{ kjoulemole}^{-1}$$

3.6 Important Characteristics of Spontaneous Process

The hot tea taken in a saucer or hot water taken in a vessel; gets cold on its own but for how long ? It is found from the general experience that when its temperature becomes equal to that of the surrounding, it stops decreasing. This way hot water goes on losing the heat until thermal equilibrium between water and surrounding does not establish. In the same way the gas filled in a bulb tries to diffuse to the bulb being evacuated till the pressure in both the bulbs become equal. This is also a type of pressure equilibrium condition.

All the chemical reactions continue spontaneously till the equilibrium condition is not established and when equilibrium state is established the concentrations of reactants and products remain constant. If we understand this statement in other way, then it can be said that the spontaneous reactions occur in the direction of establishing equilibrium between reactants and products. When equilibrium is established the reaction is also balanced. Thus, reaction attains equilibrium while going from ractants to products or from products to reactants.

3.7 Second Law of Thermodynamics

The Second law of thermodynamics explains in which direction, either the forward or the reverse, the reaction will spontaneously occur. This law can be as mentioned below :

(i) In all spontaneous processes, the entropy of the universe increases.

(ii) The free energy of the system in all the spontaneous processes decreases.

The examples of spontaneous reactions are as follows.

(i) If two substances having different temperatures are kept in contact with each other, the heat will always spontaneously flow from higher temperature to lower temperature.

(ii) Water always flows from higher level to lower level.

Entropy and free energy are necessary to understand spontaneity. Both of these are state functions.

3.7.1 Entropy and Second Law of Thermodynamics :
First, we will understand the term 'entropy' as a physical form and then as a mathematical form. What is entropy ? In order to get the answer, it is necessary to ask a second question : What is temperature ? We know that temperature of a substance does not express the quantity of heat but the level of the thermal energy in the substance and is associated with the Zeroth law of thermodynamics.

Entropy is the measurement of randomness of the substance. Also, a question will arise, what is meant by randomness ? An illustration is necessary to understand before we get the answer.

Suppose, four squares of the size 1 centimetre × 1 centimetre are drawn on a paper and one honeybee flies over it. Maximum four numbers 1, 2, 3 and 4 will be required to show the position of a honeybee. Now, this honeybee flies over nine squares on the second paper. Maximum nine numbers 1 to 9 will be required to show the position of the honeybee. Thus, more co-ordinates are required to show the position of a honeybee.

1	2
3	4

1	2	3
4	5	6
7	8	9

If we express this phenomenon in scientific language, then it can be said that if the honeybee flies and sits on the second paper then, its entropy will increase. The measurement of entropy of any system is the measure of randomness of the system.

Solid   Liquid   Gas
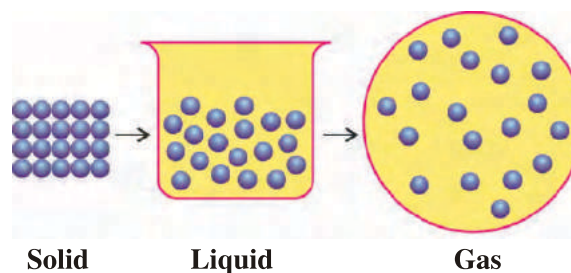
Fig 3.3

As shown in Fig 3.3 the entropy of a crystalline solid substance is the least because the arrangement of molecules is systematic in crystalline solid substance while it is maximum of molecules in the gaseous state, because the randomness of molecules in the gas is maximum. The randomness in liquid falls between these two. Thus, randomness is maximum in gaseous state, entropy in liquid state is less than that in gas but more than that in solid. In a solid, crystal arrangement is comparatively systematic and so entropy is minimum.

In this way, the volume of the gas increases when gas filled in one bulb is connected with other evacuated bulb, which means for the molecules of gas more space is available. Hence, it can be said that randomness increases by diffusion of gas in two bulbs and the entropy of the gas increases. This type of described form of entropy is not useful in understanding the spontaneity of the processes. For this, mathematical form of entropy is needed.

Entropy is expressed by symbol 'S'. Entropy is the state function. In addition, it is an extensive property. It depends on the mass of the substance. In other words, it can be said that the entropy of 1 mole substance has constant value at constant temperature and pressure.

As seen above, the state of system changes its entropy changes. The change in entropy is expressed as ΔS ($S_{final\ state} - S_{initial\ state}$) and its mathematical equation is expressed as follows.

$$S_{final\ state} - S_{initial\ state} = \Delta S = \frac{q_{rev}}{T}$$

where q_{rev} is the heat obtained or heat lost by the system reversibly at temperature T. If q_{rev} is expressed in joule unit and temperature T in kelvin unit, then the unit of change in entropy becomes joule per kelvin. It can also be expressed as entropy unit (e.u.) If the value of

entropy is taken for one mole of a substance, then the unit of entropy will be joule per kelvin per mole. The calculations for values of absolute entropies of substances can be calculated. The values of absolute entropies of some elements and compounds are given in Table 3.4.

To determine whether a reaction will occur spontaneously or not, the calculation of change in entropy of the system and the surrounding, assuming that the reaction will occur of ΔS system and ΔS surrounding is carried out.

If the sum of these two values is positive (+ve), then the forward reaction will occur spontaneously and if the sum of these two values is negative (-ve), then the reverse reaction will occur spontaneously and if the sum of these two values is zero, then reaction will be in equilibrium.

$\Delta S_{system} + \Delta S_{surrounding} > 0$, **The reaction will occur on its own (Spontaneous reaction)**

$\Delta S_{system} + \Delta S_{surrounding} < 0$, **The reaction will not occur on its own (Non-Spontaneous reaction)**

$\Delta S_{system} + \Delta S_{surrounding} = 0$, **The reaction will remain in equilibrium (Equilibrium reaction)**

The changes in entropy of the system when solid is changed to liquid state (fusion) at constant temperature or when liquid is changed to gaseous state (vapourisation) at constant temperature are called molar fusion entropy of the substance and molar vaporisation entropy of the substance. These can be determined from the values of molar enthalpy of fusion and molar enthalpy of vaporisation. We know that

$$\Delta H = q_{rev} \text{ and } \Delta S = \frac{q_{rev}}{T}$$

$$\therefore \ \Delta S = \frac{\Delta H}{T}$$

$$\Delta S_{(Fusion)} = \frac{\Delta H_{fusion}}{T} \text{ and }$$

$$\Delta S_{(Vaporisation)} = \frac{\Delta H_{vaporisation}}{T}$$

Similarly, sublimating substances (Direct change in gaseous form from solid form).

$$\Delta S_{(Sublimation)} = \frac{\Delta H_{sublimation}}{T}$$

Example 10 : 3 moles of water is boiled at 373 K and is changed to vapour state having the same temperature, what will be the change in entropy of the system ? (The molecular enthalpy of vaporistaion of water is 406.68 kjoule mole^{-1})

Solution : The heat absorbed for vaporistaion of 3 moles of water,

$$\Delta H_{vap} = 3 \times 406.68 = 1220.04 \text{ kilojoule}$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$$

$$= \frac{1220.04}{373} = 3.271 \text{ kilojoule kelvin}^{-1}$$

Example 11 : The enthalpy of vaporisation of benzene is 30.799 kilojoule mole^{-1} and its boiling point is 353 K. Find the change in entropy for the conversion of liquid benzene to its vapour at that temperature.

Solution : Here, the system absorbs the heat

$$\Delta H_{vap} = 30.799 \text{ kilojoule mole}^{-1}$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{30.799}{353}$$

$$= 0.0872 \text{ kilojoule kelvinmole}^{-1}$$

Example 12 : "Will ice having temperature 273 K placed in a surrounding having temperature 298 K will give water having temperature 273 K ?" Prove this statement. The molecular enthalpy of fusion of ice is 6.025 kjoule mole^{-1}.

Solution : 1 mole of ice will have to absorb 6.025 kilojoule mole^{-1} enthalpy from the atmosphere to change into water at 273 K temperature. Hence, the change in entropy of the system and the entropy of the surrounding can be calculated as below :

$$\Delta S_{System} = \frac{q_{rev}}{T} = \frac{\Delta H}{T} = \frac{6.025}{273}$$

$$= 0.0221 \text{ kilojoule mole}^{-1}.$$

Surrounding will lose 6.025 kjoule enthalpy but decrease of 6.025 kjoule enthalpy from very large surrounding will not make any real change in the temperature of the surrounding and so it can be neglected.

$$\Delta S_{Surrounding} = \frac{-\Delta H}{T} = \frac{-6.025}{298}$$

$$= -0.0202 \text{ kilojoule K}^{-1}\text{mole}^{-1}$$

(As it obsorbs heat from the surrounding. So it is − 6.025)

$$\Delta S_{Total} = \Delta S_{System} + \Delta S_{Surrounding}$$
$$= 0.0221 + (- 0.0202)$$
$$= 0.0019 \text{ kilojoule } K^{-1} mole^{-1}$$

Here, $\Delta S_{Total} > 0$, so the phenomenon will occur on its own.

As the value of ΔS_{total} is positive (+ve), it can be said that if an ice cube is placed in a surrounding having temperature 298 K it will melt on its own and will give water having temperature 273 K. As opposite to this, water kept at temperature 298 K, will not be changed to ice on its own (automatically). Understand the reason for this with the help of calculations.

3.7.2 Change in Entropy :
For any process (reaction), like change in enthalpy ($\Delta H = H_p - H_r$), can be calculated and similarly the change in entropy (ΔS) can also be calculated.

$$\Delta S_{reaction} = \Delta S_{System} = \text{Entropy change}$$
(Reaction or system)

The difference of entropy in initial and final states is change in entropy ΔS. For chemical reaction, this type of change can be expressed as follows :

$$\Delta S = \text{ Total entropy of product } (S_p) -$$
$$\text{Total entropy of reactant}(S_r)$$

Increase in Entropy with Increase in Temperature : With the increase in temperature the translational motion as well as rotational motion and vibrational motion increase and so there is increase in randomness at molecular level. Entropy is also a state function like internal energy (U) and enthalpy (H). Hence, entropy change will depend on initial and final states of the system and not on the path for obtaining it. Suppose, the entropy of initial state is S_i and entropy of final state is S_f. If entropy or randomness increases then $\Delta S = (S_f - S_i) > 0$.

3.7.3 Expansion of an Ideal Gas in Vacuum and Change in Entropy :
When a vessel filled with one mole of an ideal gas is connected to an evacuated vessel, there is no work done by the system during expansion of the gas on its own, because in $W = P\Delta V$ the value of P is zero because of vaccum. In addition, the gas does not lose or give the heat in this process. Hence, q = 0 and as a result $\Delta U = 0$. This process is not

reversible. Hence, $q_{irr} = 0$. Thus in the expansion of an ideal gas in vacuum, P = 0, $\Delta U = 0$ and $q_{irr} = 0$. As the volume of the gas increases during the reversible process, the change in entropy will be there. We know that, for 1 mole of gas,

$$q_{rev} = RT \, ln \, \frac{V_2}{V_1}$$

$$\therefore \; \frac{q_{rev}}{T} = R \, ln \, \frac{V_2}{V_1}$$

As, $\frac{q_{rev}}{T} = \Delta S$

$$\therefore \; \Delta S = R \, ln \, \frac{V_2}{V_1} = 2.303 \, R \, log \frac{V_2}{V_1}$$

where V_1 = initial volume of gas and
V_2 = final volume of gas

According to Boyle's law,
$$P_1 V_1 = P_2 V_2$$
$$\therefore \; \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

where P_1 = initial pressure of gas
P_2 = final pressure of gas

$$\therefore \; \Delta S = R \, ln \, \frac{P_1}{P_2}$$

$$= 2.303 \, R \, log \, \frac{P_1}{P_2}$$

3.7.4 Free Energy and Second law of Thermodynamics :
To know whether a chemical reaction will occur on its own or not can be decided on the basis of the determination of entropy of both the system and surrounding. Free energy is such a state function that in determining, whether reaction will occur on its own or not, only the change in free energy of the system is to be found out. The relation of this state function free energy (G) with enthalpy (H) of the system and the entropy (S) of the system can be shown by following equation.

$$G = H - TS$$

But, if the state of the system changes at constant temperature, there are changes in the values of all the three state functions which can be shown as below :

$$\Delta G = \Delta H - T\Delta S$$

where ΔH and ΔS are the values of change in enthalpy and change in entropy. With

the help of this the value of ΔG can be obtained. The values of these three state functions change with change in temperature.

For a reaction occurring on its own (Spontaneous) the value of ΔG obtained is negative (–ve) because there is decrease in free energy of all the reactions in the system. For reactions not occurring on their own (non-spontaneous), the value of ΔG will be positive (+ ve) and ΔG becomes zero (0) in reaction in equilibrium.

Here, the symbol G is for Gibbs free energy and it is a state function which is an extensive property. The absolute value of free energy of any substance cannot be determined because it depends on the absolute value of enthalpy of the substance. Hence, importance is given to all the three functions.

3.7.5 Standard Free Energy of Formation of Compounds :

The values of free energy of all the elements in their standard states are accepted as zero. On the basis of this, **"The value of change in free energy in direct reaction when 1 mole compound is produced from its elements in standard state will be equal to the value of change in standard free energy of formation of the compound."**

For example, water is formed by direct reaction of 1 mole of H_2 and half mole of O_2 at 298 K temperature and 1 bar pressure, water is obtained as liquid, then change in free energy of the reaction for,

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons H_2O_{(l)}$$ the value of

free energy is -237.13 kilojoule mole^{-1}

The heat of formation for

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons H_2O_{(l)}$$
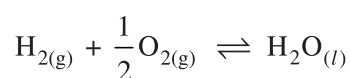
$$[\Delta_f G^0_{(H2O)_{(l)}}) = -237.13 \text{ kjoule mole}^{-1}$$

at 298 K is because the values of free energies of $H_{2(g)}$ and $O_{2(g)}$ are accepted as zero.

The values of standard free energy of formation of compounds at 298 K are given in Table 3.3.

Table 3.3. Values of standard free energy of formation of some compounds (298 K)

Compound	$\Delta_f G^0$ kJ mole^{-1}	Compound	$\Delta_f G^0$ kJ mole^{-1}
$H_2O_{(l)}$	-237.19	$CH_3OH_{(l)}$	-166.23
$H_2O_{(g)}$	-228.61	$C_2H_5OH_{(l)}$	-174.77
$CH_{4(g)}$	-50.79	$HCl_{(g)}$	-95.27
$C_2H_{2(g)}$	$+209.2$	$NH_{3(g)}$	-16.65
$CO_{(g)}$	-137.28	$NO_{(g)}$	$+86.69$
$CO_{2(g)}$	-394.38	$NO_{2(g)}$	$+51.84$
$C_6H_{6(l)}$	$+124.52$		

The change in standard free energy of the reaction can be calculated from the information about free energy of formation of compound.

$$\Delta_f G^0_{(Reaction)} = \Sigma \ \Delta_f G^0_{(Product)} - \Sigma \ \Delta_f G^0_{(Reactants)}$$

= (Total standard free energy of formation of products) – (Total standard free energy of formation of reactants)

There is a change in volume of an ideal gas when pressure is changed at constant temperature. The change in free energy associated with this can be calculated by the use of following equation :

$$\Delta G = nRT \ ln \ \frac{P_2}{P_1}$$

$$\therefore \ \Delta G = 2.303 \ nRT \ log\frac{P_2}{P_1}$$

where n is the number of moles, P_1 and P_2 are pressures at initial and final states. For an ideal gas $P_1V_1 = P_2V_2$. So the above relation can be written in the following form.

$$\Delta G = nRT \ ln \ \frac{V_1}{V_2}$$

$$\therefore \ \Delta G = 2.303 \ nRT \ log \ \frac{V_1}{V_2}$$

where n is the number of moles of the gas and V_1 and V_2 are the volumes of the gas at initial and final state.

Example 13 : The standard free energy of formation of $C_6H_{6(l)}$, $CO_{2(g)}$, and $H_2O_{(l)}$ are 124.52 kjoule mole^{-1}, −394.38 kjoule mole^{-1} and −237.13 kjoule mole^{-1} respectively. Find the change in free energy of the reaction.

Equation : $C_6H_{6(l)} + 7.5O_2 = 6CO_{2(g)} + 3H_2O_{(l)}$ at 298 K temperature.

Solution :

$\Delta_f G^0 = [\Sigma\Delta_f G^0_{products} - \Sigma\Delta_f G^0_{reactants}]$

$\therefore \Delta_f G^0 = [6(\Delta_f G^0_{CO_2}) + 3(\Delta_f G^0_{H_2O})] - [(\Delta_f G^0_{C_6H_6} + 7.5(\Delta_f G^0_{O_2})]$

$\therefore \Delta_f G^0 = [6 \times (-394.38) + 3 \times (-237.13)] - [124.52 + 7.5(0)]$

$= [-2366.28 + (-711.39)] - (124.52)$

$= -3077.67 - 124.52$

$\Delta_f G^0 = -3202.19$ k.joule mole^{-1}

3.7.6 Free Energy and Equilibrium Constant :
For, the chemical reactions occurring at constant temperature and constant pressure, free energy is related with equilibrium constant of the reaction (K) by following relation.

$\Delta_r G^0 = - RT \ln K = - 2.303 \, RT \log K$

If the system consists of gaseous state, then $K = K_p$ and if the homogeneous liquid of reactants and products is formed then $K = K_c$.

For, reactions having value of ΔG^0 negative (−ve) the value of equilibrium constant for such reactions is greater than 1 and the reactions in which the value of ΔG^0 is positive (+ ve), then the value of equilibrium constant is less than 1.

Hence, If K > 1; ΔG^0 = negative (−ve) and reaction will occur on its own (Spontaneous).

If K < 1; ΔG^0 = positive (+ve) and reaction will not occur on its own (non-spontaneous)

If K = 1; ΔG^0 = zero (0) and reaction will be in equilibrium.

Example 14 : The values of standard heat of formation of $NO_{(g)}$ and $NO_{2(g)}$ are 90.37 kjoule mole^{-1} and 33.85 kjoule mole^{-1} respectively at

298 K. The entropies of $NO_{(g)}$, $O_{2(g)}$ and $NO_{2(g)}$ 298 K temperature and 1 bar pressure are 210.45, 205 and 240.6 Joule K^{-1} mole^{-1} respectively. Then, calculate the values of ΔH^0, ΔS^0 and ΔG^0 and equilibrium constant for the following reaction at 298 K temeperature.

Reaction : $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$
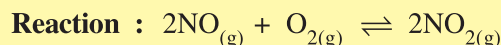
Solution :

$\Delta H^0 = [2 \times \Delta H^0_{NO_2}] - [(2 \times \Delta H^0_{NO}) + (1 \times \Delta H^0_{O_2})]$

$= [2 \times 33.85] - [(2 \times 90.37) + 1(0.0)]$

$= 67.7 - 180.74$

$= - 113.04$ kjoule

$= - 113040$ joule

$\Delta S^0 = [2 \times \Delta S^0_{NO_2}] - [(2 \times \Delta S^0_{NO}) + (1 \times \Delta S^0_{O_2})]$

$= [2 \times 240.6] - [(2 \times 210.45) + 1(205)]$

$= 481.2 - 625.9 = - 144.7$ joule K^{-1}

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

$= [- 113040] - [298 \times (- 144.7)]$

$= - 113040 + 43120.6$

$= - 69919.4$ joule

$\Delta G^0 = - 2.303 \, RT \log Kp$

$- 69919.4 = - 2.303 \times 8.314 \times 298 \log K_p$

$\log K_p = \dfrac{- 69919.4}{- 2.303 \times 8.314 \times 298}$

$= \dfrac{+ 69919.4}{+ 5705.85}$

Taking antilogarithm log $K_p = 12.2540$

$K_p = 1.795 \times 10^{12}$ bar^{-1}

Example 15 : The value of equilibrium constant of following esterfication reaction is 4. Calculate the value of ΔG^0 for this reaction.

Reaction : $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$
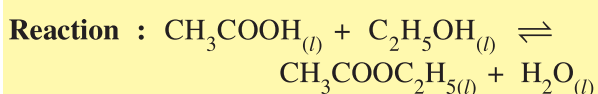
Solution : $\Delta G^0 = -2.303 \; RT \; log \; K_c$

$= -2.303 \times 8.314 \times 298 \; log \; 4$

$= -5705.84 \times 0.6021 \; (log \; 4 = 0.6021)$

$= -3435.49 \; joule$

3.7.7 Gibbs' Free Energy and Useful Work :

(i) It will be understood from the examples described above that the value of ΔG^0 is the dimension of tendency of the chemical reaction to occur on its own. In addition, free energy also possesses relation with useful work. The change in free energy associated with any process is the value of maximum possible work obtainable from that process, i.e. free energy is associated with maximum useful work viz.

$\Delta G = -W_{max}$ (negative (–ve) value for reactions occurring on its own.)

Thus, any process can be taken in use for doing the work by that process. The process for which value of ΔG is more negative (–ve), then maximum work can be done by such process.

(ii) When electrochemical cell is in operation the electrical work done by the cell W_{elect} has the following relation with free energy change of the spontaneous chemical reaction.

$\Delta G = -W_{(elect)}$

But the electrical work done by the cell is having following relation with cell potential (E_{cell}) and the quantity of electricity obtained from the cell (nf)

$W_{elect} = nFE_{cell}$

where F = Faraday constant

$= 96500$ coulomb

n = Number of electrons passing from the external path of the cell

$\Delta G = -W_{elect}$

The following relation can be deduced from the above two equations.

$\Delta G = -nFE_{cell}$

If the cell is in standard state and the change in free energy is associated with reaction and standard electrochemical cell potential, then the relation between them can be shown by following equation.

$\Delta G^0 = -nFE^0_{cell}$

where E^0_{cell} is the difference of standard reduction potentials of both the half cells of the complete cell.

Example 16 : Find the value of ΔG^0 for the reaction $Zn_{(s)} + Cu^{2+}_{(aq)} = Zn^{2+}_{(aq)} + Cu_{(s)}$ taking place in a standard cell. The value of standard cell potential (E^0_{cell}) is 1.1 volt at 298 K temperature, F = 96500 coulomb. (4.184 joule = 1 calorie)

Solution : $\Delta G^0 = -nFE^0_{cell}$

Taking n=2 for the given reaction

$= -2 \times 96500 \times 1.1$ volt coulomb

(volt coulomb = joule)

$= -212300$ joule

4.184 joule = 1 calorie

$\Delta G^0 = \dfrac{-212300}{4.184}$

$= -50740.9$ calorie

3.7.8 Limitations of Second Law of Thermodynamics :
Whether the reaction has the capacity to take place on its own or not and if it can take place on its own, then, the calculations of equilibrium constant can be done on the basis of the second law of thermodynamics. But this law is not able to give information about the rate of chemical reactions. Thus, the thermodynamics is independent of chemical kinetics.

3.8 Third Law of Thermodynamics

Generally, the value of entropy of a substance increases with increase in temperature, because, the randomness increases with increase in temperature. The value of entropy increases because there is increase in their oscillation

motion, linear motion and rotation motion as against to this, with decrease in temperature, the oscillation motion, linear motion and rotation motion of the molecules of substance decrease and so randomness decrease and decrease in randomness decrease the value of entropy.

German scientist Nernst expressed, in 1906, that the value of entropy of a completely pure crystalline substance decreases with decrease in temperature. On the basis of this, the third law of thermodynamics can be expressed as below :

"The value of entropy of a completely pure crystalline substance is zero at absolute zero temperature" i.e. the arrangement of component particles of an absolutely pure crystalline substance is completely systematic at absolute zero temperature. Hence, entropy is least in solid, more in liquid and highest in gas.

The kinetic energy of the molecules of a substance at absolute zero temperature is almost negligible but its potential energy is not zero. As a result, the value of internal energy is not zero. In addition, the internal energy is the characteristic of a substance. Therefore the value of internal energy cannot be calculated at absolute zero but the absolute value of entropy of substance can be calculated.

The entropy of one mole of a substance is called molar entropy and it is expressed as S_m. The entropy of one mole of a substance at constant temperature and standard state is called standard molar entropy S^0_m. The molar standard entropy of the substance is also called absolute entropy. The unit of molar entropy is jolue kelvin^{-1} mole^{-1}. The values of absolute entropies of some elements and compounds at 298 K are given in a Table 3.4.

Table 3.4 Values of absolute entropies of some elements and compounds at 298 K

Solid S_m^0		Liquid S_m^0		Gaseous S_m^0	
Element/ Compound	jolue K^{-1} mole^{-1}	Element/ Compound	jolue K^{-1} mole^{-1}	Element/ Compound	jolue K^{-1} mole^{-1}
C (Graphite)	5.740	$Hg_{(l)}$	76.62	$Hg_{(g)}$	130.68
C (Diamond)	2.377	$H_2O_{(g)}$	188.83	$N_{2(g)}$	191.61
S (Rhombic)	31.80	$H_2O_{(l)}$	69.91	$O_{2(g)}$	205.14
$Al_{(s)}$	28.33	$C_2H_5OH_{(g)}$	282.7	$CO_{2(g)}$	213.74
$NaCl_{(s)}$	72.13	$C_2H_5OH_{(l)}$	160.7	$NO_{(g)}$	210.76
$NaCl_{(aq)}$	115.5	$C_6H_{6(l)}$	173.3	$NO_{2(g)}$	240.06
$CaCO_3$ (Calcite)	92.9	$CH_3COOH_{(l)}$	159.8	$NH_{3(g)}$	192.45
$CaCO_3$ (Arogenite)	88.7	$CH_3OH_{(l)}$	126.8	$CH_{4(g)}$	186.26
$CaO_{(s)}$	39.75				

It can be decided from the values of the absolute entropies of the substances that the value of entropies of solid substance are less, the values of absolute entropies of the liquids are more than those of solids but less than those of gaseous substances.

SUMMARY

In this unit, the breaking of bonds in reactants and formation of bonds in products experienced in chemical reactions are discussed. Endothermic and exothermic reactions are explained. Some basic concepts like system, the very small part of the universe which is separated from the rest of the universe by a definite boundary and the observations of doing experiments are called system. The remaining part without the system is called surrounding. On the basis of exchange of matter and energy, the system is divied into three types. viz. open system in which energy and mass both are exchanged. In the closed system matter is not exchanged but only energy is exchanged. In the isolated system neither mass nor energy is exchanged. Processes like isobaric process, isothermic process and adibatic process are discussed. Extensive properties which depend on the magnitude of the mass and intensive properties which do not depend on the mass. The concept of state function is given. Internal energy (U), enthapy (H), and internal energy change (ΔU) and change in enthalpy (ΔH) are studied. The relation between them $\Delta H = \Delta U + P\Delta V$ and $\Delta H = \Delta U + \Delta n_g RT$ are studied.

The process of obtaining thermal equilibrium when two diathermic substances are connected is known as zeroth law of thermodynamics. The first law of thermodynamics in reality is the law of conservation of energy which can be expressed in different forms i.e. the total energy of the universe remains constant. The formation or destruction of energy is not possible but it is possible to transfer energy from one form to the other. The symbolic form of First law of thermodynamics is $\Delta U = q + W$ and with the help of mathematical form of First law the work done on the system and work done by the system are explained and the change in internal energy occur. Enthalpy and First law of thermodynamics $\Delta H = q_p$, enthalpy change at constant pressure and at constant volume related to ethalpy change and internal energy change can be obtained by illustrations and solutions of examples.

Enthalpy is the function only to measure the heat change in the system at constant pressure. This function is not useful to measure the heat changes at constant volume. Hence, to express the relation between changes at constant pressure or constant volume, and temperature, the function heat capacity is required. Heat capacity is not the state function. Established the concepts of specific heat capacity, molar heat capacity and the relation between C_p and C_v as $C_p - C_v = R$. For an ideal gas $\dfrac{C_p}{C_v} = \gamma$; the value of γ is 1.4. In the enthalpy of reaction the values of enthalpy of formation of solid, and gaseous molecules in standard state is taken equal to zero, studied the definitions of enthalpy of neutralisation, enthalpy of formation and enthalpy of combustion and obtained solutions of examples based on them. The Hess's law of constant heat summation was studied with the examples of combustion of carbon and formation of ammonium chloride (NH_4Cl) and its importance have been studied.

The limitation of first law of thermodynamics is brought out by examples having physical and chemical changes; the spontaneity and its characteristics are studied to predict whether a reaction will occur on its own or not ? Second law of the thermodynamics is expressed for this. According to second law of thermodynamics, the entropy of the universe increases and for any reaction occurring on its own, its free energy decreases. Entropy (S) and free energy (G) entropy change ΔS, which is determined for the surrounding to predict whether reaction will occur on its own or not ? If the value of ΔS is positive (+)

the reaction will occur on its own and if the value of ΔS is negative (–), the reaction will occur on its own, and if $\Delta S = 0$, the reaction will be in equilibrium.

$$\Delta S = \frac{\Delta q_{rev}}{T} = \frac{\Delta H}{T} \cdot \text{From this, } \Delta S_{Vaporisation} = \frac{\Delta H_{vaporisation}}{T}, \quad \Delta S_{Fusion} = \frac{\Delta H_{fusion}}{T} \quad \text{and}$$

$\Delta S_{Sublimation} = \frac{\Delta H_{sublimation}}{T}$. In the same way $\Delta S = (S_2 - S_1) > 0_1$ the reaction will occur on its own. On expansion of the ideal gas in vacuum $\Delta U = 0$ and $\Delta H = 0$ and the entropy change $\Delta S = 2.303 \text{ R} \log \frac{V_2}{V_1}$.

Whether a reaction will occur on its own or not can be determined on the basis of calculation of total entropies of system and surrounding but the free energy (G) of the system is determined from the free energy changes of the system. Its symbol is G and known as Gibbs' free energy. If the value of free energy change ΔG is negative (–) the reaction will occur on its own and if the value of ΔG is positive (+) the reaction will not occur on its own. If $\Delta G = 0$, the reaction will be in equilibrium. The reaction between free energy (G), enthalpy (H) and entropy (S) is G = H – TS. If the state of the system changes at constant temperature, there is change in the values of all the three functions. Hence, $\Delta G = \Delta H - T\Delta S$, where ΔH is enthalpy change and ΔS is entropy change. At definite temperature if the pressure of an ideal gas is changed, there will be change in volume and hence, the change in free energy occurring is $\Delta G = nRT \ln \frac{P_2}{P_1}$

$\therefore \Delta G = 2.303 \text{ } nRT \log \frac{P_2}{P_1}$ and $\therefore \Delta G = 2.303 \text{ } nRT \log \frac{V_1}{V_2}$ can be obtained. The relation between free energy change and equilibrium constant is $\Delta_f G^0 = -2.303 \text{ RT} \log K$. If the value of K is more than 1 (K > 1), $\Delta_f G^0 = $ negative (–) and if the value of K is less than 1 (K < 1), $\Delta_f G^0 = $ positive (+). The relation between free energy change and the useful work can be shown as $\Delta G = -W_{max}$ and in electrochemical cell, $\Delta G = -nFE_{cell}$. The value free energy change can be obtained. This can be understood by illustrations and definitions. The importance and limitation of second law of thermodynamies as well as the third law of thermodynamics given by Nernst can be studied. The third law of thermodynamics is "The value of entropy of a completely pure crystalline substance is zero at absolute zero." Hence, in perfectly pure crystalline substance the arrangement of its component particles is completely in order. Randomness is minimum in solid and in liquid it is more than that of solid and less than that of gas. Gases have maximum entropy. The standard molar entropy is expressed as S_m^0 and its unit is Joule Kelvin^{-1} mole^{-1}.

EXERCISE

1. **Select the proper choice from the given multiple choices :**

    (1)   Which of the following is the symbolic form of the first law of thermodynamics ?

    (A) $\Delta U = q - W$ (B) $W = \Delta U - q$

    (C) $\Delta U = q + PV$ (D) $\Delta q + W = \Delta U$

(2) The system in which the property of the system depends on the quantity of substance, such a property is called ?

(A) Specific property   (B) Physical property

(C) Thermal property   (D) Extensive property

(3) For the thermal reaction occurring in nature.

(A) Temperature is always zero   (B) Temperature is always high

(C) Temperature is always low   (D) Temperature can be of any order

(4) In which condition the relation $\Delta H = \Delta U + P\Delta V$ can be said to be true for a closed system ?

(A) Constant temperature

(B) Constant pressure

(C) Both constant temperature and pressure together

(D) Constant temperature and volume

(5) For which reaction ΔS can be maximum?

(A) $Mg_{(s)} + \dfrac{1}{2} O_{2(g)} \rightarrow MgO_{(s)}$ (B) $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

(C) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ (D) $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$

(6) In which of the following entropy decreases ?

(A) Preparing aqueous solution of common salt

(B) Change of water into ice

(C) Dry ice placed in an open vessel

(D) Melting of ice

(7) What change is observed in the isothermal condition of an ideal gas ?

(A) Decrease in enthalpy   (B) Increase in internal energy

(C) Decrease in internal energy   (D) Enthalpy will be constant

(8) Which relation shows the value of ΔS for a reversible reaction ?

(A) $T - q_{rev}$ (B) $\dfrac{q_{rev}}{T}$ (C) $q_{rev} + T$ (D) $q_{rev} - T$

(9) For a spontaneous reaction

(A) $\Delta H = +ve, \Delta S = -ve$ (B) $\Delta H = -ve, \Delta S = +ve$

(C) $\Delta G = +ve, \Delta S = -ve$ (D) $\Delta G = +ve, \Delta H = +ve$

(10) Which of the following relations is correct for free energy change and cell potential ?

(A) $\Delta G = nFE_{cell}$ (B) $\Delta G = -\dfrac{n}{F} E_{cell}$

(C) $\Delta G = -nFE_{cell}$ (D) $\Delta G = \dfrac{nF}{E_{cell}}$

(11) The reaction $A + B \rightleftharpoons C + D$ is spontaneous in forward direction, then which signs represent ΔG and ΔS respectively ?

(A) Positive and negative   (B) Positive and positive

(C) Negative and positive   (D) Negative and negative

(12) For an ideal gas, during an adiabatic raction always,

(A) Decrease in temperature   (B) $q = 0$

(C) $W = 0$ (D) $\Delta H = 0$

(13) Which of the following statements is correct ?

(A) ΔG may be less or more or equal to ΔH

(B) ΔG always changes with ΔH

(C) ΔG is always more than ΔH

(D) ΔG is always less than ΔH

(14) What will be the value of ΔG^0 if $K_c = 1$ for a reaction ?

(A) Infinite   (B) 0   (C) Negative   (D) Positive

(15) Which law of thermodynamics gives information about definite entropy of a substance ?

(A) First law   (B) Second law (C) Third law (D) Zeroth law

(16) What is the ideal condition for a reaction occurring on its own ?

(A) $T\Delta S = \Delta H$, $\Delta H = +$ve $\Delta S = +$ve

(B) $T\Delta S = \Delta H$, $\Delta H = -$ve $\Delta S = -$ve

(C) $T\Delta S > \Delta H$, $\Delta H = +$ve $\Delta S = +$ve

(D) $T\Delta S > \Delta H$, $\Delta H = +$ve $\Delta S = -$ve

(17) The reaction of quick lime with water is reversible at the room temperature and at low temperature, therefore,

(A) ΔH and ΔS both $+$ve   (B) $\Delta H = +$ve and $\Delta S = -$ve

(C) $\Delta H = -$ve and $\Delta S = +$ve   (D) ΔH and ΔS both $-$ve

(18) Which is the correct relation between ΔG^0 and K_p ?

(A) $K_p = \left(\dfrac{e}{RT}\right)^{\Delta G^0}$ (B) $K_p = \dfrac{\Delta G^0}{RT}$

(C) $K_p = e^{-\Delta G^0/RT}$ (D) $K_p = - RT \, log\Delta G^0$

(19) What can be the value of absolute entropy of free element ?

(A) Always negative   (B) Always positive

(C) Always zero   (D) Zero at 273 K

(20) Which system is indicated by the reaction of cooking rice in a pressure cooker ?

(A) Open system   (B) Closed system

(C) Isolated system   (D) All the systems

2.　　**Write the answers of the following questions in brief :**

(1)　What is meant by a system ?

(2)　What an isolated system is called ? Give example.

(3)　What is meant by closed system ? Give example.

(4)　What are called exothermic and endothermic reactions ?

(5)　What is called extensive property ?

(6)　What is called an intensive property ?

(7)　What is called a state function ?

(8)　Give definitions of internal energy and enthalpy.

(9)　Which types of work are observed in chemistry ?

(10)　Give definition of heat capacity.

(11)　Give definition of enthalpy of reaction and heat of formation.

(12)　What is called a thermal equilibrium ?

(13)　When is the total heat absorbed by the system during the process used up in work ?

(14)　Mention the equation of entropy change for the expansion of an ideal gas in vacuum.

(15)　Write the formula for the entropy of substances experiencing sublimation.

(16)　The ice cube kept at room temperature melts on its own. Which law of thermodynamics is obeyed by the reaction ?

(17)　What is meant by temperature of a substance ?

(18)　The entropy of water vapour is more than that of water. Why ?

(19)　What will be the values of ΔG at 270 K and 275 K ?

(20)　Give definition of standard free enegry of formation.

(21)　Write the equation showing relation between free energy change and cell potential.

(22)　Why does the value of entropy of a substance increase with increase in temperature ?

(23)　Write limitations of the second law of thermodynamics.

(24)　Write the third law of thermodynamics.

(25)　Mention the equation showing the relation between free energy and change in pressure of an ideal gas.

(26)　What is meant by entropy ?

(27) By which system the maximum work can be done ?

(28) What will be the value of equilibrium constant if $\Delta H < T\Delta S$ at 298 K temperature ?

(29) What will be the value of ΔS for ice kept at 275 K and 265 K temperature ?

(30) "The value of absolute free energy of any substance cannot be determined." Why ?

3.   Write answers of the following questions :

(1)   What is meant by system ? Explain giving its types.

(2)   What is meant by process ? Explain its types.

(3)   Explain extensive and intensive properties.

(4)   Explain in detail the state functions.

(5)   Explain internal energy.

(6)   Write the First law of thermodynamics and give its symbolic equation.

(7)   A system did the work of 785 joule after loss of 525 joule heat. Find the change in its internal energy.

(8)   A system absorbed 650 joule heat and did the work. Its internal energy change is 440 joules, then find out how much work has been done.

(9)   Explain the mathematical form of the first law of themodynamics.

(10) Explain enthalpy and First law of thermodynamics.

(11) Deduce the relation between C_p and C_v.

(12) Write a short note on heat capacity.

(13) Write the Second law of thermodynamics and in which forms it can be expressed ?

(14) Explain the free energy and the Second law of thermodynamics.

(15) Explain Gibbs free energy and useful work.

(16) Explain the standard free energy of formation of a compound.

(17) Explain the expansion of an ideal gas in vacuum and entropy change.

(18) Explain the Third law of thermodynamics.

(19) Give limitations of the First law of thermodynamics.

(20) Discuss characteristics of the reactions occurring on their own.

(21) What is meant by entropy ? Explain using the concept of entropy, how the direction of a reaction to occur on its own is determined.

4.   Answer the following questions in detail :

(1)   Explain internal energy and enthalpy and deduce the relation between them.

(2)   Write the First law of thermodynamics and explain it in detail in the symbolic equation and in the mathematical form.

(3)   Explain enthalpy of reaction, enthalpy of neutralisation and enthalpy of formation.

(4) Write the Hess's law of constant heat summation and explain giving example. Mention its uses also.

(5) Write the Second law of thermodynamics and explain entropy.

(6) What is meant by free energy ? What is the relation between change in free energy during a chemical reaction and the change in entropy ? On the basis of this, explain under which conditions the reaction will occur on its own.

(7) **Solve the following examples :**

(1) The change in internal energy of a given reaction at 300 K is −908 kjoule mole^{-1}, then calculate its enthalpy change.

$$4NH_{3(g)} + 5O_{2(g)} \rightarrow 6H_2O_{(l)} + 4NO_{(g)} \qquad (R = 8.314 \text{ joule})$$
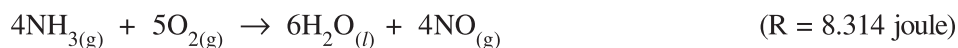
(2) The enthalpies of formation of $CO_{(g)}$, $CO_{2(g)}$, $N_2O_{(g) \text{ and }} N_2O_{4(g)}$ are −110 , −393.81, 82 and 9.7 kjoule mole^{-1}, respectively. Calculate $\Delta_f H$ for the following reaction : $N_2O_{4(g)} + 3CO_{(g)} \rightarrow N_2O_{(g)} + 3CO_{2(g)}$

(3) On the basis of the following equations, calculate the standard enthalpy of formation of $CH_3OH_{(l)}$.

$$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \quad \Delta_f H^0 = -726 \text{ kjoule mole}^{-1}$$

$$C \text{ (Graphite)} + O_{2(g)} \rightarrow CO_{2(g)} \; \Delta_f H^0 = -393 \text{ kjoule mole}^{-1}$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \; \Delta_f H^0 = -286 \text{ kjoule mole}^{-1}$$
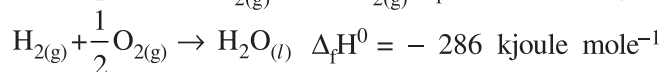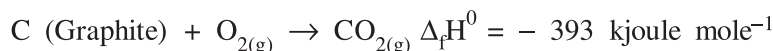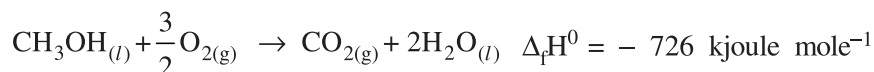
(4) If $\Delta H = 400$ kjoule mole^{-1} and $\Delta S = 0.2$ kjoule K^{-1} mole^{-1} for a reaction $2x + y \rightarrow z$, at what minimum temperature the reaction will be spontaneous ?

(5) For the following reaction, $2P_{(g)} + Q_{(g)} \rightarrow 2R_{(g)}$ $\Delta U^0 = -10.5$ kjoule and $\Delta S^0 = -44.2$ jouleKelvin^{-1} Find ΔG^0 for the reaction. Will the reaction occur on its own ? Why ?

(6) From the given data mention which of the following reactions will occur on their own at 298 K.

Reaction : X : $\Delta H = -52$ kjoule; $\Delta S = 956$ joulekelvin^{-1}

Reaction : Y : $\Delta H = -60$ kjoule; $\Delta S = -65$ joulekelvin^{-1}

(7) The changes in enthalpy and entropy for a raction $P + Q \rightleftharpoons R + S$ at 320 Kelvin temperature are 170 kilojoule and 26 joule Kelvin^{-1}. Will this reaction be spontaneous ? Why ? Find out.

(8) Find out the equilibrium constant of the follwing given reaction at 298 K temperature $NO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{2(g)}$. The values of $\Delta_f G^0$ for NO and NO_2 are 104.2 and 51.3 kjoule mole^{-1} respectively of 298 K temperature.

(9) Find the change in standard free energy of formation and equilibrium constant of the reaction $Fe_{(s)} + Cu_{(aq)}^{2+} \rightarrow Fe_{(aq)}^{2+} + Cu_{(s)}$. The standard electrochemical cell potential is 0. 78 volt and F = 96500 coulombs.

(10) The value of change in free energy for the following cell reaction at 298 K temperature is −76322 calories. Calculate the potential of the electrochemical cell. F = 96500 coulomb, 1 Calorie = 4.184 joule.

Reaction : $A_{(s)} + B_{(aq)}^{2+} \rightarrow A_{(aq)}^{2+} + B_{(s)}$
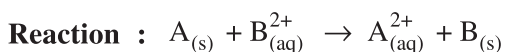
(11) The equilibrium constant of the following given reaction is Kp = 2.4 × 10^{-5} at 298 K temperarure.

Reaction : $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$. Calculate the value of $\Delta_f G^0$ for the given reaction.

•
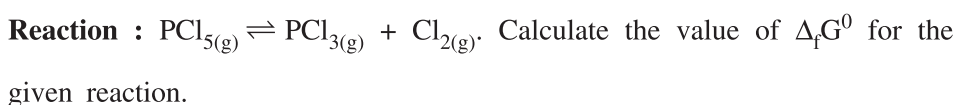
Dr. Venkat Raman Ramakrishnan

Dr. Venkat Raman Ramakrishnan is the seventh Indian (born in India) winner of the nobel prize. He got creadit for India because of his birth place in India, in the whole of the world. He was born in 1952, at Chidambaram city which is in Tehil Taluka of Cuddalore district. He, at his age of three years came to Baroda of Gujarat State with his father and mother. He obtained here his primary school education to upto graduate level. He obtained B.Sc. (Physics) degree in 1971 from Maharaja Sayajirao University. As this is also not enough, he remained as student of graduate study in biology for two years in University of California.

Ramakrishnan who did Ph.D. in Physics became postdoctorate (Special research worker after Ph.D.) by doing work on Ribosome. During 1983 to 1995 he continued his research work on Ribosome by joining Brookhaven National Laboratory. He published many research papers about this. He joined University of Utah in 1995 as Professor of Biochemistry. There he started the study on protein-RNA complex and its components. He joined Medical Research Council Laboratory of Molecular Biology, Cambridge, England in 1999 as senior scientist. There he was working as leader of the Structural Study Group. For the years dedicated to work based on Ribosome and his hard work, Dr. Venkat Raman Ramakrishnan and his team was awarded the nobel prize in Chemistry, in 2009 for the research work on 'study of structure of Ribosomes and its working.' The co-scientists this achievement were Thomas A Steitz who is professor of molecular biophysics and biochemistry and Lady Professor Ada-E-Yonath of Isarel, who is an expert in structural biology.

Equilibrium

4.1 Introduction

Equilibrium plays an important role in physical changes, chemical reactions, biological and environmental processes. e.g. evaproation of water, equilibrium between oxygen molecule and protein, production of ammonia etc. If certain changes and reactions are carried at constant temperature and pressure in closed vessels (closed systems), they remain incomplete. In the beginning of the reaction, the reactants which are in closed vessels, slowly change into products and the concentration of reactant decreases as the time proceeds. Along with this phenomenon, there is increase in concentration of product as the time proceeds. A certain point of time comes when there is no change in the concentration of reactant and product even if the time proceeds. This situation is called equilibrium state.

4.2 Dynamic Nature of Equilibrium

The most important matter in the case of equilibrium is that there is a continuous transformation of reactant to product and product to reactant. This state apprears to be steady but it is not so. This type of reaction which takes place in both the directions is called reversible reaction and it is expressed by the

symbol of two half-arrows $(\rightleftharpoons)$. This symbol indicates that such reaction occurs simultaneously in both (forward and reverse) directions. Generally, **the change of reactant to product is called forward reaction and the change of product to reactant is called the reverse reaction.** Thus, in reversible reactions, forward and reverse reactions continuously occur and we find it as equilibrium state. The mixture of reactants and products obtained at equilibrium time is called equilibrium mixture. The decomposition reaction of solid calcium carbonate in a closed vessel, at high temperature can be shown as below :

$$CaCO_{3(s)} \underset{}{\overset{\Delta}{\rightleftharpoons}} CaO_{(s)} + CO_{2(g)}$$
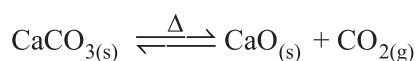
The equilibrium is dynamic and not steady or static as the forward and the reverse reactions occur with the same velocity at the equilibrium time in equilibrium reactions in closed vessels. In the above reaction obtaining CaO and CO_2 by decomposition of $CaCO_3$ and obtaining $CaCO_3$ by combination of CaO and CO_2 continuously take place. Suppose, if we deposit some amount in our bank account and withdraw the same amount, then balance in the account appears steady or static. But this can be considered operative or dynamic and not closed or static. It is very difficult to determine the dynamic nature of equilibrium, even then with the help of radioactive isotope, it can be proved viz. $^{14}CO_2$ gas containing radioactive isotope ^{14}C and $CaCO_3$ are taken in two different flasks and CO_2 obtained by decomposition is connected with vessel containing $^{14}CO_2$ gas, after some time, $Ca^{14}CO_3$ will be formed in the vessel of $CaCO_3$ and CO_2 will be obtained in the vessel containing $^{14}CO_2$. Thus, if the equilibrium would have been steady, there must not be exchange of ^{12}C and ^{14}C. With the help of suitable counter, the radioactivity can be measured and the proof for the dynamic nature of equilibrium can be obtained though the proportions of concentrations of reactants and products remain constant. The reaction can be fast or slow depending upon the nature of the reactant and the experimental conditions.

Equilibrium reactions can be divided into following three categories :

(i) Reactions which are almost at the extent of completion and concentration of reactants may be negligible. It is not possible to detect this experimentally.

(ii) Reactions in which the products are formed in very less proportions and most part of the reactant remains unchanged at the equilibrium.

(iii) Reactions in which the concentrations of reactants and products are in comparable proportions at equilibrium.

4.3   Types of Equilibrium

Physical Equilibrium : The equilibrium established in changes of pysical processes is called physical equilibrium. e.g. conversion of water into steam.

Chemical equilibrium : The equilibrium established in chemical reactions is called chemical equilibrium. e.g. Decomposition of calcium carbonate.

Equilibrium in Physical Process : At constant temperature, water in the liquid state taken in a closed vessel, gets converted into gaseous state of vapour (steam) as the time proceeds. Slowly, the concentration of vapour of water on the surface of water increases. After some time, the molecules of vapour of water get attracted to one another and converted into liquid state water. After certain time, the rates of formation of vapour from liquid water and the formation of liquid water from water vapour become equal and the equilibrium is called physical equilibrium or physical process equilibrium. In this type of process, there is no change in chemical structure of the molecule of the substance, only its physical state changes. The forward reaction of formation of water vapour from water is called evaporation of water and the reverse reaction of formation of water from vapours of water is called liquefaction.

$$H_2O_{(l)} \underset{\text{Liquefaction}}{\overset{\text{Evaporation}}{\rightleftharpoons}} H_2O_{(g)}$$
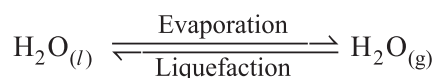
If there are changes in the factors like temperature, pressure or concentration in the physical reaction in equilibrium, there is a change in the equilibrium state.

As the substance changes from solid, liquid and gas into one another, three states can be established in physical process equilibrium.

(i) Solid-Liquid Process Equilibrium :

Take some ice and water in a thermos flask at 0^0 C (273 K). Now close the thermos flask with a cork. As you know that because of the wall having vacuum in the flask, there will not be exchange of heat between the system in the flask and the external surrounding. Hence, the quantity of ice in the thermos flask will remain constant but an equilibrium can be established between ice and water, which can be shown as below :

$$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$$
Ice (solid)   Water (liquid)
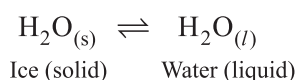
Experimentally, it is proved that even after establishment of the equilibrium in the flask, some molecules of ice get converted into water, and at the same time some amount of molecules of water get converted into ice. Hence, the quantity of ice and water in the thermos flask or the total number of molecules remain constant. This is one type of equilibrium, i.e. physical equilibrium between solid and liquid. It is important to note that there is no chemical change in the substance and therefore, this process is called physical equilibrium.

(ii) Liquid - Gas Process Equilibrium :

At constant temperature, take water in a closed vessel (system). As the time proceeds, water slowly changes into vapour (steam) depending upon the value of temperature. As the water gets converted into water vapour, vapour of water increases and the vapour pressure also increases. After sometime vapour pressure becomes constant because the temperature is constant and the change in vapour pressure stops and some constant value of vapour pressure is obtained. This equilibrium state can be expressed as below :

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$
Water (liquid)   Vapour of water (gas)
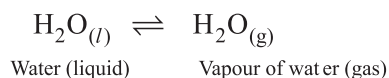
As this process is carried out in a closed vessel (system) some molecules of water change into water vapour. At the same time same number of molecules of water vapour change into water liquid. Hence, the amount of water and water vapours remain constant. Thus, this is one type of equilibrium between liquid (water) and gas (water vapour) and it is physical equilibrium.

It is important to note here that as there is no chemical change in the substance, it is the example of physical equilibrium.

(iii) Equilibrium Involving Dissolution of Solid in Solution :

For the study of this type of equilibrium the example of sugar and its solution in water can be taken. At constant temperature, take some water. Add some sugar into it and stir. In the beginning sugar easily dissolves, but as more and more amount of sugar is added, it dissolves according to its solubility and then some amount of sugar remains in solid form without dissolution. We know this state as saturated solution but in this system the equilibrium is also established between sugar (solid) and liquid (solution of sugar). This can be expressed as below :

$$Sugar_{(s)} \rightleftharpoons Sugar\ solution_{(aq)}$$
Solid   Liquid
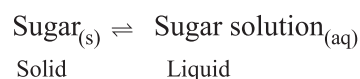
As studied earlier, equilibrium is dynamic because the forward and the reverse reactions continuously occur in each system. In this system, the amount of sugar that dissolves in water, same amount of sugar separates from solution of sugar. Hence, the number of molecules of sugar and number of aqueous molecules of sugar in the solution remain constant in this system.

(iv) Equilibrium Involving Gas and Solution :

At constant temperature and pressure, carbon dioxide can be dissolved in water in a closed vessel (system), so that a system containing gas and solution of carbon dioxide can be formed. As temperature and pressure are constant, carbon dioxide dissolves according to its pressure and temperature and forms solution of carbon dioxide and the excess carbon dioxide gas remains in equilibrium with it. Equilibrium is dynamic and so molecules of carbon dioxide gas that dissolve in water is the same as the number of molecules of the gas that release from the solution in the system. Thus, in this closed system, the total number of molecules (amount) of carbon dioxide in gaseous form and those that have dissolved in water remain constant. This equilibrium can be shown as below :

$$CO_{2(g)} \rightleftharpoons CO_{2(soln)}$$
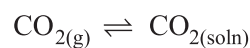
All the reactions studied above are processes in which only physical change takes place and so they all are examples of physical process equilibrium.

(v) Solid - Gas Process Equilibrium :
You know that when certain solid substances are heated, they get converted into gaseous state and on cooling are converted directly into solid from gaseous state. This process is known as sublimation. For the study of the equilibrium of this let us take example of solid iodine (I_2). In a closed vessel (system) some amount of solid iodine is taken and it is heated. At constant temperature, vapour of iodine is formed from solid iodine, which appears as a violet coloured gas. If the temperature is constant equilibrium can be expressed as below :

$$I_{2(s)} \rightleftharpoons I_{2(vap)}$$
$$\text{Solid} \qquad \text{Gas}$$
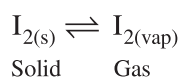
As equilibrium is dynamic at constant temperature, the number of molecules (amount) of iodine that are changed from solid iodine to vapour of iodine remain the same as the number of molecules (amount) of iodine vapour to solid iodine. Thus, in the closed vessel, the amount of iodine (solid and gaseous form) remains constant.

Table 4.1 Some Characteristics of Physical Process Equilibrium

Process	Conclusion (characteristic)
(1) Liquid $\rightleftharpoons$ Gas $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$	At constant temperature, P_{H_2O} remains constant.
(2) Solid $\rightleftharpoons$ Liquid $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$	At constant temperature melting point remains constant
(3) Solid $\rightleftharpoons$ Solution $sugar_{(s)} \rightleftharpoons$ solution of $sugar_{(aq)}$	At constant temperature, the solubility of solute in the solution remains constant.
(4) Gas $\rightleftharpoons$ Liquid $CO_{2(g)} \rightleftharpoons CO_{2(Vap)}$	At constant temperature the rates of concentration of gas dissolved in solution and concentration of gas in gaseous state remain equal.

4.4 General Characteristics of Equilibrium Involved in Physical Processes

The following are the general characteristics of systems in equilibrium for the physical systems discussed earlier.

(i) At constant temperature, equilibrium is possible only in closed system.

(ii) Both the processes (reactitons) opposite to each other that is, the forward and the reverse reactions occur at the same rates and the equilibrium involved in it remains dynamic but condition remains steady (static).

(iii) All the properties of the system which can be measured remain constant.

(iv) For physical process, when equilibrium is obtained then at constant temperature, the value of one of the factors remains constant. The list of these properties is shown in Table 4.1

(v) At any stage magnitude of such quantities show to what extent the physical process has advanced before reaching to equilibrium.

4.5 Chemical Process (Reaction) Equilibrium

Like physical processes, equilibrium state is also obtained in chemical processes (reactions). Equilibrium state is obtained when the chemical reactions occur in opposite directions to each other i.e. forward and reverse reactions and the rates of the reactions become equal. Hence concentrations of reactants and products remain constant. Chemical equilibrium is dynamic like physical equilibrium. i.e. The conversion of reactants to products and products to reactants continuously occur, and as a result all the reactants and products are present at equilibrium.

Let us think of a simple reversible reaction :

$$A + B \rightleftharpoons C + D$$
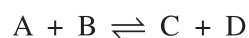
With the passing of the time, the products C and D increase and the reactants A and B decrease which is shown in Fig 4.1.
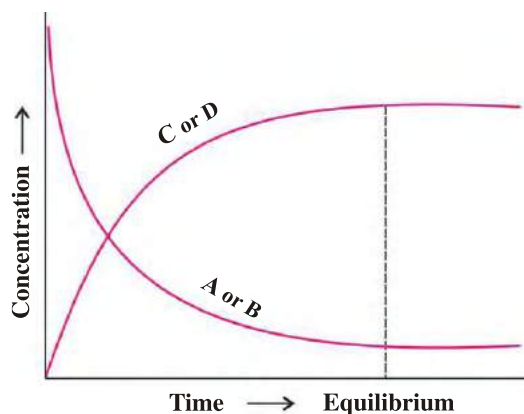
Fig. 4.1 Attainment of chemical equilibrium

It shows that at some point there is decrease in rate of forward reaction and increase in rate of reverse reaction. By chance, if both the reactions occur at the same rate, the system reaches to equilibrium state.

Suppose if we start by taking products C and D in the above reaction, even then equilibrium can be obtained. This means that even if the reaction occurs from any direction, equilibrium can be obtained.

Dynamic Nature of Chemical Equilibrium : The dynamic nature of chemical equilibrium can be demonstrated by taking example of the production of ammonia. By keeping known quantities of dinitrogen gas and dihydrogen gas at high temperature and pressure in a closed vessel, the amount of ammonia gas formed can be determined at constant intervals by a series of experiments. The quantities of unreacted dinitrogen and dihydrogen also can be determined. From this it is concluded that even if the reactants and products are in different proportions, their concentrations are same at equilibrium. This constancy in composition indicates dynamic nature of equilibrium. For this, in synthesis of ammonia, deuterium (D_2) instead of dihydrogen, (H_2) is used and ammonia gas is produced by Haber process and it is studied. The results obtained are similar to those obtained above. In the mixture proportions of N_2, D_2 and ND_3 instead of N_2, H_2, NH_3 can be determined and equilibrium can be obtained. If D_2 is added after the formation of ammonia by reaction of N_2 and H_2, the reaction may not occur but H in NH_3 is displaced by D and ND_3 can be determined by mass spectrometer. Thus, it is proved that in the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ that the reactions from reactants to

products and products to reactants that is forward and reverse reactions continuously occur with the same rates and so ND_3 instead of NH_3 is obtained. By the use of radioactive isotope, the dynamic nature of equilibrium can be proved viz. For the reaction, $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ radioactive isotope ^{131}I of iodine can be used to study the dynamic nature of chemical equilibrium. As the equilibrium is dynamic, certain properties or factors are found similar. e.g. Intensity of colour, constant pressure, constant concentration etc.

4.6 Law of Chemical Equilibrium and Equilibrium Constant

The mixture of reactants and products at equilibrium is called equilibrium mixture. We shall study the relation between concentrations of reactants and products at equilibrium state.

Let us take a simple reversible reaction as follows : $A + B \rightleftharpoons C + D$

In this reaction A and B are reactants and C and D are products. This means that in this reaction moles of reactants and products are one each but in all reactions this may not happen. Hence, it is necessary that their moles are expressed. Balanced reaction determines their moles. viz. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

From the experimental studies of many reversible reactions scientists of Norway, Guldberg and Waage mentioned in 1864 that the concentrations of substances in equilibrium mixture can be expressed by following equilibrium equation.

$$K_c = \frac{[C][D]}{[A][B]} = \frac{\text{Multiplication of concentrations of products}}{\text{Multiplication of concentrations of reactants}}$$

where K_c is equilibrium constant and [ ] bracket expresses concentration of reactant or product in mollit^{-1} or M. The equilibrium equation is also known as law of active masses because in the early years of chemistry, concentration was said to be 'active mass'.

Now, we shall derive the equation for equilibrium constant of a general reaction. Suppose, if a reaction takes place, as given below in which the reactants and products are shown in balanced form with their proper moles (a, b, c or d).

$$aA + bB \rightleftharpoons cC + dD \qquad ....4.1$$
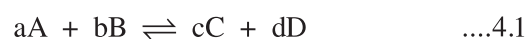
On the basis of Guldberg and Waage's law the rate of forward reaction

$$V_f \propto [A]^a [B]^b \qquad ....4.2$$

$$\text{or} \quad V_f = K_f [A]^a [B]^b ....4.3$$

where K_f is the proportionality constant for forward reaction.

The rate of reverse reaction $V_r \propto [C]^c [D]^d$....4.4

$$\text{or} \qquad V_r = K_r [C]^c [D]^d....4.5$$

where V_r is the proportionality constant for reverse reaction.

At equilibrium the rates of forward and reverse reaction will be equal and so $V_f = V_r$

that is, $K_f [A]^a [B]^b = K_r [C]^c [D]^d$

$$\therefore \frac{K_f}{K_r} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = K_c \qquad ......4.6$$

where $K_c = \dfrac{K_f}{K_r}$

Thus, when equilibrium is attained if we determine the concentration of the reactants and the products in any reaction and their stoichiometric multiples, the equilibrium constant K_c can be obtained.

Equilibrium constants of some reaction are as shown below :

(1) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_c = \dfrac{[HI]^2}{[H_2][I_2]}$

(2) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

(3) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(l)}$

$$K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$
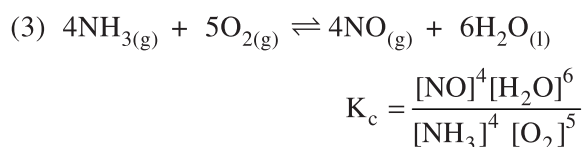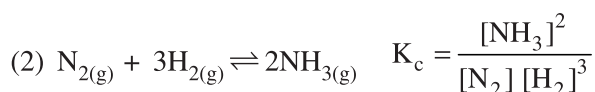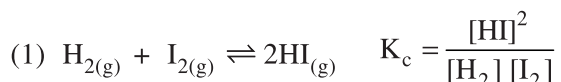
Let us think about reaction between H_2 and I_2. This reaction can be written as follows:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \quad \text{(From reactants to products)}$$

$$\therefore K_c = \frac{[HI]^2}{[H_2][I_2]}....4.7$$

Now, we write the reaction as follows :

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

$$\therefore K_c' = \frac{[H_2][I_2]}{[HI]^2} ....4.8$$

Equations 4.7 and 4.8 are inverse of each other. Hence $K_c' = \dfrac{1}{K_c}$. Thus, the equilibrium constant of forward reaction is the inverse of the equilibrium constant of reverse reaction.

The above reaction can also be written as follows :

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightleftharpoons HI_{(g)}$$
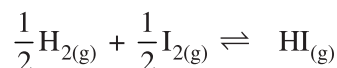
If we write the equilibrium constant for this reaction then,

$$\therefore K_c' = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}}$$

$$= \left[\frac{[HI]^2}{[H_2][I_2]}\right]^{\frac{1}{2}} ....4.9$$

$$\therefore K_c' = K_c^{1/2}$$

Multiplying reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ by n.

$$nH_{2(g)} + nI_{2(g)} \rightleftharpoons 2nHI_{(g)}$$
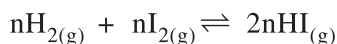
Equilibrium constant will be K_c^n

Hence, it can be written as follows :

Equation of chemical reaction	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	K_c
$cC + dD \rightleftharpoons aA + bB$	$K_c' = \dfrac{1}{K_c}$
$(n)aA + (n)bB \rightleftharpoons (n)cC + (n)dD$	$K_c^n = (K_c)^n$

Example 1 : The following reaction can be carried out in a closed vessel at 400 K. The concentration of hydrogen is 0.6 mol lit^{-1}, the concentration of iodine is 0.8 mol lit^{-1} and concentration of hydrogen iodide is 0.14 mol lit^{-1} at equilibrium state. Calculate the equilibrium constant of this reaction.

Solution :

Reaction $\qquad H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
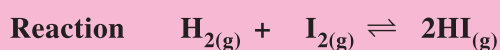
Concentration

at equilibrium :

mol lit^{-1} $\qquad\qquad$ 0.6 $\qquad$ 0.8 $\qquad$ 0.14

Equilibrium constant $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$

$$= \dfrac{(0.14)^2}{(0.6)(0.8)}$$

$$= 4.1 \times 10^{-2}$$

What will be the unit of K_c? Think and verify.

In gaseous reaction, if concentrations are expressed in partial pressures, then equilibrium constant can be obtained from partial pressures of reactants and products, and it is expressed as K_p. Let us think about a gaseous reaction :

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$
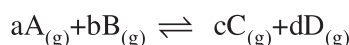
If we express partial pressures of reactants and products as p_A, p_B, p_C, and p_D respectively then the equation for chemical equilibrium K_p can be shown as below :

$$\therefore K_p = \dfrac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

4.7 Relation between K_p and K_c

As seen earlier the equilibrium constant of a gaseous reaction can be written as

$$\therefore K_p = \dfrac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} \qquad \text{........ 4.10}$$

But we know that according to simple gas equation $pV = nRT$. Hence, it can be written as

$$\therefore p = \dfrac{n}{V}RT = CRT$$

(where $\dfrac{n}{V} = C =$ concentration in mol lit^{-1}) Substituting the values of p in the above equation 4.10, it can be written as

$$\therefore K_p = \dfrac{(C_C RT)^c \, (C_D RT)^d}{(C_A RT)^a \, (C_B RT)^b}$$

$$= \dfrac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b} \cdot \dfrac{(RT)^{c+d}}{(RT)^{a+b}} \qquad \text{.........4.11}$$

$$= \dfrac{[C]^c \, [D]^d}{[A]^a \, [B]^b} \times (RT)^{(c+d)-(a+b)} \text{.........4.12}$$

$$= K_c \cdot (RT)^{\Delta n_g} \text{.........4.13}$$

where $\Delta n_g = (c + d) - (a + b)$

means number of total moles of gaseous products minus number of total moles of gaseous reactants.

Hence, it can be written as

$$K_p = K_c \cdot (RT)^{\Delta n_g} \text{..........4.14}$$

It is necessary to remember that in gaseous reaction, pressure depends on number of moles and so their partial pressures can be taken as concentrations. Atmosphere is the unit used for pressure but according to SI unit it is expressed as Pascal. A summary of K_p and K_c with respect to values Δn_g, can be written as follows : **(1) if $\Delta n_g = 0$ then $K_p = K_c$ (2) if $\Delta n_g > 0$ then $K_p > K_c$ (3) if $\Delta n_g < 0$ then $K_p < K_c$**

Example 2 : 1 mole H_2O and 1 mole CO are heated in a colsed vessel of 10 litres at 725 K temperature. At equilibrium H_2O 40% by mass reacts with CO gas as follows :

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$
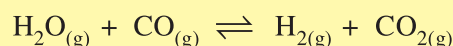
Calculate equilibrium constants K_p and K_c for this reaction :

Solution :

Reaction : $H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$

Initial concentration

mol lit^{-1}

$\dfrac{1}{10}$	$\dfrac{1}{10}$	0	0

Concentration at equilibrium mol

$\dfrac{1(100-40)}{100}$	$\dfrac{1(100-40)}{100}$	$\dfrac{40}{100}$	$\dfrac{40}{100}$
$= 0.6$	$= 0.6$	$= 0.4$	$= 0.4$

concentration mol lit^{-1}

$\dfrac{0.6}{10}$	$\dfrac{0.6}{10}$	$\dfrac{0.4}{10}$	$\dfrac{0.4}{10}$
$= 0.06$	$= 0.06$	$= 0.04$	$= 0.04$

Now, $K_c = \dfrac{[H_2][CO_2]}{[H_2O][CO]} = \dfrac{0.04 \times 0.04}{0.06 \times 0.06} = 0.44$

Now $K_p = K_c \cdot (RT)^{\Delta n_g}$

In this reaction (number of moles of gaseous products) − (number of moles of gaseous reactants)

$(1 + 1) − (1 + 1) = \Delta n_g = 0$

Hence, $K_p = K_c \cdot (RT)^0 = K_c$

Hence, the values of K_p and K_c will be same i.e. 0.44

Example 3 : The equilibrium constant of the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ at 700 K temperature is 54.8. The concentration of HI at equilibrium is 0.5 mollit^{-1}. Suppose reaction is carried by taking $HI_{(g)}$ find concentrations of $H_{2(g)}$ and $I_{2(g)}$ at equilibrium.

Solution :

Reaction : $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
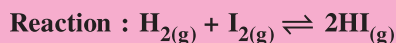
$K_c = \dfrac{[HI]^2}{[H_2][I_2]} = \dfrac{(0.5)^2}{[H_2][I_2]}$

i.e. $54.8 = \dfrac{(0.5)^2}{[H_2][I_2]}$

$\therefore [H_2][I_2] = \dfrac{(0.5)^2}{54.8}$ But at equilibrium

$H_{2(g)} = I_{2(g)}$ and

$[H_2][I_2] = \dfrac{(0.5)^2}{54.8} = 4.56 \times 10^{-3}$

$[H_2] = [I_2] = \sqrt{4.56 \times 10^{-3}} = 0.0675$ mollit^{-1}

Activity : Derive relation amongst K_c, K_p and K_x.

Hint : According to Dalton's law of partial pressures, if the total pressure is P atmosphere, the partial pressures of reactants A and B and partial pressures of products C and D will be $X_A \cdot P_A$, $X_B \cdot P_B$, $X_C \cdot P_C$ and $X_D \cdot P_D$ respectively, where X is mole fraction. Using this derive the following relations :

$K_p = K_x \cdot P^{\Delta n_g}$ and $K_c = K_x \cdot V^{-\Delta n_g}$

4.8   Types of Chemical Equilibrium

The equilibrium is of two types :

(i) Homogeneous equilibrium and

(ii) Heterogeneous equilibrium.

(i) Homogeneous equilibrium : In homogeneous system all the reactants and the products are in one similar phase viz.

The product ammonia produced by reaction of reactants dinitrogen and dihydrogen, all are in gaseous phase. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$. Similarly, the hydrolysis of methyl acetate is also homogeneous equilibrium because, the reactants and the products in it are also in the same phase (liquid phase).

$CH_3COOCH_{3(l)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(l)} + CH_3OH_{(l)}$
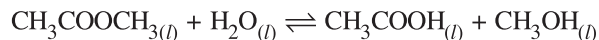
In addition to this, the reaction between aqueous solution containing Fe^{3+} ions and aqueous solution containing SCN^- ions is also an example of homogeneous equilibrium. But the only change in it is that this equilibrium is ionic equilibrium.

$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}_{(aq)}$
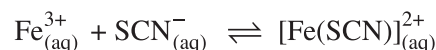
We shall study this, later on in this unit.

All the equilibrium reactions and their equilibrium constants that we discussed earlier are the examples of homogeneous equilibrium and also derived from the relations between K_p, K_c and K_x related to them. For calculation of values of K_p pressures must be expressed in unit of bar because, bar is the unit in standard condition but in SI unit it is pascal. The relation between them is as follows :

1 Pascal Pa = 1 Nm^{-2} (Newton meter^{-2}) and 1 bar = 10^5 Pa.

For calculation of equilibrium constants of homogeneous equilibrium constant, we understand the following examples :

Example 4 : $PCl_{5(g)}$ can be obtained by chemical reaction between $PCl_{3(g)}$ and $Cl_{2(g)}$ in closed vessel. The concentrations of PCl_3, Cl_2, and PCl_5 in this reaction at 500 K are 1.59 m, 1.59 M and 1.41 M respectively, calculate equilibrium constant of this reaction.

Solution :

Reaction : $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$
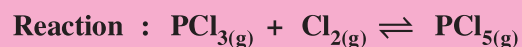
$K_c = \dfrac{[PCl_5]}{[PCl_3][Cl_2]} = \dfrac{1.41}{1.59 \times 1.59}$

$= 5.58 \times 10^{-3}$ mollit^{-1}

Suppose, we want to calculate K_p for this reaction. According to relation,

$K_p = K_c (RT)^{\Delta n_g}$

$K_p = 5.58 \times 10^{-3} (0.0831 \times 500)^{-1}$

because Δn_g = number of moles of gaseous product − number of moles of gaseous reactants
= 1 − 2 = −1

$$\therefore K_p = \frac{5.58 \times 10^{-3}}{(0.0831 \times 500)}$$

$$= 1.3 \times 10^{-4} \text{ bar}^{-1}$$

Example 5 : Ethyl acetate is obtained by reaction of ethanol with acetic acid in presence of H^+ ions. Suppose 1 mole acetic acid and 0.18 mole ethanol are taken in this reaction. At equilibrium 0.171 mole ethylacetate is obtained. Calculate equilibrium constant of this esterification reaction.

Solution :

Reaction :

$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$
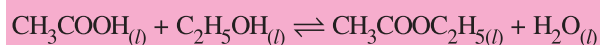
Initial

concentration :

1 mol   0.18 mole   0   0

concentration

at equilibrium

(1-0.171)mole (0.18-0.171)mole 0.171mole 0.171mole

0.829mol   0.009mole   0.171mole 0.171mole

$$K_c = \frac{[CH_3COOC_2H_5] [H_2O]}{[CH_3COOH] [C_2H_5OH]}$$

$$= \frac{0.171 \times 0.171}{0.829 \times 0.009} = 3.92$$

Example 6 : The value of equilibrium constant for the reaction $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$ is obtained as 0.033 bar at 1060 K temperature, then what will be the value of K_c for this reaction ?

Solution :

Reaction : $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$
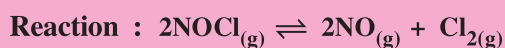
As we know, that $K_p = K_c (RT)^{\Delta n_g}$

Δn = Moles of $NO_{(g)}$ + Moles of $Cl_{2(g)}$ − (Moles of $NOCl_{(g)}$)

= (2 + 1−2) = 3−2 = 1

Putting the values, $0.033 = K_c (0.0831 \times 1060)^1$

$$\therefore K_c = \frac{0.033}{0.0831 \times 1060}$$

$$= 3.7 \times 10^{-4} \text{ mol.lit}^{-1}$$

(ii) Heterogeneous Equilibrium : If reactants and products, possess more than one phase, the equilibrium is called heterogeneous equilibrium. The equilibrium between water (liquid) and water vapour (steam) in a closed vessel is the example of heterogeneous equilibrium.

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$
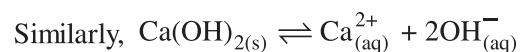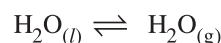
Similarly, $Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$ is also the example of heterogeneous equilibrium. (Equilibrium between solid and liquid). It is necessary to note here that this is an example for ionic equilibrium.

Generally, in heterogeneous equilibrium, pure solid or liquid are associated, the concentrations of reactants and products can be separated, viz. The concentration of pure solid or liquid is its density and density is constant at constant temperature. Hence, concentration can also be taken as constant or the pure solid or liquid which are present will be independent of concentration. Suppose, some substance X is involved in this, then concentrations $X_{(s)}$ and $X_{(l)}$ will be taken as constant in whatever proportion they are present while concentrations of $X_{(g)}$ and $X_{(aq)}$ will change and will vary with volume.

Let us take example of thermal decomposition of calcium carbonate.
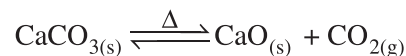
$$CaCO_{3(s)} \xrightleftharpoons{\Delta} CaO_{(s)} + CO_{2(g)}$$

If we write the equation for heterogeneous equilibrium on the basis of stoichiometry then,

$$K_c = \frac{[CaO_{(s)}] [CO_{2(g)}]}{[CaCO_{3(s)}]} \qquad ....4.15$$

As discussed earlier, $CaO_{(s)}$ and $CaCO_{3(s)}$ are in solid state, their concentrations can be taken equal to their densities, i.e. they remain constant. Hence, the above equation can be written as below :

$$K_e \times K_1 = K_c = [CO_{2(g)}] \qquad ....4.16$$

where, $K_1 = \dfrac{[CaCO_{3(s)}]}{[CaO_{(s)}]}$ or $K_p = p_{CO_2}$

where P_{CO_2} is the concentration or pressure of CO_2 gas at equilibrium. The equilibrium constant of above reaction is found to be 2.0×10^5 at 1100 K temperature. Hence, $K_p = P_{CO_2} = 2.0 \times 10^5$ Pa. Converting it into bars,

$$\dfrac{2 \times 10^5 \text{ Pa}}{1 \times 10^5 \text{ Pa / bar}} = 2.0 \text{ bar}$$

It is necessary to remember that in heterogeneous equilibrium, even if the solid and liquid are in very less proportion, their concentrations or partial pressures are not considered in equilibrium constant, viz. For the reaction,

$$Ag_2O_{(s)} + 2HNO_{3(aq)} \rightleftharpoons 2AgNO_{3(aq)} + H_2O_{(l)}$$
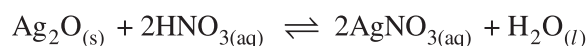
$$K_c = \dfrac{[AgNO_{3(aq)}]^2 \, [H_2O_{(l)}]}{[Ag_2O_{(s)}] \, [HNO_{3(aq)}]^2}$$

$$= \dfrac{[AgNO_{3(aq)}]^2}{[HNO_{3(aq)}]^2}$$

because, $[H_2O_{(l)}]$ and $[Ag_2O_{(s)}]^2 = $ constant.

4.9 Characteristics of Equilibrium

(i) During chemical equilibrium, the properties like colour, concentration, pressure or temperature of the system remain constant and they are similar in the total area of the system.

(ii) When chemical equilibrium is attained, the rates of forward and reverse reactions become equal.

(iii) If the factors like concentration, pressure, temperature etc. which affect the chemical equilibrium are changed, they produce effect on equilibrium.

(iv) Even if the initial concentrations are different, the equilibrium constant remains constant at constant temperature.

(v) The value of equilibrium constant changes if the temperature changes.

(vi) For attainment of equilibrium, the reaction can be carried out from left to right (reactants to products) or from right to left (products to reactants).

(vii) There is no effect of catalyst on the equilibrium constant and so the proportions of products remain same but the rate of reaction to attain equilibrium increases.

Units of Equilibrium Constant : To express equilibrium constant K_c, the concentrations are required in mol lit^{-1} or M and for K_p, Pa, kPa, bar or atmosphere is taken. Hence, after selecting these units, if the numerator and denominator become equal, then there will be no unit or equilibrium constant and will be unitless and ratio will become 1. But if the concentrations of substances are expressed in their stoichiometric proportions, and are written accordingly, then the unit will be there. Some reactions and units of their K are expressed below :

Reaction :	Unit
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	Unitless

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
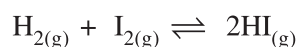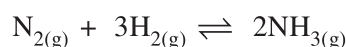
$$\dfrac{(mol.lit^{-1})^2}{(mol.lit^{-1})(mol.lit^{-1})^3}$$

$$= (mol. \ lit^{-1})^{-2}$$

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons$$

$$CH_3COOC_2H_{5(l)} + H_2O_{(l)} \quad \text{Unitless}$$
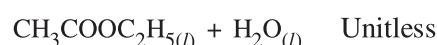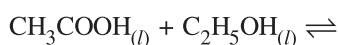
Example 7 : The equilibrium constant of the reaction $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$, K_c is 4.25 at 810 K. Suppose, if this reaction begins with reactants having concentrations 0.1 mol.lit^{-1} or M, then calculate the concentrations of $CO_{(g)}$, $H_2O_{(g)}$, $CO_{2(g)}$ and $H_{2(g)}$ at equilibrium at 810 K.

Solution :

Reaction : $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$
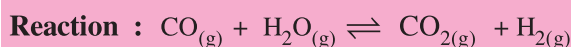
Initial concentration

0.1M	0.1M	0	0

Concentration at equilibrium

$(0.1 - x)$M	$(0.1 - x)$M	xM	xM

where xM is the concentration of $CO_{2(g)}$ and $H_{2(g)}$ at equilibrium. Now, equilibrium constant

$$K_c = \frac{[CO_{2(g)}]\,[H_{2(g)}]}{[CO_{(g)}]\,[H_2O_{(g)}]}$$

$$= \frac{[x]\,[x]}{[0.1-x]\,[0.1-x]}$$

$$\therefore 4.25 = \frac{x^2}{[0.1-x]^2}$$

$$\therefore x^2 = 4.25(0.01 - 0.2x + x^2)$$

$$\therefore x^2 = 0.0425 - 0.850x + 4.25x^2 = 0$$

$$\therefore 3.25x^2 - 0.850x + 0.0425 = 0$$

The coefficients of quadratic equation are $a = 3.25$, $b = -0.850$ and $c = 0.0425$. The solution of quadratic equation $ax^2 + bx + c = 0$ is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{+0.850 \pm \sqrt{(0.85)^2 - 4(3.25)(0.0425)}}{(2 \times 3.25)}$$

$$\therefore x = \frac{0.850 \pm 0.41}{6.50}$$

$\therefore$ One out of the two solutions

$x_1 = \dfrac{0.850 + 0.41}{6.50} = 0.19$ and second solution

$x_2 = \dfrac{0.850 - 0.41}{6.50} = 0.068$. But initial concentration is 0.1M. Hence, the value 0.19M is not acceptable. Hence, $x = 0.068$M is acceptable.

Thus, $x = [CO_{2(g)}] = [H_{2(g)}] = 0.068$M and concentration of $CO_{(g)}$ at equilibrium will be $(0.1 - x) = (0.1 - 0.068) = 0.032$ M. and concentration of $H_{2(g)}$ at equilibrium will be $(0.1 - x) = (0.1 - 0.068) = 0.032$M.

4.10 Applications of Equilibrium Constant

Some of the important applications of equilibrium constants are as follows :

(i) Prediction of completion of reaction : The value of equilibrium constant shows proportion of completion of the reaction. If the value of $K_c > 1$, then more proportion of products will be obtained, i.e. the reaction of getting products from the reactants will be towards completion. If the value of K_c is less than 1, then the proportions of reactants will be more as compared to products and so there will be decrease in the tendency for the completion of the reaction. If value of K_c is 1, then the proportions of reactants and products will be in equilibrium state.

(ii) Prediction about the forward or reverse direction of the reaction : The prediction about the reaction at any stage will occur in which direction can be decided from the value of equilibrium constant. For this we have to calculate the reaction quotient (Q_c). As mentioned earlier, the value of K_c for the reaction $aA + bB \rightleftharpoons cC + dD$.

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} = Q_c$$

If $Q_c < K_c$, or $K_c > Q_c$, then reaction will occur in forward direction, i.e. from reactants to products. If $Q_c > K_c$ or $K_c < Q_c$, then the reaction will occur in reverse reaction, i.e. from products to reactants. If $Q_c = K_c$, the reaction will remain in equilibrium.

Example 8 : The value of K_c for the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ is found to be 57.0 at 700 K temperature. Suppose in reaction mixture the concentrations of reactants and products at some determined time are as follows : $[H_2] = 0.05$M, $[I_2] = 0.10$M and $[HI] = 0.20$M. Determine in which direction the reaction will proceed :

Solution :

Reaction : $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
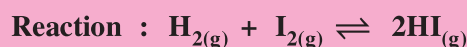
$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = Q_c$$

$$Q_c = \frac{(0.20)^2}{(0.05)\,(0.1)} = \frac{0.04}{0.005} = 8$$

Thus, $Q_c = 8$ and $K_c = 57.0$. Hence, $Q_c < K_c$ i.e. The reaction will occur in forward direction which means that reaction will occur in the direction of obtaining product from reactant.

(iii) Calculation of Equilibrium Concentration : If we know the concentrations of reactants and products at equilibrium time we can calculate the value of equilibrium constant and if the initial concentration of the reactants and the value of equilibrium constant are known, equilibrium concentrations can be calculated. For this the following steps are to be followed.

Step 1 : Write chemical reaction in balanced form.

Step 2 : (a) Mention the initial concentrations of reactants and products below them and (b) Mention the changes that take place when equilibrium is reached. Mention concentration in $mol\,lit^{-1}$ or pressure in bar. Write x for the unknown concentrations and then mention their stoichiometry.

Step 3 : Put the values of equilibrium concentration in the equation of chemical equilibrium and solve the equation. If quadratic equation is obtained, find out the two values using formula for it and determine the acceptable value.

Step 4 : From the value of x, determine the acceptable value.

Step 5 : Verify the value of equilibrium constant by putting the values of equilibrium concentrations in the equation for equilibrium constant.

Example 9 : 6.9 gram N_2O_4 is taken in a closed versel of 0.5 litre volume. Temperature is 400 K. Required time passes to obtain equilibrium. If the reaction is $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ and at equilibrium total pressure is 9.15 bar, calculate K_c, K_p and partial pressures at equilibrium. $R = 0.082$ lit atm mol^{-1} $kelvin^{-1}$

Solution :

Reaction : $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
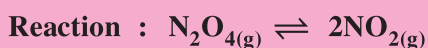
$$\text{Moles of } N_2O_4 = \frac{\text{Mass of } N_2O_4}{\text{Molecular mass}}$$

$$= \frac{6.9}{92} = 0.075$$

The volume of closed vessel is 0.5 lit.

Now, $PV = nRT$

$$P = \frac{n}{V}RT$$

$$= \frac{0.075}{0.5} \times 0.082 \times 400 = 4.92\,\text{bar}$$

At equilibrium total presure is 9.15.

Reaction : $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
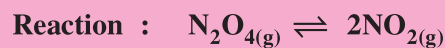
Initial concentration 4.92 bar   0 bar (pressure)

At equilibrium

concentration (pressure)

$\quad\quad\quad\quad$ $(4.92 - x)$ bar $2x$ bar

where x = concentration (pressure) of NO_2

Now, total pressure = partial pressure of $N_2O_{4(g)}$ + partial pressure of $NO_{2(g)}$

$\therefore$ $9.15 = (4.92 - x) + 2x$

$\therefore$ $9.15 = 4.92 - x + 2x = 4.92 + x$

$\therefore$ $x = 9.15 - 4.92 = 4.23$ bar

Partial pressure of $N_2O_{4(g)}$ at equilibrium

$p_{N_2O_4} = 4.92 - 4.23 = 0.69$ bar

Partial pressure of $NO_{2(g)}$, at equilibrium.

$p_{NO_2} = 2x = 2 \times 4.23 = 8.46$ bar

Now, $K_p = \dfrac{(p_{NO_2})^2}{(p_{N_2O_4})}$

$$= \frac{(8.34)^2}{0.69} = 103.73 \text{ bar}$$

$K_p = K_c\,(RT)^{\Delta n_g}$

$\therefore$ $103.73 = K_c\,(0.082 \times 400)^1$

Here Δn_g = (moles of gaseous NO_2 −

$\quad\quad\quad\quad\quad\quad$ moles of gaseous N_2O_4)

$\quad\quad\quad$ $= (2 - 1) = 1$

$\therefore$ $K_c = \dfrac{103.73}{0.082 \times 400}$

$\quad\quad$ $= 3.162 \approx 3.2$ mol lit^{-1}

4.11 Relation Between Reaction Quotient Q_c, Equilibrium Constant K and Gibbs' Free Energy

Chemical equilibrium has no relation with chemical kinetics, but it is definitely related to thermodynamics. In thermodynamics, the change in free energy ΔG is known as Gibbs free energy change. This difference is the difference

between total free energy of products and total free energy of reactants. Three possibilites are there : negative, zero and positive. We shall discuss its relation with equilibrium constant.

(i) If the value of ΔG is negative, then the reaction will be spontaneous (will occur on its own) and it will always proceed in the direction toward products i.e. forward reaction.

(ii) If the value of ΔG is positive then the reaction will not be spontaneous and will always proceed in the direction from products to reactants.

(iii) If the value of ΔG is zero, then the reaction will be in equilibrium i.e. the concentrations of reactants and products will be in equilibrium and the reaction will not proceed towards either of the forward or reverse reactions.

In the thermodynamics, the relation between changes in free energy and concentration Quotient (Q_c) is as follows :

$$\Delta G = \Delta G^0 + RT \ln Q_c \quad .... \; 4.17$$

where ΔG^0 = standard Gibbs free energy change or it is the value of Gibbs standard free energy change.

As we have seen, ΔG = 0 at equilibrium,

Hence, $Q_c = K_c$ and in putting the value equation 4.17,

$$\Delta G = \Delta G^0 + RT \ln K = 0 \quad ...... \; 4.18$$

or $\Delta G^0 = - RT \ln K \quad ...... \; 4.19$

If we write this equation by taking antilogaritham it can be written as

$$K = e^{-\Delta G^0/RT} \quad ...... \; 4.20$$

Hence, equation 4.20 can be used and related to the spontaneity and ΔG of the reaction.

(i) If $\Delta G^0 < 0$, then $-\Delta G^0/RT$ will be positive. Hence, it can be said that K > 1 or the values of ΔG is negative, the reaction will always proceed in the direction of forward reaction and proportions of products will be more.

(ii) If $\Delta G^0 > 0$ then $-\Delta G^0/RT$ will be negative and so K < 1. This shows that the reaction will not be spontaneous and the proportion of products will be less than those of reactants.

Example 10 : The value of equilibrium constant in reaction of phosphorylation of glucose during glycolysis was obtained 3.8×10^{-3} at 298 K temperature. Calculate the value of ΔG^0 for this reaction and mention your opinion about this reaction.

Solution : $K = 3.8 \times 10^{-3}$ and T = 298 K

Now, $\Delta G^0 = - RT \ln K$

$= - 2.303 RT \log K$

$= -2.303 \times 8.314 \times 298 \times \log 3.8 \times 10^{-3}$

$= -2.303 \times 8.314 \times 298 \times (-2.4202)$

$= 13809 \; Jmol^{-1} \approx 13.81 \; kJmol^{-1}$

The value of ΔG^0 being positive, the reaction will not be spontaneous.

4.12 Factors Affecting Chemical Equilibrium

In industries, the intention is to obtain maximum product with minimum expenses. Hence, the study of factors affecting the equilibrium constant and their aggregation (interpretation) becomes more important in the method to keep the equilibrium. In the study of factors affecting equilibrium concentration or pressure of reactants, temperature, and use of catalyst are studied. The production of ammonia by Haber process, using dinitrogen and dihydrogen is an important reaction, because it is used in the industrial production of several tons of artificial fertilizers. Hence, the study of factors affecting such reactions becomes essential.

Equilibrium constant is independent of initial concentration of reactant but, if change is carried out in concentration or pressure, there is an effect on equilibrium, the equilibrium tries to nullify this effect. Reaction can be endothermic or exothermic. Hence the heat absorbed or evolved, functions like that of the reactant and that of the product and its effect is on equilibrium which tries to nullify the effect. Le Chatelier studied the effect of concentration and temperature and his presentation is called Le Chatelier's principle whose statement can be written as below :

"If from the factors determining the equilibrium state, any one factor is changed, there will be such a change in the system that the effect will be nullified or made negligible so that the value of equilibrium constant at that temperature will remain constant." This principle

can be applied to both physical and chemical equilibrium.

We shall study in detail the factors like (1) change in concentration (2) change in pressure (3) addition of inert gases (4) change in temperature and (5) use of catalyst affecting the equilibrium.

(1) Effect of change in concentration : If we add or remove the reactant or the product from the reaction in equilibrium, its effect on equilibrium according to Le Chatelier's principle will be as follows :

(a) If the concentration of reactant or product is increased by addition of reactant or product, the reaction will occur in such a way that the increase in concentration will be taken for use i.e. the increase in concentration of reactant, the concentration of product will increase and if concentration of product is increased the reaction will result in the direction of increase in concentration of the reactant.

(b) If the concentration of reactant or product is decreased by removing reactant or product, the reaction will occur in such a way that product or reactant will be established again.

Hence, if any change in concentration of reactant or product is carried out then the equilibrium will try to make this effect minimum and equilibrium will be established accordingly. If we take this as an example, in the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_3$, if concentration of reactants dinitrogen or dihydrogen is increased, the reaction will proceed towards right hand side and the product ammonia obtained will be more. If the concentration of dinitrogen or dihydrogen is decreased, the reaction will proceed towards left hand side and reactants of dinitrogen or dihydrogen will be obtained back i.e. production of ammonia will decrease. Here, it is necessary to remember that 1 mole dinitrogen combines with 3 moles of dihydrogen in this reaction and forms 2 moles of ammonia. Hence, increase in concentration of dihydrogen rather than dinitrogen, will give more product. We take another example of heterogeneous equilibrium. If solid $CaCO_{3(s)}$ is heated in closed vessel, the following decomposition reaction will occcur.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

Hence, if more $CaO_{(s)}$ is to be obtained then, the $CO_{2(g)}$ formed in the reaction should be removed because $CO_{2(g)}$, gas can combine with solid $CaO_{(s)}$ and carry out reverse reaction then proportion of product will decrease. Hence, by removing $CO_{2(g)}$ from the reaction vessel, more $CaO_{(s)}$ can be obtained.

Activity : Let us think about one example from ionic equilibrium $Fe^{3+}_{(aq)}$ ion reacts with $SCN^-_{(aq)}$ ion and forms $[Fe(SCN)]^{2+}_{(aq)}$ ion.

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}$$
light yellow colour   colourless   colour like blood
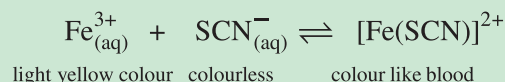
In this reaction, if concentration of reactant is increased by addition of $Fe^{3+}_{(aq)}$ or $SCN^-_{(aq)}$ ion, then more $[Fe(SCN)]^{2+}_{(aq)}$ will be formed and so the red colour will become more dark. If concentration of product is increased by addition of $[Fe(SCN)]^{2+}_{(aq)}$, then concentration of $[Fe(SCN)]^{2+}_{(aq)}$ will decrease and the darkness of red colour will decrease because the reaction will move towards reactant.

This is given as an experiment for demonstration in practical book. Hence, it can be carried out as the activity.

(2) Effect of change of pressure : The change in pressure can be carried out by increasing or decreasing the concentration of the gas or respectively decreasing or increasing the volume of the vessel. By carrying out this type of change, there will be change in proportions of gaseous reactants or products or total products. Le Chatelier's principle can also be applied to such reactions. In heterogeneous equilibrium if we do not take into consideration the effect of pressure on solid or liquid substances in equilibrium, it can work because their volumes and concentration are independent of change of pressure. Let us take the following example.

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$$
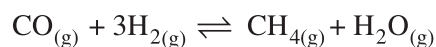
In this reaction 1 mole of reactant $CO_{(g)}$ reacts with three moles of reactant $H_{2(g)}$ and forms 1 mole product $CH_{4(g)}$ and 1 mole product $H_2O_{(g)}$. Thus, 2 moles product is obtained from 4 moles of reactants. Hence, there is decrease in number of moles during reaction.

Suppose, the pressure on the closed vessel in which the reaction is carried out at constant temperature and the volume of equilibrium mixture is made half, then what will happen? Total pressure will be double because

PV = constant. the concentrations or pressures of reactants or products are increased. Hence, according to Le Chatelier's principle, the equilibrium will try to attain the original state. As pressure is doubled and 2 moles of products are obtained and 4 moles of reactants, there is decrease in number of moles and the reaction will go in forward direction i.e. more product will be obtained.

As a reverse of this, if in reaction $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ the number of moles of product increases (from 0 to 1). If pressure is increased by addition of $CO_{2(g)}$, then, the reaction will become reverse reaction and will decrease the product.

(3) Addition of inert gas : If the volume of the system is kept constant and inert gas not taking part in the reaction is added, then there will be no effect on equilibrium. As inert gas does not react with reactant or product, their partial pressure will not change and as a result there will not be any effect on equilibrium. As seen earlier that K_c which depends on Q_c, there is no change on it.

(4) Effect of temperature : The value of equilibrium constant is associated with temperature i.e. the value of equilibrium is constant at constant temperature. If temperature changes its value also changes. Reactions can be of two types (1) Exothermic and (2) Endothermic. With the change in temperature, there is a change in absorbed or evolved heat. In exothermic reaction when heat is absorbed it works as a reactant. In exothermic reaction when heat is evolved, it works as a product. Hence, it can be said that the equilibrium constant increases with increase in temperature in endothermic reaction; equilibrium constant decreases with increase in temperature in exothermic reaction. Especially, let us make it clear that the increase or decrease in temperature affects the rate of reaction. Let us think about reaction of production of $NH_{3(g)}$.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92.38 \text{ kJmol}^{-1}$$
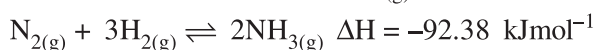
ΔH means change in enthalpy which is the difference in total enthalpies of products and reactants. Its positive value indicates endothermic reaction and negative value indicates exothermic reaction. Hence, the above reaction is exothermic. As seen earlier that increase in temperature is not favourable for exothermic reaction because

reaction will go in reverse direction and will decrease the product. Hence, decrease in temperature is advantageous to obtain more product but by decreasing the temperature the rate of reaction decreases. Hence, more time is required for completion of the reaction.

Hence, as a compromise, at the lowest possible temperature and at the highest possible pressure, catalyst is used. Hence, more possible product is obtained in less possible time. This type of state is called optimization state.

Activity : The effect of temperature on equilibrium can be studied by following reaction.

$$2NO_{2(g)} \underset{+\Delta}{\overset{-\Delta}{\rightleftharpoons}} N_2O_{4(g)} \quad \Delta H = - \text{ ve}$$

Brown coloar   Colourless
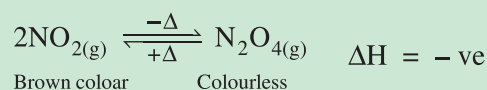
This reaction is exothermic and so the effect of decrease in temperature can be studied using ice and the effect increase in temperature can be studied by keeping the flask in a hot water vessel. For this activity, perform the experiment according to the experiment for demonstration given in a practical book and obtain conclusion regarding effect of temperature.

(5) Effect of catalyst : The use of suitable catalyst always helps to increase the rate of reaction, viz. iron powder is used as the catalyst in the production of ammonia by Haber's process. Use of catalyst is associated with chemical kinetics because it affects the rate of reaction. The function of catalyst is to decrease the energy of activation. Hence, the reaction easily moves forward towards product. During this reaction, the energy of activation decreases but has no effect on equilibrium constant, that is, more proportion of product cannot be obtained. Let us examine the case of reaction of ammonia gas obtained by combination of dinitrogen gas and dihydrogen gas with the help of Haber's process.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92.38 \text{ kJmol}^{-1}$$
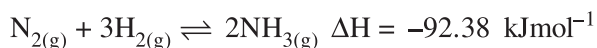
In the above reaction, total 2 moles product are obtained from total 4 moles of reactants. Hence, according to Le Chatelier's principle, increase in pressure is advantageous to get more ammonia but for the reactions occurring in closed vessel and so the pressure has to be kept limited. In addition, this reaction is exothermic and so according to Le Chatelier's principle, the decrease in temperature is advantageous but decrease in

temperature affects the rate of reaction. Hence, more time is required for completion of the reaction, which is not economically advantageous in industry. Hence, temperature is also to be restricted. By making compromise with these two and using catalyst whereby the energy of activation is decreased and increasing rate of reaction, more possible product is obtained in less time. Hence, Haber used iron powder as catalyst in the production reaction of ammonia and satisfactory results were obtained. In the production of ammonia, the values of optimum pressure and temperature are 200 bar and 773 K temperature respectively and iron powder is used as catalyst. If the value of equilibrium constant of the reaction K_c is very low then the use of catalyst is not fruitful or helpful.

4.13 Ionic Equilibrium in Solution

In this unit on equilibrium, we have so far studied the reactions in which molecular reactions are included. Now, the equilibrium that we shall study in this remaining part of the unit will be reactions in which ions are included. In the previous part of this unit, we have studied the chemical equilibrium and now we shall study ionic equilibrium in the remaining part of the unit. There is an experiment on ionic equilibrium in your practical book. When potassium thiocyanate solution is added to ferric nitrate solution blood like red colour can be obtained. This equilibrium reaction can be written in ionic form as below :

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}_{(aq)}$$

Light yellow colour   Colourless   Red colour like blood
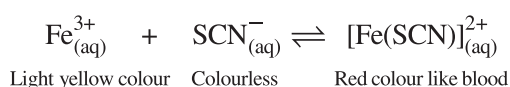
If we write the equilibrium constant, K_c for the reaction by expressing concentrations of ions, then $K_c = \dfrac{[Fe(SCN)]^{2+}}{[Fe^{3+}][SCN^-]}$. As the concentration of ions are expressed in $mollit^{-1}$ or molarity, equilibrium constant is expressed as K_c. Ions are mostly present in aqueous solutions.

You know that electric current can pass through the aqueous solution of sodium chloride and if we increase the concentration of sodium chloride, conductivity increases. When electric current is passed through water, negligible electric current is passed through it. In aqueous solution the electric current is conducted by ions. Hence, it can be said that in aqueous solution of sodium chloride, the ions are present in the solution. On the basis of this Michael Faraday classified

substances into two sections (1) electrolyte and non-electrolyte. In the above example, sodium chloride is an electrolyte because it conducts electricity and gets decomposed by electricity while pure water does not get decomposed by electricity and so it is a non-electrolyte.

Afterwards, it was found that electrolytes can be divided into two parts, viz. some compounds are in the form of ions obtained by complete ionisation of the compound and so their ionisation is almost 100%. e.g. solution of NaCl. Some compounds possess incomplete ionisation i.e. the number of ions in their aqueous solution is less (about 2 to 3%). The conduction of current in aqueous solutions, depend on the number of ions and so it can be said that substances like sodium chloride are completely ionised and so they are called strong electroleytes but substances like water are incompletely ionised and so they are called weak electrolytes. Examples are mentioned in the following Table 4.2.

Table 4.2

Type of Electrolyte	Examples
(1) Strong electrolyte	Aqueous solutions of HCl, NaOH, KCl, NaCl, etc.
(2) Weak electrolyte	Aqueous solutions of CH_3COOH, NH_4OH, CH_3NH_2 etc.

As strong electrolytes are completely ionised, the reaction takes place in forward direction and so equilibrium is not possible but weak electroytes are incompletely ionised and so the reaction occurs both in forward and reverse reactions so that equilibrium becomes possible. Thus, the study of equilibrium constant, factors affecting equilibrium can only be applied to weak electrolytes.

4.14 Acid, Base and Salt

We come in contact with acid, base and salt in our everyday life. In the stomach of a human being about 1.2 to 1.5 litres per day HCl is secreted. In addition, lemon juice, tamarind water etc. are acids. Bases like NaOH and KOH are used in preparation of soap. We also use salts like washing soda, baking soda and salt. Washing soda can be classified as weak base and acetic acid in vinegar as weak acid.

Most of the acids are sour in taste. Word 'Acidus' is there for sour in taste in Latin language. The word Acid is derived from it.

4.14.1 Definition of Acid and Base :

Earlier you have already studied about acids and bases and accordingly their definitions can be given as follows :

Acid means such a substance which is (1) Sour in taste (2) turns wet blue litmus paper red (3) forms salt and water by reacting with base (4) In certain circumstances produces hydrogen gas by reacting with metals. Similarly, base means such a substance which is (1) Bitter in taste (2) turns wet red litmus blue (3) forms salt and water by reaction with acid.

The above definitions have been derived from the properties of the acids and bases. Hence, they are called 'Operational' definitions. Their limitation is that they cannot explain why acids are sour and bases are bitter. Hence, operational definitions are called old definitions. The modern definitions used at present are called 'Conceptual' definitions in which Arrhenius, Bronsted-Lowry and Lewis definitions of acid and base are included which we shall study later on.

In the unit of solid state, you have studied that Na^+ and Cl^- ions are present in solid NaCl. Even then they do not conduct electricity because each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. i.e. the ions remain fixed and so are not available free for conduction of electricity but its aqueous solution or in its molten state conducts elecricity because the ions move apart from each other and become capable of conducting electricity. The reason for conduction of electricity in aqueous solution is due to the nature of water as polar solvent. Water can be expressed as $\overset{-\delta}{O}$ with $_{+\delta}H$ $H_{+\delta}$ on oxygen partial negative charge and on hydrogen partial positive charge are present. Na^+ from NaCl, gets attracted towards negatively charged oxygen $O^{\delta-}$ and Cl^- ion gets attracted towards the positively charged $H^{+\delta}$ in H_2O. Hence,

$$Na^+ + \overset{-\delta}{O}\big(^{+\delta H}_{+\delta H}\big) \longrightarrow Na^+_{(aq)} \quad \text{is formed}$$

$$Cl^- + \overset{H^{+\delta}}{\underset{H_{+\delta}}{O^{-\delta}}} \longrightarrow Cl^-_{(aq)} \quad \text{is formed}$$
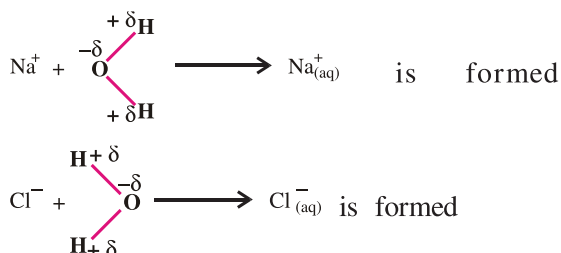
which try to separate from each other. Hence, conduction of electricity takes place.
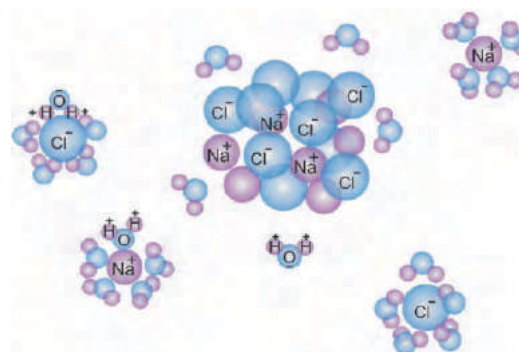
Fig. 4.2 Dissolution of sodium chloride in water

Na^+ and Cl^- ions are stabilised by their hydration with polar water molecules.

Hydrogen chloride and acetic acid are polar covalent compounds. When dissolved in water hydrogen chloride (HCl) is completely ionised viz. $HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$ but acetic acid (CH_3COOH) gets incompletely ionised viz.

$$CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

This type of reaction with water is called hydration reaction and for solvents other than water it is called 'Solvation'. Let us, understand the difference between two terms (1) Dissociation and (2) Ionisation. In dissociation, the positive ion and the negative ion present in the original substance are separated showing dissociation, viz.,

$$Na^+Cl^-_{(s)} + H_2O_{(l)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$
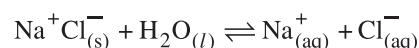
but in ionisation original substance is changed into ion form in aqueous solution. viz.

$$CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$
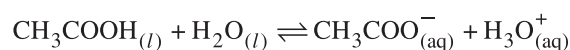
At this stage, we can consider both the terms having same meaning. (Note) : Thermal dissociation can be there, viz.,

$$NH_4Cl_{(s)} \underset{\Delta}{\rightleftharpoons} NH_{3(g)} + HCl_{(g)}$$ and ions are not obtained, only dissociate. The thermal ionisation is not known.

Arrhenius Concept about Acid and Base : According to Arrhenius concept, substances which dissociate in water and give hydrogen ion (H^+) are called acids and substances which dissociate in water and give hydroxyl ions (OH^-) are called bases e.g.

(1) $HCl_{(g)} \xrightarrow{+H_2O} H^+ + Cl^-$ \quad Acid

(2) $NaOH_{(s)} \xrightarrow{+H_2O} Na^+ + OH^-$ \quad Base
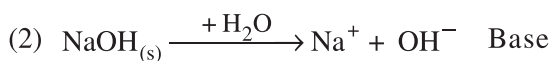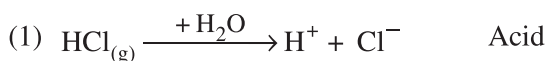
The limitations of this concept are as follows :

(i)   Proton (H^+) is highly unstable.

(ii) It can not exist independently.

(iii) It immediately combines with molecules of solvent water and gives H_3O^+ ions. Its addition in certain bases OH^- is not present even then they show properties of base, viz., NH_3. Similarly compounds like BF_3 do not possess H^+, even then they act as acid.

(iv) This concept can only be applied to aqueous solutions because salt like NH_4Cl reacts as acid in solvent like liquid NH_3. Hence, it is difficult to accept Arrtenius concept as the universal one, because ionisation is given importance. (In addition it is necessry to know that ionic radius of H^+ ion is about 10^{-15} meter and so it is very small in size.) Hence, it easily gets combined with molecules of water and forms H_3O^+ ion which is called hydronium ion. One estimate is that H^+ can be combined with four molecules of water showing. $H^+ + 4H_2O \rightarrow H_9O_4^+$ ion.

Concept of Bronsted - Lowry for Acid and Base : Danish chemist Bronsted and English chemist Lowry presented the concept of acid and base. They made H^+ (Proton) as a base. According to their concept, the substance which gives a proton or donates a proton is called the acid and the substance which receives a proton or accepts a proton is called the base. Thus, acid is a proton donor and base is a proton acceptor. Let us take the dissociation reaction of hydrogen chloride in water.

Similarly,
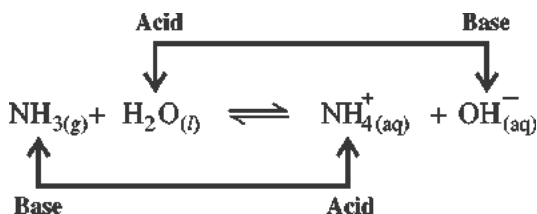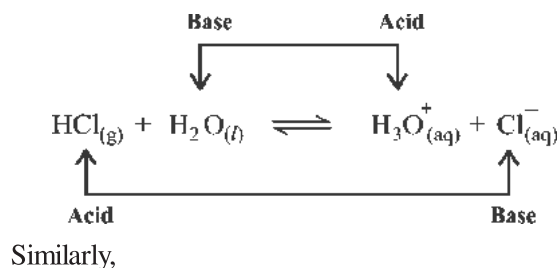
We shall understand in detail the first from the above reactions :

$$HCl \rightleftharpoons H^+ + Cl^-$$
Acid - 1   Proton   Conjugate base - 1
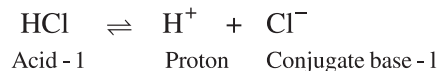
As it gives proton, HCl is an acid

$$H_2O + H^+ \rightleftharpoons H_3O^+$$
Base - 2   Proton   Conjugate acids - 2
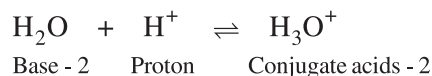
As it accepts a proton, H_2O is a base.

Total reaction :

$$HCl + H_2O \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$
Acid - 1   Base - 2   Acid - 2   Base - 1
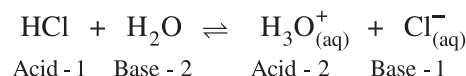
In the above reaction giving-taking of proton is not shown. Hence, it can be said that only transfer of proton takes place, it is not obtained free. Every acid will lose proton and so its conjugate base will be formed and every base will accept a proton and so its conjugate acid will be formed. Hence, this concept is known as proton transfer or conjugate acid-base concept.

We have earlier seen in limitations of Arrhenius concept that OH^- is not present in NH_3 even then it acts as a base but according Bronsted - Lowry concept it can be explained.

$$NH_3 + H_2O \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$$
Base - 1   Acid - 2   Acid - 1   Base - 2
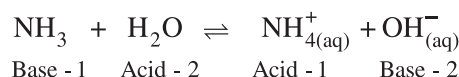
In the reaction, base NH_3 accepts a proton and forms conjugate acid NH_4^+ ion and acid H_2O loses proton and forms conjugate base OH^-.

Thus the concept of Bronsted - Lowry is found to be more applicable and acceptable than Arrhenius concept. Even then its limitations are also known. The difficulties are observed in the study of reactions in organic chemistry and complex salts. BF_3 has no proton even then it acts as an acid. Hence, the third concept has come in to existence, which is known as Lewis acid-base concept. Proton is given importance in Bronsted-Lowry concept.

Lewis Concept of Acid and Base : Lewis, in presenting this concept, in 1923, mentioned that acid means a substance which can accept a pair of electrons and base means a substance which can donate a pair of electrons. Thus, instead of the concepts of proton, ionisation, conjugate acid or base, he made electrons associated with all reactions and substances and

its arrangement as the base of the concept. As seen earlier BF_3 can be said an acid or not and NH_3 can be said a base or not can be solved by this concept. It will be clear from the following reaction :

| Acid | Base | Salt |
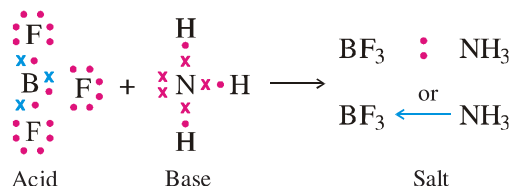
Thus, BF_3 accepts the pair of electron and so it is acid and NH_3 donates a pair of electron, so it is base. Electron deficient substances or ions like $AlCl_3$, Co^{3+}, Mg^{2+}, will act as acid and substances like H_2O, NH_3, OH^-, F^- will act as base. They are respectively called Lewis acid and Lewis base.

Activity : Study the above concepts and then give reason for the following statement. Discuss it with your teacher also. "All Bronsted-Lowry acids can be Lewis acids but all Lewis acids are not Bronsted-Lowry acid." Make a list of such acids and bases.

4.15 Ionisation of Acid and Base

Arrhenius concept of acid and base is useful in understanding ionisation of acid and base in most of the chemical and biochemical reactions, ionisation is there in aqueous medium. Acids like $HClO_4$, HCl, HNO_3, HBr, H_2SO_4, are called strong acids because they are completely ionised in aqueous solutions. Similarly bases like $NaOH$, KOH, $Ba(OH)_2$ are strong bases because they are completely ionised in aqueous medium. The magnitude of ionisation determines the strength of acid or base. According to Bronsted - Lowry, the magnitude of accepting or donating a proton delides the strong or weak (HA) acid or base.

Let us take the following example :

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$
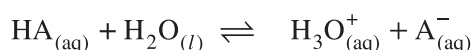
Thus, in above dissociation, equilibrium is attained and equilibrium is dynamic, that is the transfer of proton in forward and reverse reaction takes place continuously. If above reaction is more in forward reaction, then strength of acid will be more and if in reverse reaction, the strength of acid will be less and so their

respective conjugate base will be weak and strong respectively. e.g. The conjugate bases of strong acids HCl, H_2SO_4, HNO_3 etc. namely Cl^-, SO_4^{2-} and NO_3^- will be weak bases. In the same way the conjugate acids of strong bases $NaOH$, KOH etc, namely Na^+ and K^+ etc. will be weak acids. Weak acid or base may not ionise completely and so equilibrium is obtained. Indicator like phenolphthalein is colourless in presence of acid and shows pink colour in presence of base.

4.16 Ionic Product of Water

Water is an amphoteric oxide when acid is added to it; it accepts the proton and act as base and when base is added to it, it donates a proton and acts as acid. When reaction between two molecules of water takes place, one molecule donates proton and other molecule receives proton and shows conjugate acid-base reaction.

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

| Acid - 1 | Base - 2 | Conjugate acid - 2 | Conjugate base - 2 |
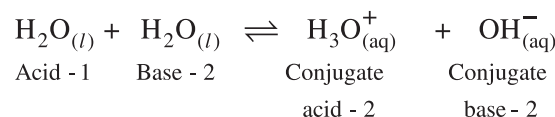
If we express the equilibrium constant of the above reaction then.

$$K_a = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$$

where K_a is the dissociation constant of acid. There is no significant change in concentration of water (55.5M) because H_2O is a weak acid (possesses about 10^{-7}M H^+). Thus, if H_2O is considered constant,

$$K_a \times [H_2O]^2 = [H_3O^+][OH^-] = K_w$$

where K_w is ionic product of water. Water is neutral and so $[H_3O^+]$ and $[OH^-]$ in it are 10^{-7} M. Hence, $K_w = [H_3O^+][OH^-] = (10^{-7})(10^{-7}) = 10^{-14}$ which is constant and equilibrium constant remains constant at constant temperature; so the value of K_w will be constant at constant temperature, viz., the value of K_w is 1×10^{-14} at 298 K. If we find the ratio of concentrations of dissociated and undissociated water, $10^{-7}/55.5 = 1.8 \times 10^{-9}$ equilibrium remain on left hand side, i.e. the number of undissociated molecules or its concentration will be more.

From the above study, three possibilities arise :

(i) $[H_3O^+] > [OH^-]$ i.e. concentration of $[H_3O^+]$ is more in solution and so solution is acidic.

(ii) $[H_3O^+] < [OH^-]$ i.e. concentration of $[OH^-]$ is more in solution and so solution is basic.

(iii) $[H_3O^+] = [OH^-]$ i.e. concentration of both $[H_3O^+]$ and $[OH^-]$ are equal and so solution will remain neutral.

4.17 pH Scale

If we express the concentration of hydronium ion $[H_3O^+]$ in molarity then values like 10^{-12} to 10^{-2} are possible. It is difficult to express these values on simple graph paper. Hence, scientist Sorensen found a scale which is called pH scale. According to him pH = $-\log_{10}[H_3O^+]$. The values 10^{-12} to 10^{-2} shown above can be converted to +12 to +2 if calculated on the basis of this relation and plotting of graph can be easy. The definition of pH can be given like this, "pH of a solution is the negative logarithm to the base 10, of the molar concentration of hydrogen or hydronium ion". According to thermodynamics, activity is more proper word instead of concentration but in dilute solutions activity and concentration can be considered to be the same. Now as seen earlier a solution containing 10^{-7}M $[H_3O^+]$ and $[OH^-]$ is neutral. Hence,

pH = $-\log_{10}[H_3O^+] = -\log_{10}10^{-7}$M = 7 and for acidic solution $[H_3O^+] > 10^{-7}$M, pH < 7 Similarly, for basic solution $[H_3O^+] < 10^{-7}$M, Hence, pH > 7. Therefore, it can be written as :

pH < 7 Acidic solution

pH > 7 Basic solution

pH = 7 Neutral solution

As seen above,

$K_w = [H_3O^+][OH^-]$

Putting the values, $K_w=(10^{-7})\,(10^{-7})=10^{-14}$

and $-\log K_w = -\log(10^{-14})$

$\therefore$ $pK_w = 14$

$\therefore$ pH + pOH = pK_w = 14

Temperature affects the values of pH, pOH, pK_w. The above discussion can be shown in the following table :

Concent-ration (M)	Acidic	Neutral	Basic
$[H_3O^+]$	more than 10^{-7}	10^{-7}	less than 10^{-7}
$[OH^-]$	less than 10^{-7}	10^{-7}	more than 10^{-7}
pH	less than 7	7	more than 7
pOH	more than 7	7	less than 7

pH paper, litmus paper or universal indicator can be used to test whether the solution is acidic or basic but the exact values of pH can be determined with the help of instrument called pH meter.

Example 11 : In one drink, the concentration of hydrogen ion is found to be 4×10^{-3}. What will be the value of its pH ? Also calculate the value of pOH.

Solution :

pH = $-\log_{10}[H_3O^+]$

= $-\log_{10}(4 \times 10^{-3})$ = $-(0.6021 - 3.0)$

= $+2.3979 \approx 2.4$

pK_w = pH + pOH

$\therefore$ 14 = 2.4 + pOH

$\therefore$ pOH = 11.6

Example 12 : Calculate pH and pOH of solution containing 0.03M NaOH.

Solution :

NaOH is a base so; $[OH^-]$ = 0.03M

Now, pOH = $-\log_{10}[OH^-]$

= $-\log_{10}(0.03)$

= $-(-2.000 + 0.4771)$

= $+1.5229 \approx 1.52$

Now, pK_w = pH + pOH

$\therefore \ 14 = pH + 1.52$

$\therefore \ pH = 12.48$

Solution 13 : 0.1 ml 0.001M HCl solution is diluted with water to make 10 litres. Calculate pH of the dilute solution.

Solution : According to

$$N_1V_1 \ = \ N_2V_2$$

$0.1 \times 0.001 = 10000 \times x$

$\therefore \ x = \dfrac{0.1 \times 0.001}{10000}$

$\therefore \ x = 10^{-8}M$

Now, $pH = -\log_{10}[H_3O^+]$

$= -\log_{10}(10^{-8})$

$\therefore \ pH = 8$

If the pH of solution is 8, solution must be basic but we have diluted HCl, so it is wrong. The principle says that when concentration of HCl becomes $10^{-8}M$, the concentration of $[H_3O^+]$ of water is $10^{-7}M$ and so it cannot be neglected. It should be taken into calculation. Hence,

$[H_3O^+]$ in solution = concentration of HCl + concentration of $[H_3O^+]$ ion in water.

$= 10^{-8} + 10^{-7} = 1.1 \times 10^{-7}$

$\therefore \ pH = -\log_{10}[H_3O^+]$

$= -\log_{10}(1.1 \times 10^{-7}) = 6.98$

This value is acceptable because it is less than 7 and solution is acidic.

Thus, in solutions of acids having very low concentration, the concentration of $[H_3O^+] = 10^{-7}M$ cannot be neglected. It should be taken in calculation so that correct pH can be obtained.

4.18 Ionisation Constant of Weak Acid and Weak Base

4.18.1 Ionisation Constant of Weak Acid (K_a) :
In aqueous solution of weak monobasic acid HA, there is a partial ionisation and so the equilibrium is obtained as below :

$$HA_{(aq)} + H_2O_{(l)} \ \rightleftharpoons \ H_3O^+_{(aq)} + A^-_{(aq)}$$
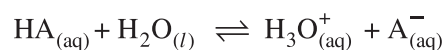
Suppose the initial concentration of weak acid (HA) is C mollit^{-1} and degree of ionisation is α, then following can be written :

Reaction :

$$HA_{(aq)} + H_2O_{(l)} \ \rightleftharpoons \ H_3O^+_{(aq)} + A^-_{(aq)}$$
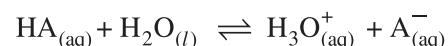
	HA	H₃O⁺	A⁻
Initial concentration(M)	C	0	0
Degree of ionisation(α)	$1-\alpha$	α	α
Concentration at equilibrium(M)	$(1-\alpha)C$	αC	αC

Equilibrium constant $K_e = \dfrac{[H_3O^+][A^-]}{[HA][H_2O]}$

$$= \dfrac{(\alpha C)(\alpha C)}{(1-\alpha)C[H_2O]} \quad .....4.21$$

But $[H_2O]$ is accepted as constant and so

$$K_e[H_2O] = \dfrac{(\alpha C)(\alpha C)}{(1-\alpha)C}$$

$$= \dfrac{\alpha^2 C}{(1-\alpha)} = K_a \quad ....4.22$$

where K_a is the ionisation constant or dissociation constant of the acid HA. (At this stage we consider both the terms same) Hence, for any weak monobasic acid, following can be written

$$K_a = \dfrac{[H_3O^+][A^-]}{[HA]} \quad ....4.23$$

The unit of K_a will be mollit^{-1}.

As the values of K_a depend on $[H_3^+O]$ the values of K_a will be different for different $[H_3O^+]$. Lesser the value of K_a, weaker will be the acid. The value of K_a will be constant at definite temperature. In table 4.3 the values of ionisation constants of some weak acids are given.

Table 4.3

The Ionisation Constants (K_a) of some weak acids at 298K

Acid	K_a
Hydrofluoric acid (HF)	3.5×10^{-4}
Nitrous acid (HNO$_2$)	4.5×10^{-4}
Formic acid (HCOOH)	1.8×10^{-4}
Acetic acid (CH$_3$COOH)	1.74×10^{-5}
Benzoic acid (C$_6$H$_5$COOH)	6.5×10^{-5}
Hypochlorus acid (HClO)	3.0×10^{-8}
Hydrocyanic acid (HCN)	4.9×10^{-10}
Phenol (C$_6$H$_5$OH)	1.3×10^{-10}

According to the relations seen earlier,

$$pH = -\log_{10}[H_3O^+]$$

$$pOH = -\log_{10}[OH^-]$$

Similarly, $pK_a = -\log_{10}[K_a]$

$p_{A^-} = -\log_{10}[A^-]$ can be written.

where $[A^-]$ is the concentration of negative ion.

It is apparent from above relations that if the values of initial concentration $[H_3O^+]$ and K_a are known, then at equilibrium, $[H_3O^+]$ concentration can be determined and pH can be calculated.

Suppose, if we take 0.1M CH$_3$COOH as weak acid HA and its ionisation constant K_a as 1.74×10^{-5} at 298 K, temperature then $[H_3O^+]$, [CH$_3$COOH], pH, pOH, pK$_w$ etc. at equilibrium can be calculated.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$
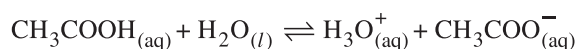
$$K_e = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]} \quad \text{and}$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

If we take α as the degree of ionisation of weak CH$_3$COOH then

$$K_a = \frac{(0.1 \times \alpha)(0.1 \times \alpha)}{0.1(1-\alpha)}$$

$$K_a = \frac{(0.1)^2 \alpha^2}{(1-\alpha)(0.1)}$$

$$K_a = \frac{(0.1)\alpha^2}{(1-\alpha)}$$

The value of K_a is given as 1.74×10^{-5} and so,

$$\frac{(0.1)\alpha^2}{(1-\alpha)} = 1.74 \times 10^{-5}$$

The value of α being very small (0.02 to 0.03); $(1-\alpha)$ can be written as ≈ 1

$$\therefore \ 0.1 \times \alpha^2 = 1.74 \times 10^{-5}$$

$$\therefore \ \alpha^2 = \frac{1.74 \times 10^{-5}}{0.1} = 1.74 \times 10^{-4}$$

$$\therefore \ \alpha = \sqrt{1.74 \times 10^{-4}} = 1.32 \times 10^{-2}$$

Now, $[H_3O^+] = \alpha C = 1.32 \times 10^{-2} \times 0.1$

$$= 1.32 \times 10^{-3}M$$

$$\therefore \ pH = -\log_{10}[H_3O^+]$$

$$= -\log_{10}(1.32 \times 10^{-3}) = 2.88$$

In the same way CH$_3$COO$^-$ = 2.88

The amount of undissociated CH$_3$COOH will be $(1-(1.32 \times 10^{-2}) \times 0.1)$.

According to $(1-\alpha)C$.

$$= (1-1.32 \times 10^{-2}) \times 0.1$$

$$= 0.09668M$$

Though the solution is acidic, if we want to know concentration of OH$^-$, it is possible.

$$pH + pOH = pK_w$$

$$2.88 + pOH = 14$$

$$\therefore \ pOH = 11.12$$

$$\therefore \ -\log_{10}[OH^-] = 11.12$$

$$\therefore \ \log_{10}[OH^-] = -11.12 = -12.00 + 0.88$$

$$\therefore \ [OH^-] = \text{antilog} \ -12.00 + 0.88$$

$$= 7.586 \times 10^{-12} \ M$$

Activity : The pH of 0.1M monobasic weak acid HA is 4.40. Calculate the values of $[H_3O^+]$, $[A^-]$, $[HA]$, K_a, pK_a in the solution at equilibrium.

Solution : Use the above method and try to calculate the values and verify that they are as follows :

$$[H_3O^+] = [A^-] = 4.0 \times 10^{-5}M$$
$$[HA] \approx 0.1M$$
$$K_a = 1.6 \times 10^{-8}, \quad pK_a = 7.80$$

4.18.2 Ionisation Constant (K_b) of Weak Base :
The ionisation of monoacidic weak base MOH will take place in aqueous solution as follows :

$$MOH_{(aq)} \xrightarrow{H_2O} M^+_{(aq)} + OH^-_{(aq)}$$
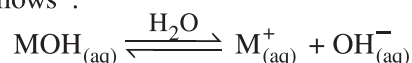
As base is weak, incomplete ionisation will occur and so equilibrium will be obtain and it can be expressed as below :

$$K_e = \frac{[M^+][OH^-]}{[MOH][H_2O]} \qquad ....4.24 \text{ and}$$

$$K_e \times [H_2O] = \frac{[M^+][OH^-]}{[MOH]} = K_b \qquad ....4.25$$

where K_b is the ionisation or dissociation constant of monoacidic weak base. If we know the initial concentration of weak base and its degree of ionisation, we can calculate the value of K_b as we have studied earlier. $[M^+] = [OH^-]$. Let us study with the following example.

Example 14 : Calculate the values of $[NH_4^+]$, $[OH^-]$, pOH, pH of 0.1M NH_4OH solution at equilibrium. The ionisation constant of NH_4OH is 1.8×10^{-5}

Solution : NH_4OH is a weak base, so it can be written in the same manner as the earlier one.

Reaction :

$$NH_4OH_{(aq)} \xrightarrow{H_2O} NH^+_{4(aq)} + OH^-_{(aq)}$$
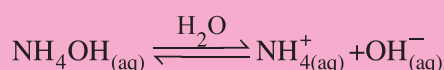
Initial concentration (M)   0.1   0   0
Degree of ionisation $(1-\alpha)$ α α
Concentration at equilibrium (M) $(1-\alpha)C$ αC αC

But $C = 0.1$

At equilibrium M $(1-\alpha)\times 0.1$ $\alpha \times 0.1$ $\alpha \times 0.1$

$$K_b = \frac{(\alpha C)(\alpha C)}{(1-\alpha)C} = \frac{\alpha^2 C}{1-\alpha}$$

But $K_b = 1.8 \times 10^{-5}$ is given and the value of α being very small $(1-\alpha)$ can be taken nearly equal to 1.

$$K_b = \alpha^2 C$$

$$\therefore 1.8 \times 10^{-5} = \alpha^2 C = \alpha^2 \times 0.1$$

$$\therefore \alpha^2 = \frac{1.8\times 10^{-5}}{0.1} = 1.8\times 10^{-4}$$

$$\therefore \alpha = \sqrt{1.8 \times 10^{-4}} = 1.34 \times 10^{-2}$$

$$[NH_4^+] = [OH^-]$$

$$\alpha C = 1.34 \times 10^{-2} \times 0.1$$

$$= 1.34 \times 10^{-3}M$$

$$pOH = -\log_{10}[OH^-]$$

$$= -\log_{10}(1.34 \times 10^{-3}) \approx 2.87$$

$$pH + pOH = 14$$

$$\therefore pH = 14 - pOH$$

$$= 14 - 2.87 = 11.13$$

In table 4.4 the values of ionisation constants of some monoacidic bases at 298 K are given.

Table 4.4 The Ionisation Constants (K_b) of some weak bases at 298 K

Base	K_b
Ammonium hydroxide (NH_4OH)	1.77×10^{-5}
Methyl amine (CH_3NH_2)	4.4×10^{-5}
Dimethyl amine $(CH_3)_2NH$	5.4×10^{-5}
Trimethyl amine $(CH_3)_3N$	6.45×10^{-5}
Aniline $(C_6H_5NH_2)$	4.27×10^{-10}
Urea (NH_2CONH_2)	1.3×10^{-14}

Example 15 : The ionisation constant of dimethyl amine $[(CH_3)_2NH]$ is 5.4×10^{-4}. If the initial concentration of dimethyl amine is 0.02 M, calculate $[OH^-]$, $[(CH_3)_2NH]$, $[H_3O^+]$, pH and pOH in solution at equilibrium.

Solution :

Reaction :

$(CH_3)_2NH_{(aq)} + H_2O_{(l)} \rightleftharpoons (CH_3)_2NH_{2(aq)}^+ + OH_{(aq)}^-$

The following values will be obtained by calculation, compare them :

$[OH^-] = [(CH_3)_2NH_2^+] = 3.28 \times 10^{-4}$ M

$[H_3O^+] = 3.0 \times 10^{-9}$ M

pOH = 3.48, pH = 10.52

Relation between K_a and K_b : As seen earlier the values of K_a and K_b show the strength of acid and base respectively. In reference to conjugate acid base, every acid has conjugate base and every base has conjugate acid; viz.

$\underset{\text{Acid - 1}}{NH_{4(aq)}^+} + \underset{}{H_2O_{(l)}} \rightleftharpoons \underset{\text{Base - 1}}{NH_{3(aq)}} + \underset{\text{Acid - 2}}{H_3O_{(aq)}^+}$
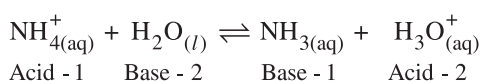
The value of K_a for the reaction will be

$K_a = \dfrac{[H_3O^+]\,[NH_3]}{[NH_4^+]}$ 4.25

$= 5.6 \times 10^{-10}$

$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_{4(aq)}^+ + OH_{(aq)}^-$
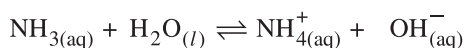
$K_b = \dfrac{[NH_4^+]\,[OH^-]}{[NH_3]}$ 4.26

The value of this K_b is found to be 1.8×10^{-5}. On adding the above reactions,

$NH_{4(aq)}^+ + H_2O_{(l)} \rightleftharpoons H_3O_{(aq)}^+ + NH_{3(aq)}$

$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons OH_{(aq)}^- + NH_{4(aq)}^+$

─────────────────────────────

$2H_2O_{(l)} \rightleftharpoons H_3O_{(aq)}^+ + OH_{(aq)}^-$
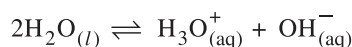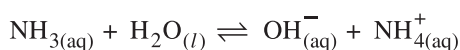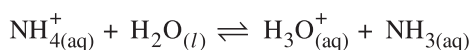
and $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ 4.27

K_w is ionic product of water, K_a is ionisation constant of NH_4^+ acid and K_b is the ionisation constant of base NH_3.

$\therefore K_a \times K_b =$

$\left[[H_3O^+]\,[NH_3] \middle/ [NH_4^+] \right] \times \left[[NH_4^+]\,[OH^-] \middle/ [NH_3] \right]$

........4.28

$= [H_3O^+]\,[OH^-] = K_w$ 4.29

$\therefore K_a \times K_b = 5.6 \times 10^{-10} \times 1.8 \times 10^{-5}$

$= 1.008 \times 10^{-14} \approx 1.0 \times 10^{-14} = K_w.$

Hence, it can be concluded that the constant for the net reaction is the product of the equilibrium constants of two or more reactions involved in it.

$\therefore K_{net} = K_1 \times K_2 \times K_3$ 4.30

If we know ionisation constant of conjugate acid or base, then the ionisation constant of their conjugate base or acid can be known with the help of K_w viz. The ionisation constant of CH_3COOH is $K_a = 1.7 \times 10^{-5}$ so the ionisation constant of its conjugate base CH_3COO^- ion will

be $K_b = \dfrac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.75 \times 10^{-10}$

or $pK_a + pk_b = 14$ 4.31

$\therefore pk_b = 14 - pK_a$ or

$- \log K_b = 14 + \log K_a$ 4.32

and from the value of $- \log K_b$, the value of K_b can be calculated.

Example 16 : The dissociation constant of formic acid (HCOOH) is 1.8×10^{-4}. What will be the value of dissociation constant of conjugate base formate ion $(HCOO^-)$?

Solution :

$K_a = 1.8 \times 10^{-4}$ and $K_w = 1.0 \times 10^{-14}$

$K_a \times K_b = K_w$

$\therefore K_b = \dfrac{K_w}{K_a} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.5 \times 10^{-9}$

**Dissociation constants of dibasic or polybasic (diprotic or polyprotic) acids :** Sulphuric acid, oxalic acid etc. are dibasic acids and phosphoric acid, citric acid are tribasic acids. Their dissociation constants are two K_{a_1} and K_{a_2} for dibasic and three K_{a_1}, K_{a_2} and K_{a_3} for tribasic acids respectively. Suppose, dibasic weak acid is expressed as H_2A, then its dissociation will occur in the following two steps and corresponding K_{a_1} and K_{a_2} will be obtained. For tribasic acid dissociation will occur in three steps and corresponding K_{a_1}, K_{a_2} and K_{a_3} will be obtained.

(1) $H_2A_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HA^-_{(aq)}$

$$K_{a_1} = \frac{[H_3O^+][HA^-]}{[H_2A]} \quad ....4.33$$

(2) $HA^- + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^{2-}_{(aq)}$

$$K_{a_2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} \quad ....4.34$$
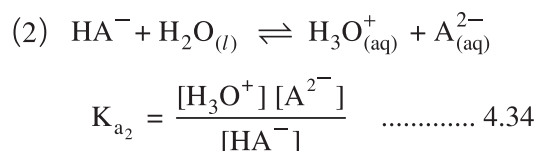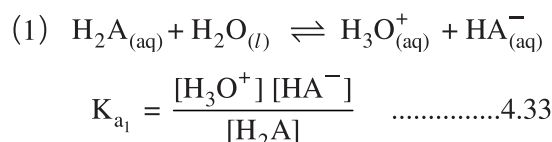
4.18.3 Factors Affecting Strength of Acid : From the study of dissociation constant, pH value etc., it is found that their values are different. The reason for this is that $[H_3O^+]$ available can be more or less. What may be the reason for this? If the acid is strong, its value of K_a will be high and the value of pH will be low. The dissociation of acid will depend on strength of acid and the polarity of H–A bond. As the strength of H–A bond decreases, the energy required for breaking that bond will decrease and HA will be stronger. When difference between electronegativities of A and B will increase, apparently ionisation will occur and will be easy to break the structure of the bond. Hence, acidity will increase.

On comparing the elements of the same group of periodic table, the strength of H–A bond will be more important factor than polar nature. As we go down in the group the size of A will increase and so strength of H–A bond will decrease and hence acid strength will increase.

Increase in Size

HF << HCl << HBr << HI

Increase in acid strength
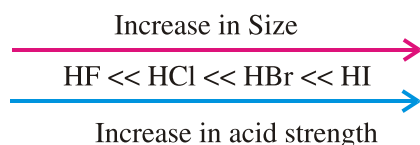
For this reason, H_2S is stronger acid than H_2O, but if we discuss the elements in the same period of periodic table, the polarity of H–A bond will determine the strength of acid. As the electronegativity of A increases, the strength of acid will increase.

Increase in electronegativity

CH_4 << NH_3 << H_2O << HF

Increase in acid strength
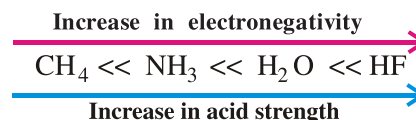
4.18.4 Effect of common ion on ionisation constant of weak acid and base : Let us take the example of weak acid, acetic acid (CH_3COOH)

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

OR

$$HAc + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Ac^-_{(aq)}$$
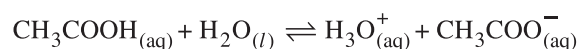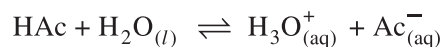
where HAc and Ac⁻ are the short forms of CH_3COOH and CH_3COO^- ion.

$$K_a = \frac{[H_3O^+][Ac^-]}{[HAc]} \quad ....4.35$$
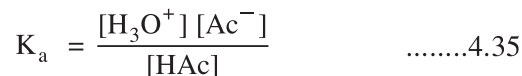
Suppose we add salt CH_3COONa or HCl, to the solution of HAc in equilibrium, then what will happen ? As studied earlier in chemical equilibrium if HCl is added, $[H_3O^+]$ will increase and if CH_3COONa is added, $[Ac^-]$ will increase. Hence, according to Le Chatelier's principle, the equilibrium will make negligible change and will keep the same value of equilibrium constant. This means that the equilibrium will be shifted towards left and concentration of HAc will increase i.e. the amount of undissociated acid will increase and there will be decrease in $[H_3O^+]$ and hence, there will be increase in pH. By addition of HCl due to increase in $[H_3O^+]$ similar result will be obtained. This effect is known as effect of common ion effect on dissociation constant of acid.

In the same way, in the case of ionisation of weak base NH_3, if we increase $[NH_4^+]$ by adding salt like NH_4Cl then, according to Le Chatelier's principle, as $[NH_4^+]$ increases the equilibrium will shift towards left and hence, undissociated NH_3 will increase, i.e. $[OH^-]$ will decrease. As a result, pH will decrease. We can prove these two effects by following examples.

Example 17 : What will be the change in pH of 0.1M CH_3COOH acid if 0.1M CH_3COONa is added to its solution? pK_a of CH_3COOH = 4.74

Solution : Firstly in absence of common ion (CH_3COO^-), for weak acid

$$[H_3O^+] = \sqrt{K_a \cdot C}$$

pK_a = 4.74

$\therefore -\log K_a = 4.74$

$\therefore \log K_a = -4.74 = \bar{5} + 0.26$

K_a = Antilog $(\bar{5} + 0.26)$

$\therefore K_a = 1.8 \times 10^{-5}$

$\therefore [H_3O^+] = \sqrt{K_a \cdot C_o}$

$= \sqrt{1.8 \times 10^{-5} \times 10^{-1}}$

$= \sqrt{1.8 \times 10^{-6}} = 1.3416 \times 10^{-3}$

$\therefore pH = -\log_{10}[H_3O^+]$

$= -\log_{10}(1.3416 \times 10^{-3}) = 2.87$

Now, if 0.1M CH_3COONa is added, then,

$$K_a = \frac{[H_3O^+][Ac^-]}{[HAc]}$$

$$K_a = \frac{[H_3O^+][0.1]}{[0.1]} \qquad ....4.36$$

$[Ac^-]$ = Ac^- available from CH_3COONa and Ac^- from dissociation of HAc. But concentration of Ac^- available from dissociation of HAc can be neglected in comparison to Ac^- (0.1M)

available from CH_3COONa. Hence, Ac^- = 0.1M can be taken.

$\therefore [H_3O^+] = 1.8 \times 10^{-5}$

$\therefore -\log_{10}[H_3O^+] = pH$

$= -\log_{10}(1.8 \times 10^{-5}) = 4.81$

Hence, it can be proved that the dissociation of acid decreases due to effect of common ion and so $[H_3O^+]$ decreases and so pH increases.

Example 18 : What will be the change in pH of 0.1M weak base NH_4OH if 0.1M NH_4Cl is added to the solution? K_b for NH_4OH = 1.77×10^{-5}

Solution : As mentioned above calculate on the basis of method of determination of ionisation constant. Compare the values obtained with the following values.

pH of 0.1M NH_4OH in absence of NH_4Cl = 11.13, pH of 0.1M NH_4OH in presence of NH_4Cl = 9.25. Thus, this example shows that the pH of a solution of weak base decreases due to effect of common ion.

4.19 Hydrolysis of Salt and pH of Their Solutions

Salt is obtained by combination of acid and base in definite proportion. When the salt is dissolved in water, ionisation occurs. The following types of salts are obtained depending on acid or base being strong or weak.

Acid	Base	Salt	Property	Example
(1) Strong	Strong	Neutral	Neutral	$NaOH + HCl \rightarrow NaCl + H_2O$
(2) Strong	Weak	Acidic	Acidic	$HCl + NH_4OH \rightleftharpoons NH_4Cl + H_2O$
(3) Weak	Strong	Basic	Basic	$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$
(4) Weak	Weak	Neutral or Acidic or Basic	Neutral or Acidic or Basic	$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$ $HCOOH + NH_4OH \rightleftharpoons HCOONH_4 + H_2O$ $C_6H_5COOH + NH_4OH \rightleftharpoons C_6H_5COONH_4 + H_2O$

Salt formed from strong base and strong acid is neutral and so its pH is 7.0. e.g. NaCl. But if salt is formed from strong acid and weak base, it will be acidic and pH of its aqueous solution will be less than 7 e.g. NH_4Cl. Similarly

salt formed from weak acid and strong base is basic and its pH in aqueous solution will be more than 7, e.g. CH_3COONa. The reason is that salt reacts with water and undergoes hydrolysis reaction.

Hydrolysis reaction is an equilibrium reaction and so its corresponding equilibrium constant can be calculated which is known as hydrolysis constant (K_h). It can be determined with the help of the example of weak acid and strong base e.g. CH_3COONa
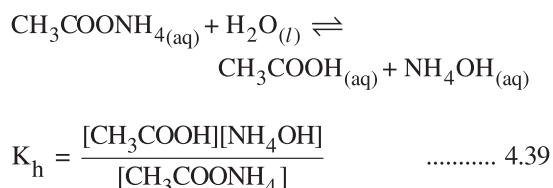
(1) For salt of weak acid and strong base,

$$CH_3COONa_{(aq)} + H_2O_{(l)} \rightleftharpoons$$
$$CH_3COOH_{(aq)} + NaOH_{(aq)}$$

$$K_h = \frac{[CH_3COOH][NaOH]}{[CH_3COONa]} \quad \text{.........4.37}$$
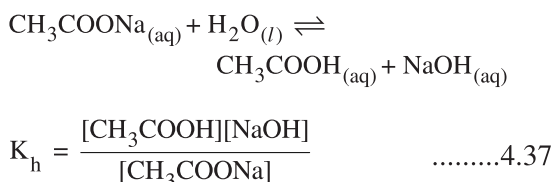
(2) For salt of strong acid and weak base (e.g. NH_4Cl)

$$NH_4Cl_{(aq)} + H_2O_{(l)} \rightleftharpoons$$
$$NH_4OH_{(aq)} + HCl_{(aq)}$$
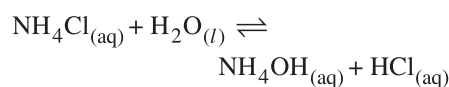
$$K_h = \frac{[NH_4OH][HCl]}{[NH_4Cl]} \quad (4.38)$$

(3) For salt of weak acid and weak base(e.g. CH_3COONH_4),

$$CH_3COONH_{4(aq)} + H_2O_{(l)} \rightleftharpoons$$
$$CH_3COOH_{(aq)} + NH_4OH_{(aq)}$$

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COONH_4]} \quad \text{.......... 4.39}$$

Earlier you have studied about K_a and K_b. The equation of K_h can be obtained from them as shown below :

Salt	Hydrolysis constant	PH of solution
Strong acid weak base	$K_h = \dfrac{K_w}{K_b} = \dfrac{[H_3O^+]^2}{C_O}$	< 7
Weak acid strong base	$K_h = \dfrac{K_w}{K_a} = \dfrac{[OH^-]}{C_O}$	> 7
Weak acid weak base	$K_h = \dfrac{K_w}{K_a \cdot K_b} = \dfrac{[H_3O^+][OH^-]}{C_O}$	= 7

where C_o is the initial concentration of salt.

Thus, from the nature of the salt pH of its aqueous solution can be calculated.

Example 19 : Calculate pH of 0.1M sodium acetate (CH_3COONa) solution. K_a of $CH_3COOH = 1.8 \times 10^{-5}$ $K_w = 1.0 \times 10^{-14}$

Solution :

$$CH_3COONa_{(aq)} + H_2O_{(l)} \rightleftharpoons$$
$$CH_3COOH_{(aq)} + NaOH_{(aq)}$$

OR

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons$$
$$CH_3COOH_{(aq)} + OH^-_{(aq)}$$
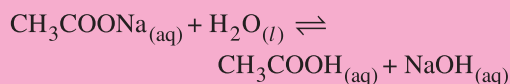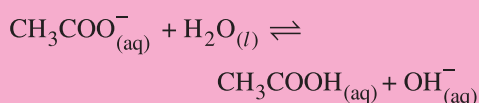
$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$$

But $K_h = \dfrac{[OH^-]^2}{C_o}$

$$\therefore 5.5 \times 10^{-10} = \frac{[OH^-]^2}{0.1}$$

$$\therefore [OH^-]^2 = 5.5 \times 10^{-10} \times 0.1$$
$$= 5.5 \times 10^{-11}$$

$$\therefore [OH^-]^2 = \sqrt{5.5 \times 10^{-11}}$$
$$= 7.4 \times 10^{-6}$$

Now, $pOH = -\log_{10}[OH^-]$
$$= -\log_{10}(7.4 \times 10^{-6}) = 5.13$$

$pH = 14 - pOH$

$$\therefore pH = 14 - 5.13 = 8.87$$

4.20 Buffer Solutions

The pH of the fluids like blood in our body and urine is almost constant. If there is change in this pH, it affects biochemical reaction in the body. The pH of chemical and biochemical reactions in our body are constant, viz. the pH of human saliva is 6.4. In addition,

hydrochloric acid is present in human stomach which helps in digestion. The pH of cosmetics are also kept constant. Hence, the question arises that how pH in any solution can be kept constant. Such solutions are called buffer solutions. Its definition can be given as below :

"The solution which resists the change in pH carried out by addition of acid or base in small proportion to them or are being diluted, and the values of their pH remain constant are called buffer solutions". Buffer solutions can be acidic or basic. If pK_a of weak acid and pK_b of weak base are known, buffer solutions of known pH can be prepared. Buffer solutions can be of three types as follows :

(i) Acidic buffer solution : Acidic buffer solution can be prepared by mixture of weak acid and its salt with strong base.

(ii) Basic buffer solution : Basic buffer solution can be prepared by mixture of weak base and its salt with strong acid.

(iii) Neutral buffer solution : Neutral buffer solution can be prepared by neutralisation of weak acid and weak base. These types of buffer solutions are shown below :

Type	Substances	Value of pH
Acidic	$CH_3COOH + CH_3COONa$	< 7
Basic	$NH_4OH + NH_4Cl$	> 7
Neutral	$CH_3COOH + NH_4OH$	≈ 7

Buffer solution of known pH can be prepared by using the following Henderson-Hasselbalch equation.

For acidic solution,

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} \qquad ....4.40$$

where [acid] is concentration a weak acid and its dissociation constant is K_a and [salt] is concentration of the salt of this weak acid with strong base. For an acidic buffer solution, it can be written as

$$pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

Similarly, for basic buffer solution e.g. $NH_4OH + NH_4Cl$ can be written that,

$$pH = pK_b + \log \frac{[NH_4Cl]}{[NH_4OH]}$$

Such buffer solutions can be used in chemical and biochemical reactions and esepcially in analytical chemistry. In human body buffer solutions containing $[HCO_3^-]$ and $[CO_3^{2-}]$ as well as $[H_2PO_4^-]$ and $[HPO_4^{2-}]$ are present.

4.21 Solubility Product of Sparingly Soluble Salts

We have studied earlier that ionic substances like NaOH are highly soluble in water. It absorbs moisture from the air and dissolves. While covalent compounds like LiF are less soluble in water and non-ionic compounds like CdS are almost insoluble in water. Hence, substances can be divided into three types :

Type 1 : Soluble : The substances whose solubility in water is more than 0.1M. e.g. NaCl, HCl, NaOH

Type 2 : Insoluble : The substances whose solubility is very less in water. e.g. CdS, PbS

Type : 3 Sparingly soluble : The substances whose solubility is less than 0.01M. e.g. AgCl, $BaSO_4$, $PbSO_4$

The basis of solubility is on the lattice enthalpy and hydration enthalpy of the substance. If hydration enthalpy is more than lattice enthalpy, the substance will be soluble in water. The second thing is that polar substance dissolves in polar solvents and non-polar substance dissolves in non-polar solvents. e.g. Polar substance like NaCl is soluble in polar solvent like water and nonpolar substance like naphthalene can dissolve in non-polar solvent like benzene.

Sparingly soluble substances are soluble in less proportion and so possess equilibrium and whatever substance is dissolved, it completely gets ionised. We shall study the equilibrium constant of sparingly soluble salt and effect of common ion on its solubility.

Solubility Product Constant of Sparingly Soluble Salt : Suppose, if we dissolve sparingly soluble substance like AgCl in water and prepare its saturated solution, then following reaction will occur and equilibrium will be established.

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

Equilibrium constant $K_e = \dfrac{[Ag^+][Cl^-]}{[AgCl]}$ 4.41

For pure solid substance, its concentration is its density and density remains constant at constant temperature, so concentration can be considered constant. Hence,

$$K_e \cdot [AgCl_{(s)}] = [Ag^+][Cl^-] = K_{sp} \qquad ....4.42$$

where K_{sp} is the solubility product constant of sparingly soluble salt AgCl which is also expressed only as solubility product. Now, if we determine concentration of Ag^+ and Cl^- ions, then solubility product can be obtained. At 298 K, the solubility of AgCl is found to be 1.3×10^{-5} M

Hence, $[Ag^+] = [Cl^-] = 1.3 \times 10^{-5}$ M

$\therefore K_{sp} = [Ag^+][Cl^-]$

$\qquad = (1.3 \times 10^{-5})(1.3 \times 10^{-5})$

$\qquad = (1.69 \times 10^{-10})(mollit^{-1})^2$ or M^2

If solubility is to be determined in grams, it can be obtained by multiplying with molecular mass.

Example 20 : The concentration of $Mg(OH)_2$ in its saturated solution is found to be 8.2×10^{-4} gramlitre^{-1} at 298 K temperature. Calculate K_{sp} of $Mg(OH)_2$. The molecular mass of $Mg(OH)_2$ is 58.0 grammole^{-1}.

Solution : Concentration of $Mg(OH)_2$ is 8.2×10^{-4} grammole^{-1}

Solubility of $Mg(OH)_2$ in mol lit^{-1}

$$\dfrac{8.2 \times 10^{-4}}{58} = 1.41 \times 10^{-5} \text{ M}$$

Now, $Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$
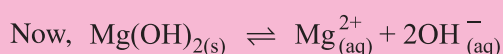
Hence, $[Mg^{2+}] = 1.41 \times 10^{-5}$ M but

$[OH^-] = 2 \times 1.41 \times 10^{-5}$ M

so, according to $K_{sp} = [Mg^{2+}][OH^-]^2$

$K_{sp} = (1.41 \times 10^{-5})(2 \times 1.41 \times 10^{-5})^2$

$\qquad = 1.076 \times 10^{-14}$ M^3

The types of sparingly soluble salts and the formula of calculation of the values of Ksp are as follows :

Type	Example	Formula for K_{sp} and unit
1 : 1	AgCl	$K_{sp} = S^2$ M^2
1 : 2	CaF_2	$K_{sp} = 4S^3$ M^3
2 : 2	$BaSO_4$	$K_{sp} = S^2$ M^2
2 : 1	$Mg(OH)_2$	$K_{sp} = 4S^3$ M^3

where S = solubility in mollit^{-1} or M.

If solubility is given in grams and volume is given in mililitres, the solubility in gramlitre^{-1} or M can be obtained.

Activity : Mention the formula and units of solubility products of the following substances AgBr, $PbSO_4$, $Al(OH)_3$, Bi_2S_3 and $Zr_3(PO_4)_2$.

Utility of Solubility Product :

(1) If the values of solubility products are known, the solubilities of the substances in the solutions can be compared.

(2) Whether precipitation of soluble substance into insoluble substance will take place or not can also be determined, viz. we want to know whether precipitates of AgCl will be obtained or not by addition of solution of NaCl to a solution of $AgNO_3$. For this get $[Ag^+]$ in M from the solution of $AgNO_3$ and $[Cl^-]$ in M from the solution of added NaCl. Multiply them. Mention this product or multiplication as I_p and compare its value with the value of its K_{sp}. Three possibilities are there. according to which precipitatres of sparingly soluble salt can be obtained or not can be predicted.

(i) $I_p > K_{sp}$ Precipitates of sparingly soluble salt will be obtained or precipitation will occur.

(ii) $I_p < K_{sp}$ Precipitates of sparingly soluble salt will not be obtained or precipitation will not occur.

(iii) $I_p = K_{sp}$ Shows equilibrium, Hence precipitation will not occur but solution will remain in saturated state.

4.22 Effect of Common Ion on Solubility of Sparingly Soluble Salt

The sparingly soluble salt that has dissolved in solution that is completely dissociated and so it is in ionic form. Hence, it is a strong electrolyte. Earlier, in chemical equilibrium, effect of concentration, application of Le Chatelier's principle etc. have been studied. Solubility product is ionic equilibrium and the effect of concentration can be studied. As it is equilibrium constant, it will depend on temperature, but its value will be constant at constant temperature.

What will happen if we add soluble ionic substance like KCl in the solution of a sparing soluble salt like AgCl?

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$
$$KCl_{(s)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$
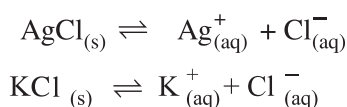
The Cl^- from AgCl in equilibrium and Cl^- ion obtained by complete ionisation of KCl, the concentration of Cl^- will increase. Hence, according to Le Chatelier's principle, the equilibrium will shift towards left side so as to nullify the effect of Cl^- i.e. more AgCl will be formed. In other words, there will be decrease in solubility of AgCl. Hence, it can be said that because of the effect of common ion on sparingly soluble salt its solubility decreases and sparingly soluble salt precipitates more.

Example 21 : The value of solubility product of K_{sp} sparingly soluble salt $Mg(OH)_2$ is $1.8 \times 10^{-11} M^3$ at 298 K. If a solution of 0.1 M NaOH is added to it, what will be the concentration of $Mg(OH)_2$? Discuss the results.

Solution : Sparingly soluble salt $Mg(OH)_2$ is 2:1 type of salt and so $K_{sp} = 4S^3$ where S = concentration of $Mg(OH)_2$ in mollit^{-1}.

Now, $K_{sp} = 4S^3 \therefore 1.8 \times 10^{-11} = 4S^3$

$$\therefore S = \sqrt[3]{\frac{1.8 \times 10^{-11}}{4}} = 1.65 \times 10^{-4} \text{ M.}$$

Thus, solubility of $Mg(OH)_2$ in water in absence of NaOH will be 1.65×10^{-4} M.

Now, concentration of OH^- in presence of 0.1 M NaOH will be equal to concentration of OH^- available from complete ionisation of NaOH and concentration of OH^- available from ionisation of $Mg(OH)_2$ but the solubility of $Mg(OH)_2$ is less and so concentration of OH^- available from its ionisation can be neglected in comparison to 0.1 M OH^- from NaOH. Hence, for

$$K_{sp} = [Mg^{2+}] [OH^-]^2$$
$$1.8 \times 10^{-11} = [S] (2 \times 0.1)^2$$

$$\therefore [S] = \frac{1.8 \times 10^{-11}}{4 \times 10^{-2}}$$

$$= 0.45 \times 10^{-9} = 4.5 \times 10^{-10} \text{ M}$$

Thus, the solubility of sparingly soluble salt $Mg(OH)_2$ decreases from 1.65×10^{-4} M to 4.5×10^{-10} M in presence of common OH^- ion. Thus, solubility of sparingly soluble salt decreases in presence of common ion.

The use of effect of common ion can be made to separate one ion from the other in presence of other ion in qualitative analysis. It can also be used for decrease in solubility of the components in the mixture. In qualitative analysis, the solubility products of sulphides of metal ions of second group are less in comparison to solubility products of sulphides of metal ions of III B group ions, therefore, HCl is added before adding H_2S water to test the second group ions.

$$H_2S_{(aq)} \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$$
$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$
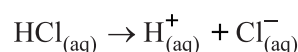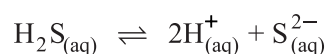
The common ion available from HCl creates common ion effect on the equilibrium and decreases concentration of S^{2-} ions. Hence, the sulphides of the ions included in second group can only be precipitated because their solubility

products are less. In the same way, for precipitation of ions of group III A ammonium chloride (in excess) is added along with NH_4OH. The concentration of OH^- available from ionisation of NH_4OH gets decreased due to common ion effect due to NH_4^+ available from NH_4Cl. Hence, the hydroxides of the ions of III A group only will be precipitated because the values of solubility products of the hydroxides of III A group are low. Above this, if HCl gas is passed through saturated solution of $NaCl$, $NaCl$ becomes insoluble and separates as precipitates due to the common ion effect of Cl^- ions.

It is necessary to note that under certain situations the solubility increases instead of decreasing. The solubility of salt like phosphate increases when acid is added to their solutions or pH of the solution decreases. The reason for this is that, phosphate ion combines with H^+ available from acid and converts into acid by accepting proton. Hence, solubility of phosphate salt increases.

SUMMARY

It is said that equilibrium is established when number of molecules moving from liquid state to vapour state and number of molecules moving from vapour state to liquid state are same and it is dynamic. Equilibrium is established in both physical and chemical types of reactions. At this point of time the rates of forward and reverse reactions become equal. Equilibrium constant K_c is expressed as the ratio of the multiplication of concentration of products to the multiplication of concentration of reactants; concentration of each can be expressed as power of their stoichiometric coefficient.

For reaction $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Equilibrium constant has constant value at constant temperature and at this stage macroscopic properties like concentration, pressure, etc become constant. For gaseous reaction K_p is taken instead of K_c and partital pressure of gaseous reactants and products are expressed instead of concentrations. The relation between K_p and K_c is expressed as $K_p = K_c(RT)^{\Delta n_g}$. In which direction reaction will occur (forward or reverse) can be expressed by reaction quotient Q_c which is equal to K_c at equilibrium. Le Chatelier's principle, mentions that if the equilibrium gets disturbed by change in factors like concentration, temperature, pressure etc., then equilibrium will move in the direction whereby the effect has been minimised or made negligible and the value of equilibrium constant will not change. This can be used in industries to know how equilibrium can be obtained by study of changes in factors like concentration, pressure, temperature, inert gas etc. In industries, we can change or control factors accordingly so that reaction shifts from reactants to products (left to right). If catalyst is used, only the rate of required reaction will increase but no change will occur in amounts of reactants or products because the effect on forward and reverse reactions will be the same and so equilibrium constant will not change.

The substances which allow the electric current to pass through their aqueous solutions are called electrolytes. Acid, base and salt are electrolytes because their aqueous solutions conduct electric current. The reason for the conduction of electric current in aqueous solution of electrolyte is the formation of ions due to dissociation or ionisation which conducts electric current. While the weak electrolytes are incompletely dissociated and so the equilibrium is established between its ions and undissociated molecules. This is called ionic equilibrium.

According to Arrhenius ionisation theory, acid is called a substance which gives hydrogen ion (H^+) and base is called a substanec which gives hydroxyl ion (OH^-) on ionisation. According to Bronsted - Lowry theory, acid is defined as a proton donor and base is defined as proton acceptor. Each acid has its conjugate base and each base has its conjugate acid. Hence, it is known as conjugate acid - base or proton - transfer theory. Proton is tranferred between acid and base. Bronsted - Lowry is more general than Arrhenius definition. According to Lewis' definition, acid means a substance which accepts a pair of electrons and base is a substance which donates a pair of electrons. This definition can be applied to organic chemistry, complex compounds chemistry in addition to acid-base. Hence, it is considered universally acceptable. Ionisation constant is also an equilibrium constant. The ionisation constants of weak acid (K_a) and weak base (K_b) can be determined. Concentration of acid can be expressed as $pH = -\log_{10}[H_3O^+]$. Hence, pH scale is determined for acid - base. Similary, concentration of OH^- can be expressed as $pOH = -\log_{10}[OH^-]$, ionisation constant of water as $pK_w = -\log_{10}K_w [H_3O^+]$ and $[OH^-]$ can be calculted by the use of relation $pK_w = pH + pOH$. If $pH < 7$ solution will be acidic, $pH > 7$ solution will be basic and $pH = 7$ solution will be neutral.

Different salts can be obtained by neutralisation of strong or weak acid and strong or weak base. In such salts, acidic, basic and neutral salts are included. When such salts react with water, hydration (hydrolysis) reaction occurs and solution obtained can be acidic, basic or neutral. This is also an equilibrium reaction and so corresponding equilibrium constant for it can be determined. Hydrolysis constant is expressed as K_h. pH or pOH can be calculated from the values of K_a and K_b and the value of K_h characteristic for the particular salt. Some solutions are such whose pH does not change by addition of small amount of acid or base or in case they are being diluted. Such solutions are called buffer solutions which can be acidic, basic or of neutral type. The control of pH is useful in the control of biological reactions in our body and chemical reactions in analytical chemistry, industries etc.

Sparingly soluble salts (whose solubility is less than 0.01M in water) dissolve in water depending on their solubility and equilibrium is established. Hence, equilibrium constant for this can be obtained which is known as solubility product constant or solubility product of the sparingly soluble salt. The study of effect of common ion, acid, etc. on the solubility of sparingly soluble salt can be carried out by application of Le Chatelier's principle. Generally, the solubility of sparingly soluble salt decreases due to effect of common ion. This is used in qualitative analysis. By mixing two solutions, whether precipitates will be obtained or not, can be predicted by comparing concentration product I_p with the solubility product K_{sp}. If $I_p > K_{sp}$ precipitation will occur and if $I_p < K_{sp}$ the precipitation will not occur and if $I_p = K_{sp}$, the precipitation will not occur but solution will remain in saturated state.

EXERCISE

1. **Select the proper choice from the given multiple choices :**

    (1) Chemical equilibrium is

    (A) Dynamic   (B) Steady state

    (C) Dynamic or stable state   (D) None from the above

    (2) The example of homogeneous equilibrium is

    (A) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ (B) $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$

    (C) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ (D) $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

(3)   Mention Lewis acid from following compounds

(A) HCl   (B) CH_3OOH (C) H_2O (D) BF_3

(4)   Mention conjugate base of acid $H_2PO_4^-$

(A) PO_4^{3-} (B) HPO_4^{2-} (C) H_3PO_4 (D) $H_2P_2O_7$

(5)   According to which theory NH_3 cannot be said to be base?

(A) Bronsted-Lowry   (B) Lewis   (C) Arrhenius   (D) None from the above

(6)   In a reaction, what is necessary for precipitation?

(A) $I_p < K_{sp}$ (B) $I_p = K_{sp}$ (C) $I_p > K_{sp}$ (D) $K_{sp} > I_p$

(7)   The solubility of sparingly soluble salt by the effect of common ion

(A) Decreases   (B) Increases

(C) Remains constant   (D) Increases very high

(8)   Le Chatelier's principle is applicable to

(A) Chemical equilibrium only   (B) Ionic equilibrium only

(C) Both chemical and ionic equilibrium. (D) All of the above

(9)   Ferric chloridc solution will be

(A) Basic   (B) Neutral   (C) Acidic   (D) Cannot be said

(10)   With the use of catalyst, the value of equilibrium constant

(A) Increases   (B) Decreases

(C) Remains constant   (D) Increases or Decreases

2.   Answer the following questions in brief :

(1)   Mention the relation between K_p and K_c.

(2)   Describe effect of concentration on chemical equilibrium.

(3)   Write the formula for the ionic product of water.

(4)   Mention the relation between equilibrium constants of forward and reverse reactions.

(5)   Write definitions of acid and base according to Arrhenius theory.

(6)   Write definitions of Lewis acid and base.

(7)   Mention conjugate acid-base theory giving suitable example.

(8)   Explain the terms solubility product and ionic product.

(9)   Mention the relation amongst hydrolysis constant of the salt, dissociation constant and ionic product of water.

(10)   Write three examples of conjugute acid-base and conjugate base-acid.

3.   Write answers of the following questions :

(1)   Mention the operational and conceptual definitions of acid and base.

(2)   Derive the formula for dissociation constant of a weak acid.

(3)   Derive the formula for dissociation constant of a weak base.

(4)   Obtain the relation between equilibrium constants K_c and K_p.

(5)   Derive the formula for the solubility product of sparingly soluble salt CaF_2.

(6)   Mention the use of effect of common ion in qualitative analysis.

(7)   Giving definition of buffer, explain acidic, basic and neutral buffer, giving suitable examples.

(8)   Bronsted-Lowry acid can be a Lewis acid but all Lewis acids cannot be Bronsted-Lowry acid. Explain giving suitable example.

(9)   Derive the formula of ionic product of water.

(10)   Explain calculation of pH of a solution from dissiociation constant.

4.   Calculate the following examples :

(1)   Calculate pH and pOH of following solutions.

     (a) 0.1 M HCl, 0.1 M H_2SO_4, 0.1 M, HNO_3

     (b) 0.1 M NaOH, 0.1 M KOH, 0.1 M, $Ba(OH)_2$

(2)   Calculate pH of following solutions.

     (a) 3.65 gram HCl in 250 ml solution

     (b) 9.80 gram H_2SO_4 in 500 ml solution

     (c) 1.6 gram NaOH in 250 ml solution

     (d) 11.2 gram KOH in 500 ml solution

(3)   Calculate pH of 250 ml solution containing 6 gram acetic acid. Dissociation constant of acetic acid is 1.8×10^{-5}

(4)   Calculate pH of 500 ml ammonium hydroxide solution containing 7 gram ammonium hydroxide. Dissociation constant of ammonium hydroxide is 1.8×10^{-5}

(5)   The dissociation constant of benzoic acid is 6.5×10^{-5} at 298 K. What will be the pH of its 0.15 M solution and its $[H_3O^+]$ ion concentration ?

(6) The dissociation constant of dimethyl amine is 5.4×10^{-5} at 298 K. What will be the pH of its 0.25 M solution and $[H_3O^+]$ ion concentration ?

(7) To prepare one acidic buffer solution 0.125 M sodium acetate is added to 0.25 M solution of acetic acid. If dissociation constant of acetic acid is 1.8×10^{-5}, what will be the pH of this buffer solution ?

(8) To prepare one basic buffer solution, 0.250 M NH_4Cl is added to a solution of 0.125 M ammonium hydroxide. If dissociation constant of ammonium hydroxide is 1.8×10^{-5}, what will be the pH of this buffer solution ?

(9) 20 ml 0.04 M NaCl solution is added to 10 ml 0.06 M $AgNO_3$ solution. If solubility product of AgCl is 1.8×10^{-10} at 298 K, predict whether precipitation will occur or not ?

(10) 20 ml 0.025 M K_2CrO_4 solution is added to 20 ml 0.05 $BaCl_2$ solution. If solubility product of $BaCrO_4$ is 1.2×10^{-10} at 298 K, predict whether precipitation will occur or not ?

(11) Calculate hydrolysis constant and pH of a solution of 0.1 M sodium acetate. Dissociation constant of acetic acid is 1.8×10^{-5} at 298 K and ionic product of water is 1.04×10^{-14}

(12) Calculate hydrolysis constant and pH of 0.30 M NH_4Cl solution. The dissociation constant and ionic product of water are 1.8×10^{-5} and 1.04×10^{-14} respectively at 298 K.

(13) If 20 ml 0.15 M NaOH solution is added to a 10 ml 0.1 M 10 H_2SO_4 solution, what will be the pH of the resulting mixture ?

(14) If 20 ml 0.15 M HCI solution is added to 10 ml 0.1 M $Ba(OH)_2$ solution, what will be the pH of the resulting mixture ?

(15) If dissociation constant of aniline is 4.27×10^{-10} at 298 K, what will be the dissociation constant of its conjugate acid ? $K_w = 1.04 \times 10^{-14}$.

(16) If dissociation constant of acetic acid is 1.76×10^{-5} at 298 K, what will be dissociation constant of its conjugate base ? $K_w = 1.04 \times 10^{-14}$.

Some p -Block Elements - I

5.1 Introduction

The elements (except He) having outermost valence shell electronic configuration $ns^2 np^1$ to $ns^2 np^6$ are called p-Block Elements where n = 2 to 6. Since p-orbitals can accommodate maximum six electrons, there are six groups of p-block elements. In periodic table group 13 to 18 are called p-block elements. The p-block elements are situated on the right side to the transitonal elements in periodic table. Due to difference in inner core electronic configuration, the elements show variation in physical and chemical properties. The first element of the group shows anomalous behaviour in some properties from the other elements of that group. In this unit, let us study the elements of group 13 (IIIA) and group 14 (IVA). The first element of group 13 and 14 are Boron and Carbon respectively, so these groups are also known as Boron group and Carbon group respectively. Due to catenation properties of carbon, carbon forms number of organic compounds which are included in Organic Chemistry. Now, we shall study the general introduction to p-block elements.

General Introduction to p-Block Elements : Group 13 to 18 means p-block elements show variation in physical and chemical properties. Allthough their trends in some properties can be indicated as given below.

							He
		13	14	15	16	17	18
2p		B	C	N	O	F	Ne
3p		Al	Si	P	S	Cl	Ar
4p		Ga	Ge	As	Se	Br	Kr
5p		In	Sn	Sb	Te	I	Xe
6p		Tl	Pb	Bi	Po	At	Rn

(Left axis, downward arrow) Atomic radius, metallic character

(Right axis, upward arrow) Electronegativity, Ionisation-enthalpy, Oxidising agent

(Bottom axis, leftward arrow) **Atomic radius, metallic character**

Generally in the period, eletronegativity, ionisation enthalpy and oxidising power increases as the atomic number increases. While in group it decreases as the atomic number increases. Generally, in group atomic radius, van der Waals radius and metallic character increases as the atomic number increases. Due to these characteristics of the p-block elements, metal, nonmetal and metalloids are included in same group and these characteristics are decreasing in a period as the atomic number increases.

p-Block elements have valence shell electronic configuration $ns^2 np^{1-6}$ where n = 2 to 6 and hence **the value of maximum oxidation state of these elements is obtained by subtracting 10 from its group number.** On moving down the group from 13 to 16 the oxidation state which is two units less than the highest oxidation state becomes more stable. This trend is called inert pair effect. The common oxidation states are as shown in Table 5.2.

Table 5.2 Common Oxidation States of p-Block Elements

Group	13	14	15	16	17	18
Oxidation state	B +3	C +4, −4	N +5 to −3	O −1, −2	F −1	Ne −
	Al +3	Si +4,	P, As +3, +5, −3	S, Se, Te − 2, +2 +4, +6	Cl, Br, I −1, +1, +3 +5, +7	Xe +2, +4 +6, +8
	Ga, In, Tl +3, +1	Ge, Sn, Pb +4, +2	Sb, Bi, +4, +2	−	−	−

We shall study in detail some properties of the elements of group 13 and 14 after the general introduction of p-block elements.

Group 13 elements (Boron group) : Electronic configuration :

The group 13 includes elements. Boron **(B)**, Aluminium **(Al)**, Gallium **(Ga)**, Indium **(In)** and Thallium **(Tl)**. The valence shell electronic configuration is ns^2, np^1 where n = 2 to 6. Hence, there are two electrons in s orbital and one electron in p orbital, therefore, in total three electrons are there. The electronic configurations of elements of group 13 are as shown in table 5.3.

Table 5.3 Electronic Configuration of Elements of Group 13

Element	Atomic No.	Electronic Configuration	
		Complete	**With inert gas core**
Boron (B)	5	$1s^2\ 2s^2\ 2p^1$	[He] $2s^2\ 2p^1$
Aluminium (Al)	13	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$	[Ne] $3s^2\ 3p^1$
Gallium (Ga)	31	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^1$	[Ar] $3d^{10}\ 4s^2\ 4p^1$
Indium (In)	49	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$ $4d^{10}\ 5s^2\ 5p^1$	[Kr] $4d^{10}\ 5s^2\ 5p^1$
Thallium (Tl)	81	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$ $4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^1$	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$

Occurrence : The abundance of boron in earth's crust is less than 0.0001% by weight. It occurs in ore form. The main important ores of boron are

Borax	: $(Na_2B_4O_7 \cdot 10H_2O)$,
Kernite	: $(Na_2B_4O_7 \cdot 4H_2O)$,
Colemanite	: $(Ca_2B_6O_{11} \cdot 2H_2O)$
Orthoboric acid	: (H_3BO_3).

The boron is found in California (USA) and in Turkey State. While in India it is found as borax in Puga valley of Ladakh region in Kashmir and also in Sambhar lake of Rajasthan. Aluminiun is the third most abundant element found in earth's crust, while the first is oxygen (45.5% by weight), the second is silicon (27.7% by weight) and the third is aluminiam (8.3% by weight). Some important ores of aluminium are given below :

Bauxite	: $Al_2O_3 \cdot XH_2O$
Orthoclase	: $KAlSi_3O_8$
Cryolite	: Na_3AlF_6
Corundum	: Al_2O_3
Beryl	: $Be_3Al_2Si_6O_{18}$
Mica	: $KAl_2(Si_3AlO_{10})(OH)_2$

The important ores of aluminium are bauxite and cryolite. In India mica is found in Madhya Pradesh, Karnataka, Orissa and Jammu. India is the world's largest supplier of mica. Gallium, Indium and Thallium are less abundant. Gallium $(0.1 - 1\%)$ is found in the mineral Germanite which is a complex sulphide of Zn, Cu, Ge and As, while the traces of Indium are found in sulphide ore of zinc.

Variation in properties : Variation in some properties are observed in elements of Boron group which are as shown in Table 5.4.

Table 5.4 Some physical properties of group 13 elements

Physical Property	Elements				
	B	**Al**	**Ga**	**In**	**T*l***
Atomic number	5	13	31	49	81
Atomic mass	10.81	26.98	69.72	114.82	204.38
Atomic radius (pm)	85	143	135	167	170
Ionic radius m^{3+} (pm)	27	53.5	62.0	80.0	88.5
Ionic radius m^{1+} (pm)	—	—	120	140	150
Ionisation enthalpy (kJmol^{-1}) (I)	800	577	578	558	590
(II)	2427	1816	1979	1820	1971
(III)	3659	2744	2962	2704	2877
(IV)	25026	11578	6200	5200	—
Electronegativity (Pauling scale)	2.0	1.5	1.6	1.7	1.8
Density (g cm^{-3})	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
$E^0_{(V)}$ 298 K $M^{3+}_{(aq)} + 3e^- \rightarrow M_{(s)}$	——	− 1.66	− 0.56	− 0.34	+ 1.26
$E^0_{(V)}$ 298 K $M^+_{(aq)} + e^- \rightarrow M_{(s)}$	——	+ 0.55	——	− 0.18	− 0.34

pm = Picometer = 10^{-12} meter

(i) Atomic radii and ionic radii : In elements of boron group as the atomic number increases, new electron shell gets added and so the distance between the nucleus and outermost orbital having electron increases; hence the atomic radius increases. Similar trends can be observed in ionic radius. Anyhow, there is exception in atomic radius of Al and Ga. The atomic radius of Al (143 pm) is more than atomic radius Ga (135 pm) because there is no d-orbital in electronic configuration of Al while there is d-orbital in electronic configuration of Ga. As the d-orbitals are large in size, hence the magnitude of screening effect dereases with nucleus by eletrons present in them. Now, the nuclear charge of Gallium is high; as a result the attraction towards the nucleus by outermost orbital electron increases. Hence, atomic radius of Ga is less than that of Al. However a regular trend is observed in ionic radii.

(ii) Ionisation enthalpy : The order of first ionisation enthalpy $(\Delta_i H_1)$ for boron group elements is **B > Al < Ga > In < Tl.** The first ionisation enthalpy of Al is less than that of B because in Al the new valence shell is added and so the atomic size of Al increases which in turn increases the screening effect in Al that results in decreasing attractive forces towards the nucleus by the outermost orbital electrons. So first ionisation enthalpy is less than that of B, but the first ionisation enthalpy of Ga is little more (1 kJ mol^{-1}) compared to Al because in Ga the addition of new valence shell and also presence of 3d-orbital, which decreases the screening effect. This means it does not remain more effective so in Ga the attractive forces of electron towards the nucleus increases and hence, the first ionisation enthalpy is little more. In the same way Indium possesses 4d-orbital, which reduces the magnitude of screening effect and

increase in nuclear charge $(49 - 31 = 18 \text{ units})$ which is overweighing the screening effect towards nucleus by the electron arranged in outermost orbital is less compared to Ga. Hence, the first ionisation enthalpy of Induim is less compared to that of Ga. Now, the first ionisation enthalpy of Tl is higher than that of Induim because in Tl as the nuclear charge increases $(81 - 49 = 32 \text{ units})$ and also presence of 4f and 5d-orbitals still the decreases in reactivity of screening effect is overweighed by nuclear charge. **As a result force of attraction towards nucleus by the outermost orbital electrons increases.** So, the first ionisation enthalpy incereases.

Moreover, the value of second ionisation enthalpy $(\Delta_i H_2)$ and third ionisation enthalpy $(\Delta_i H_3)$ are very high because when first electron is removed, then the size of ion decreases and the effective nuclear charge increases and so the force of attraction towards the nucleus increases. Moreover, the second and third electrons are removed from s-type orbital which has more attractive forces towards the nucleus, so more energy is required to remove electron from them. Hence the values of $\Delta_i H_2$ and $\Delta_i H_3$ are very high.

(iii) Metallic character : The elements of group 13 show variation in metallic character. The metallic character is higher in Al than that of B. So Al is good conductor of heat and electricity. The reduction potential values go on increasing from Al to Tl, so the values of electropositivity decreases as a result, metallic character increases. Thus, B is non-metal, while Al is metal and in Indium, Ga and Tl the metallic character increases successively.

(iv) Electronegativity : On moving down the elements of group 13, electronegativity decreases suddenly from B to Al and after that it increases gradually as moving from Al to Tl, because the atomic volume increases as the atomic number increases. As the atomic volume increases, the attractive force for electron towards nucleus decreases.

(v) Melting points and Boiling points : The elements of group 13 show irregular trends in melting points, viz the melting point of B is the highest, while melting point of Al is low and melting point of Ga is the lowest; the melting point of In is more than that of Ga and Tl has little more. The order of melting points of group 13 elements are in order **B > Al > Ga < In < Tl.** The crystal structure of element is responsible for this. The boiling points of the elements of group 13 on moving down the group show regular trend. As the atomic number goes on increasing the boiling point decreases regularly.

(vi) Density : The density goes on increasing as the atomic number increases for the elements of group 13 because as the atomic number increases the volume increases but the increase in atomic mass is more compared to volume and hence, density increases.

(vii) Characteristic as reducing agent : The characteristic as reducing agent goes on decreasing on moving down the group, which means moving from Al to Tl, because the values of reduction potential increase from Al to Tl and so the reduction power decreases and the characteristic as reducing agent also decreases.

(viii) Nature of compounds : The elementes of group 13 have a decreasing tendency to form covalent bond compounds. The elements of group 13 have increasing tendency to form ionic compounds because the size of B is small and to form B^{3+} ion the sum of three ionisation enthalpy values $(\Delta_i H_1 + \Delta_i H_2 + \Delta_i H_3)$ is high, so boron does not form B^{3+} ion easily and hence, it forms covalent bond. Now, as the atomic number goes on increasing the atomic size also increases and total ionisation enthalpy value decreases. So, the tendency to form covalent bond decreases and tendency to form ionic bond increases. Boron forms compounds having covalent bond, while Al forms covalent bond and also to some extent has tendency to form ionic bond. While in Ga, In and Tl as the atomic number increases, the tendency to form compounds having ionic bond becomes prominent.

Oxidation state : In the electronic configurations of elements of group 13 they have two electrons in s-type orbital and one electron in p-type orbitals, so total three electrons in outermost orbital, hence it possesses +3 oxidation state. The oxidation state of boron and aluminium is +3 while Ga, In and Tl have both +1 and +3 oxidation states. As the atomic number is increasing the stability of +3 oxidation state decreases and stability of +1 oxidation state increases because on going down the group as the atomic number is increasing the tendency of s-electron to participate in bond formation decreases which means ns^2 electron of Ga, In and Tl remain paired because of intervening of d and f orbitals. The screening effect of ns^2 orbitals becomes poor and inert pair effect becomes more predominant as atomic number increases and so the ns^2 orbital electrons are more strongly attracted towards the nucleus and therefore, it is difficult to remove that electron, so the stability of oxidation state +1 increases and that of +3 oxidation state decreases. The stability of oxidation state is supported by following reaction.

$$Tl^{3+}_{(aq)} + 2e^- \rightarrow Tl^+_{(aq)} \quad E^0 = + 1.25 \ V$$
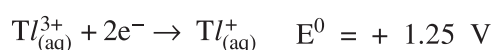
The reaction indicates that the +1 oxidation state is more stable than + 3 because **the reduction potential of this reaction has positive value.**

Trends in Chemical Reactivity : The variation is observed in chemical reactivity of group 13 elements, because in the electronic configuration of B and Al they have $ns^2 \ np^1$ type electronic configuration after the noble gas electronic configuration. While in electronic configuration of Ga and In, the intervening of d-orbital after the noble gas electronic configuration is followed by $ns^2 \ np^1$-type electronic configuration. Now in electronic configuration of Tl there is intervening of both d and f-type orbitals and after that $ns^2 \ np^1$ type electronic configuration takes place so that chemical reactivity of group 13 elements is as given below :

(i) Hydride compounds : Elements of group 13 do not combine directly with dihydrogen but they combine indirectly with dihydrogen to form hydride compounds e.g. Boron hydride is obtained by reaction of BF_3 with LiH.

$$2BF_3 + 6LiH \xrightarrow{450 \ K} B_2H_6 + 6LiF$$
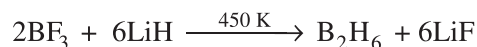
Boron forms number of hydrides, most of hydrides having molecular formula, **$B_n H_{n+4}$** and **$B_n H_{n+6}$** which is known as **Borane.** Other hydride elementes are polymeric e.g. $(AlH_3)_n$, $(GaH_3)_n$ and $(InH_3)_n$ their structure contains M.....H......M bridge (M = Al, Ga, In). The stability of hydrides decreases with increasing atomic number and so thalium hydride is quite unstable. These hydrides are Lewis acids which readily combine with strong Lewis base (B :).

$$B : + MH_3 \rightarrow [B \rightarrow MH_3] \ (M = Al \ or \ Ga)$$

In addition to these polymeric hydrides, Al or Ga also form complex tetrahydrides e.g. lithium tetrahydro aluminate (III). This is also known as lithium aluminium hydride, which can be obtained by the reaction of LiH and $AlCl_3$ in presence of dry ether.

$$4LiH + AlCl_3 \xrightarrow{Dry \ ether} Li^+[AlH_4]^- + 3LiCl$$
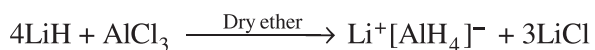
Particularly in organic reaction $LiAlH_4$ is used as a reducing agent.

(ii) Halide Compounds : Elements of group 13 form MX_3 type trihalides where X = F, Cl, Br and I. TlI_3 is unknown. Due to small size and high ionisation enthalpy boron atom has tendency to form covalent bond by sp^2 hybridisation and form trihalide. The trihalides BX_3 act as Lewis acid and the order of its strength is **$BI_3 > BBr_3 > BCl_3 > BF_3$.** In vapour form $AlCl_3$ exists in dimer form due to bridging of chlorine atoms and its structure is as shown in Figure 5.1.
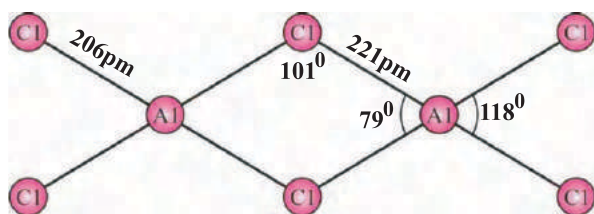
Fig 5.1 Structure of Al_2Cl_6 (dimer) (gaseous state)

$AlCl_3$ is Lewis acid. **BF_3 and $AlCl_3$ are strong Lewis acids and therefore used as a catalyst in Friedel and Crafts alkylation reaction and electrophilic aromatic substitution reaction.** Ga and T*l* also form MX type halides where M = Cl, Br, I. The stability of MX type halide increases as the atomic number increases, so that TlX is more stable than GaX.

(iii) Oxide and Hydroxide Compounds :

The group 13 elements form oxides having formula **M_2O_3** and hydroxide having formula **$M(OH)_3$.** As the atomic number of element goes on increasing the acidic character of oxide and the hydroxide decreases, and at the same time the basic character goes on increasing .e.g. oxide and hydroxide of boron are acidic, those of Al and Ga are amphoteric and In are basic while those of T*l* are strong base.

(iv) Complex and Double Salt Compounds :

In elements of group 13, in the electronic configuration of boron the d-orbital is absent, so it forms only tetrahedral complex like $[BH_4]^-$, $[BI_4]^-$, etc. The electronic configuration of Al, Ga, In and T*l* have d-orbital (in Al it is in form of $3d^0$), so they form octahedral complexes like $[AlF_6]^{3-}$, $[GaCl_6]^{3-}$, $[InCl_6]^{3-}$, and $[TlCl_6]^{3-}$, with octahedral aqua ions can be described as $[M(H_2O)_6]^{3+}$, (where M = Al, Ga, In, and T*l*). Aluminium sulphate reacts with sulphate of NH_4^+ and alkali metal ions and form double salts known as alums with formula $M_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ or $MAl(SO_4)_2 \cdot 12H_2O$ (where M = Na^+, K^+, Rb^+ and NH_4^+). The uses of this **double salts are to change hard water to soft water and as a mordant in chemicals of colour dye.**

The anomalous behaviour of the first element (boron) of group 13 : The first element of group 13, boron shows anomalous behaviour. For example,

(i) Boron is non-metal while other elements except boron show metallic characters.

(ii) Boron trihalide is monomeric while in other elements trihalides exist as a dimer or polymer.

(iii) Boron hydride is monomeric while in other elements hydrides exist as a dimer or polymer.

(iv) Boron does not react with water while other elements react with water and form oxides.

(v) Oxides and hydroxides of boron are acidic while the oxides and hydroxides of other elements are amphoteric or basic.

(vi) Except boron, trihalides of other elements on hydrolysis result in complex ions.

5.2 Physical and Chemical Properties of Boron (Chemical Reactions)

Physical properties of boron :

(i) Boron is extremely hard subtance. In order of hardness, it comes next to diamond.

(ii) The melting point and boiling point of boron are very high.

(iii) Boron is poor conductor of heat and electricity.

(iv) Boron has two isotopes ^{10}B and ^{11}B and its relative abundances is 20% and 80% respectively.

(v) Boron has two allotropes. The colour of amorphous form is dark brown whereas the crystalline form is found in black metallic luster.

Chemical properties (Chemical reactions) : Boron is chemically less reactive. It is almost inert towards normal chemical

reagents at normal temperature, but however, it reacts with strong oxidising agent and with some typical reagents as given below :

(i) Reaction with non-metal : Non-metal dinitrogen, dioxygen and dihalogen react with boron at high temparature.

$$4B + 3O_2 \xrightarrow{\Delta} 2B_2O_3$$

$$2B + N_2 \xrightarrow{\Delta} 2BN$$

$$2B + 3X_2 \xrightarrow{\Delta} 2BX_3 \ \ (\text{where } X = Cl, Br, I)$$
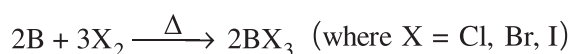
(ii) Reaction with acid : Boron does not react with HCl but it reacts with con. HNO_3 and H_2SO_4 and oxidises to boric acid.

$$2B + 3H_2SO_4 \xrightarrow{\Delta} 2H_3BO_3 + 3SO_2$$

$$B + 3HNO_3 \xrightarrow{\Delta} H_3BO_3 + 3NO_2$$
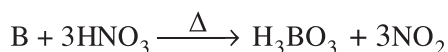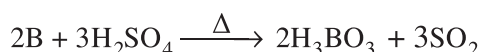
(iii) Reaction with alkali : Boron reacts with fused alkalis like NaOH and KOH and converts into corresponding borates and liberates dihydrogen.

$$2B + 6NaOH_{(l)} \xrightarrow{\Delta} 2Na_3BO_3 + 3H_2$$
$$\text{Sodium borate}$$

$$2B + 6KOH_{(l)} \xrightarrow{\Delta} 2K_3BO_3 + 3H_2$$
$$\text{Potassium borate}$$
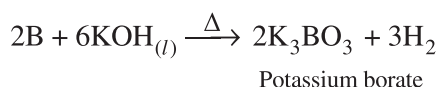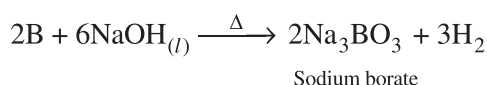
(iv) Reaction with metal : Boron reacts with some metals on heating and converts in to borides which are very hard and solid substances having high melting points. e.g.

$$B + Cr \xrightarrow{\Delta} CrB \ \ \text{(Chromium boride)}$$

5.3 Some Important Compounds of Boron

(1) Borax Powder ($Na_2B_4O_7$) : The important compound of boron is borax or **sodium tetraborate** $(Na_2B_4O_7)$. The impure form of borax is Tincal which contains 55% borax. It is found in certain dried up lakes of India, Tibet, Sri Lanka and California.

Preparation :

(i) Borax from Tincal : Tincal is dissolved in water and boiled. On filteration insoluble impurities like sand, clay etc are removed. While borax remains soluble in solution, the solution is concentrated, and on cooling crystals of borax separates out.

(ii) Borax from colemanite : On boiling mineral colemanite with sodium carbonate, the borax, $CaCO_3$ and sodium metaborate are formed. The $CaCO_3$ which is obtained as insoluble so it is in form of precipitates and removed by filteration and solution is obtained. Concentrating the solution and on cooling crystals of borax are obtained. Mother liquor still having sodium metaborate is converted to borax by passing CO_2 in the solution.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \xrightarrow{\Delta}$$

$$2CaCO_{3(s)} + \underset{\text{Borax}}{Na_2B_4O_7} + \underset{\substack{\text{Sodium} \\ \text{metaborate}}}{2NaBO_2}$$

$$\underset{\substack{\text{Sodium} \\ \text{metaborate}}}{4NaBO_2} + CO_2 \rightarrow \underset{\text{Borax}}{Na_2B_4O_7} + Na_2CO_3$$
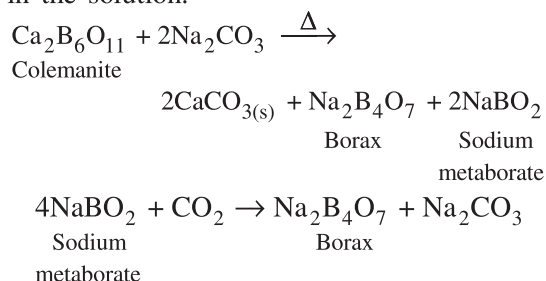
(iii) Borax from boric acid : On neutralization of boric acid by Na_2CO_3 borax is obtained.

$$\underset{\text{Boric acid}}{4H_3BO_3} + Na_2CO_3 \xrightarrow{\Delta}$$

$$\underset{\text{borax}}{Na_2B_4O_7} + 6H_2O + CO_2$$
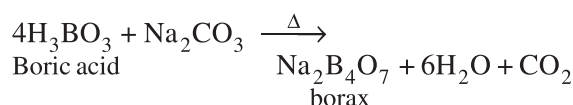
The mixture is heated and on cooling borax separates as crystals.

Properties of Borax :

(1) Borax is found in three forms. **(a) Prismatic $Na_2B_4O_7 \cdot 10H_2O$ (b) Octahedral $Na_2B_4O_7 \cdot 5H_2O$ (c) Borax glass $Na_2B_4O_7$**

(2) Borax is white, crystalline solid substance sparingly soluble in cold water and highly soluble in hot water.

(3) Aqueous solution of borax is basic due to its hydrolysis.

$$Na_2B_4O_7 + 2H_2O \rightarrow H_2B_4O_7 + 2NaOH$$
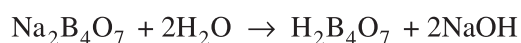
(4) On heating borax, due to its decomposition swells and loses water of crystalization and becomes anhydrous; on further heating it melts and forms glassy, transparent bead known as borax bead.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow{\Delta} \underset{\substack{\text{Sodium} \\ \text{metaborate}}}{2NaBO_2} + \underset{\substack{\text{Boron oxide or} \\ \text{boric anhydride}}}{B_2O_3}$$

$$\text{glassy transparent borax bead.}$$
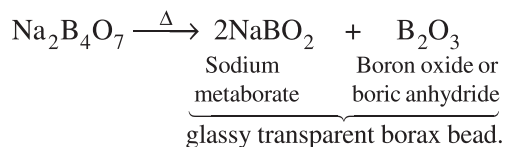
(5) When the glassy, transparent bead is dipped in coloured ions like Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+} and heated, they are converted into their metaborates respectively and they are coloured and their colours are brown, blue, green and pink respectively e.g.

$$NiO + B_2O_3 \xrightarrow{\Delta} \underset{\substack{\text{Nickel metaborate} \\ \text{(Brown colour)}}}{Ni(BO_2)_2}$$
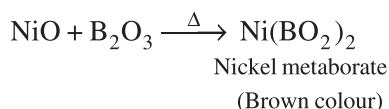
Uses :

(i) It is used in laboratory to perform borax bead test in qualitative analysis.

(ii) It is used in manufacturing of enamels and glazing of earthen pots.

(iii) Used in preparation of candles.

(iv) Due to its antiseptic properties it is used in preparation of medicinal soap.

(v) It is used in making optical glass.

(vi) Used in softening of hard water.

(2) Boric acid (H_3BO_3) : Its trivial name is **orthoboric acid.**

Preparation :

(i) Boric acid from borax : Acidifying the aqueous solution of borax by adding HCl or H_2SO_4, Boric acid is obtained which on concentrating and cooling gives crystals of boric acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \xrightarrow{\Delta} 4H_3BO_3 + 2NaCl$$

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \xrightarrow{\Delta} 4H_3BO_3 + Na_2SO_4$$
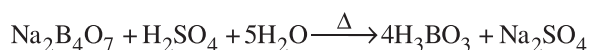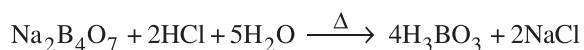
(ii) Boric acid from mineral colemanites : Powder the mineral colemanite, add water and boil it. On passing SO_2 gas boric acid and calcium bisulphite are obtained. Calcium bisulphite is highly soluble in water while boric acid is sparingly soluble, so on cooling boric acid gets separated.

$$Ca_2B_6O_{11} + 11H_2O \xrightarrow{\Delta} 2Ca(OH)_2 + 6H_3BO_3$$

$$2Ca(OH)_2 + 4SO_2 \xrightarrow{\Delta} 2Ca(HSO_3)_2$$

net reaction :

$$Ca_2B_6O_{11} + 11H_2O + 4SO_2 \xrightarrow{\Delta} 6H_3BO_3 + 2Ca(HSO_3)_2$$
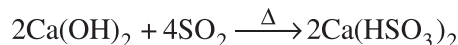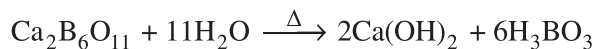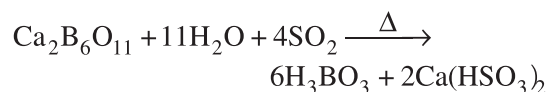
(iii) Boric acid from hydrolysis of boron compounds : On hydrolysis of BCl_3 and BN, they give boric acid.

$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$$

$$BN + 3H_2O \rightarrow H_3BO_3 + NH_3$$
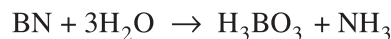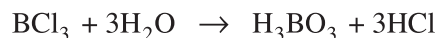
Properties :

(i) Boric acid is a white crystaline solid substance with a soft soapy touch.

(ii) It is sparingly soluble in cold water but fairly soluble in hot water.

(iii) At different temperatures the effects of heat on it are as given below :

$$\underset{\text{Orthoboric acid}}{4H_3BO_3} \xrightarrow[-H_2O]{373\ K} \underset{\text{Metaboric acid}}{4HBO_2} \xrightarrow[-H_2O]{433\ K}$$

$$\underset{\text{Tetraboric acid}}{H_2B_4O_7} \xrightarrow[-H_2O]{\text{red hot}} \underset{\text{Boron oxide}}{2B_2O_3}$$
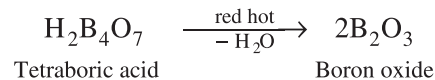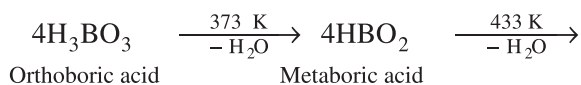
(iv) It is a weak monobasic acid and acts as a Lewis acid.

(v) In presence of H_2SO_4 it reacts with ethanol and form ethyl borate.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{[H^+]} \underset{\text{Ethyl borate}}{B(OC_2H_5)_3} + 3H_2O$$
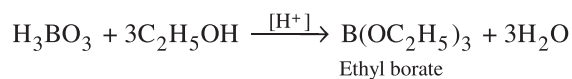
(vi) The structure of boric acid having H—bond is given in Fig. 5.2.
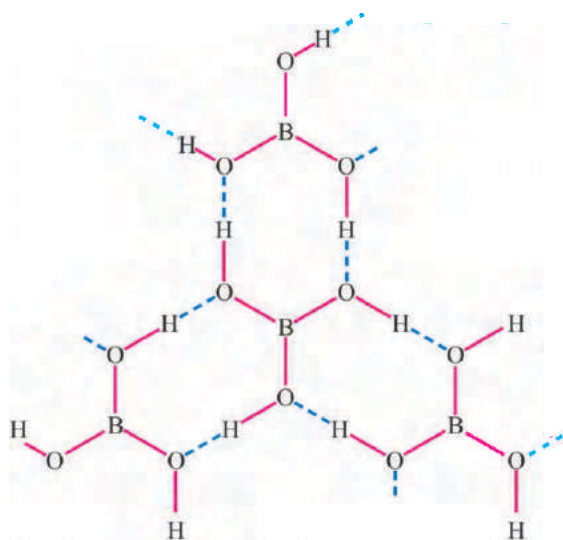
Fig. 5.2 Structure of boric acid having H-bond

(**The dotted lines represent hydrogen bonds**)

Uses :

(i) In food industry it is used as a preservative for the preservation of food.

(ii) Used in the preparation of pigments and borax.

(iii) It is used (in medicine) as an eye wash.

(iv) Used in the manufacturing of enamels and pottery glazes.

(3) Boron hydrides : Boron forms a number of hydride compounds having general formula B_nH_{n+4} **and** B_nH_{n+6}. **Boron hydrides are also called Boranes.** B_2H_6 **(diborane) is a boron hydride.**

Preparation of Diborane (B_2H_6) **:** In the laboratory, diborane is prepared by the reaction of iodine with sodium-borohydride in the presence of polyether as a solvent.

$$2NaBH_4 + I_2 \xrightarrow{\text{polyether}} B_2H_6 + 2NaI + H_2$$
$$\text{Diborane}$$
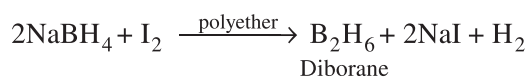
On an industrial scale, diborane is obtained by the reaction of boron trifluoride or boron trichloride with lithium hydride at 450 K temperature.

$$2BF_3 + 6LiH \xrightarrow{450\,K} B_2H_6 + 6LiF$$

$$2BCl_3 + 6LiH \xrightarrow{450\,K} B_2H_6 + 6LiCl$$
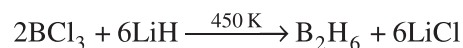
Properties :

(i) Diborane is colourless and highly toxic gas.

(ii) Diborane has strong affinity for O_2 and therefore it catches fire spontaneously on exposure to air and releases energy. The heat of combustion is very high.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$
$$\Delta H = -2008 \text{ kJ mol}^{-1}$$
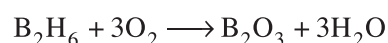
(iii) At 450 K temparature, if diborane is heated with NH_3, forms **Borazine** $(B_3N_3H_6)$ having structure like benzene and hence it is also called inorganic benzene.

$$3B_2H_6 + 6NH_3 \xrightarrow{450\,K} 2B_3N_3H_6 + 12H_2$$
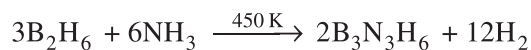
(iv) Diborane on hydrolysis gives boric acid and liberates H_2 gas.

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$$
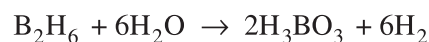
(v) The structure of diborane is given in Figure 5.3.
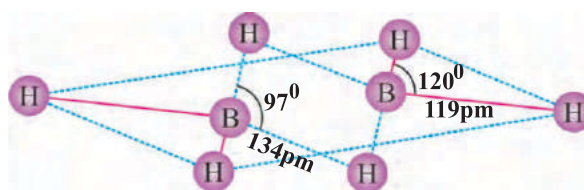
Fig. 5.3 The structure of diborane, B_2H_6

Uses of Boron and its Compounds :

(i) Isotope of boron ^{10}B has ability to absorb neutrons and therefore used as metal borides, in nuclear reactor as a **protective shield** and the **controlling rod**s and also used in chemotherapy to cure cancer.

(ii) Boron fibres are used in making light composite materials for air craft industries.

(iii) Boron and boric acid are used in manu-facturing of **heat resistant borosilicate pyrex glass.** They are also used in metallurgy as **a flux for soldering** metals.

(iv) Borax is used for making **porcelain enamels.**

(v) In laboratory, borax powder is used in **borax bead test** for detection of coloured metallic ions.

(vi) Aqueous solution of boric acid is used as **a mild antiseptic.**

(vii) In leather industry borax is used for cleaning **skin (leather)** while in food industry it is used as a **preservative.**

(viii) The heat of combustion for diborane is very high, so it is used as a high energy fuel.

5.4   Properties of Aluminium

(i) Aluminium is a light, silvery white metal.

(ii) It has high **tensile strength,** high electrical and thermal conductivity. (twice than that of Cu).

(iii) It is highly electropositive.

(iv) It readily reacts with O_2 and forms a protective layer of Al_2O_3 on its surface, which makes it passtive.

Uses :

(i) Aluminium is used extensively in industries and in daily life.

(ii) It forms useful alloys with Cu, Mn, Mg, Si and Zn.

(iii) Al and its alloys are used in making utensils, aeroplane parts and also in some preparations.

(iv) It is used in **Aluminothermite process** for obtaining the chromium and manganese metals from their oxides.

(v) Aluminium is used as a **strong reducing agent.**

Reaction of Aluminium with acids and bases :
Aluminium reacts both with acid and base. Thus, it is amphoteric.

With acid : Aluminium dissolves in dil HCl, dil H_2SO_4 and liberates H_2 gas slowly.

$$2Al + 6HCl + 12H_2O \longrightarrow 2[Al(H_2O)_6]Cl_3 + 3H_2$$
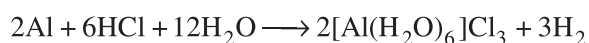
On heating with concentrated H_2SO_4 aluminium produces SO_2 gas.

$$2Al + 6H_2SO_4 \xrightarrow{\Delta} Al_2(SO_4)_3 + 3SO_2 + 6H_2O$$
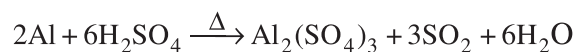
Aluminium reacts with concentrated HNO_3 and forms inactive, passive protective layer of Al_2O_3 on surface which stops the further reaction on its surface.

Reaction with base : Aluminium dissolves in strong alkali $(NaOH$ or $KOH)$ to form sodium aluminate or potassium aluminate and H_2 gas is evolved.

$$2Al + 2NaOH + 6H_2O \longrightarrow 2Na[Al(OH)_4] + 3H_2$$

5.5   General Introduction of Group 14 Elements

Group 14 includes the elements. Carbon (C), Silicon (Si), Germanium (Ge), Tin (Sn) and Lead (Pb). The first element of this group is carbon, so they are also called carbon group elements. **Carbon shows catenation characteristic due to its small size, high eletronegativity** and very high carbon-carbon bond enthalpy. Due to typical character of catenation, it forms chain and cyclic compounds having carbon-carbon $\sigma-$bond as well as $\pi-$bond. Moreover, one carbon can form one or more than one bond with another carbon or with other atoms. also e.g. $C = C$, $C \equiv C$, $C - O$, $C = O$, $C - N$, $C = N$, $C \equiv N$ and compounds having such type of bonding are studied in Organic Chemistry. Compounds of carbon with metals, metalliods and with non-metals are called binary inorganic compounds. The compounds like calcium carbide, silicon carbide, carbon monoxide, carbon dioxide, hydrogen cyanide are inorganic compounds. Organic compounds have their contribution in the fields like living organism, non-living organisum, medicine, plastic etc.

Electronic Configuration : Carbon group elements have **electronic configuration $ns^2\,np^2$ in outermost valence orbital** where n = 2 to 6. The electronic configurations of carbon group elements are given in Table 5.5.

Table 5.5 Electronic Configurations of Elements of Group 14

Element	Atomic No.	Electronic Configuration	
		Complete	**With inert gas core**
Carbon (C)	6	$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$	[He] $2s^2\ 2p_x^1\ 2p_y^1$
Silicon (Si)	14	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1$	[Ne] $3s^2\ 3p_x^1\ 3p_y^1$
Germanium(Ge)	32	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p_x^1\ p_y^1$	[Ar] $3d^{10}\ 4s^2\ 4p_x^1\ 4p_y^1$
Tin (Sn)	50	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}$ $5s^2\ 5p_x^1\ 5p_y^1$	[Kr] $4d^{10}\ 5s^2\ 5p_x^1\ 5p_y^1$
Lead (Pb)	82	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}$ $4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p_x^1\ 6p_y^1$	[Xe] $4f^{14}\ 5d^{10}\ 6s^2$ $6p_x^1\ 6p_y^1$

Occurrence : Carbon is the seventeenth most abundant element by weight out of elements obtained from the earth's crust. In earth's crust it occurs in form of coal, petroleum and metal carbonate of eletropositive metals. In atomosphere it is in the form of CO_2. All living organisms contain carbon in form of organic compounds. Silicon is present in nature in the form of silica (SiO_2) and silicates. Moreover it is an important component used in ceramics, glass and cement. Silicon is the second most abundant (27.7 %) by weight in the earth's crust. Germanium occurs as a trace element and is mainly recovered from the flue dust arising from roasting of zinc ores. Tin and Lead are found in nature in the amount 2 ppm and 13 ppm respectively. **Galena (PbS)** is the principal ore of lead. Found along with **zinc blende (ZnS).** Other ores of lead are **anglesite $(PbSO_4)$** and **cerussite $(PbCO_3)$**

Variation in properties : Group 14 elements have variation in some properties as shown in Table 5.6.

Table 5.6 Some Physical Properties of Group 14 Elements

Property	Elements				
	C	**Si**	**Ge**	**Sn**	**Pb**
Atomic number	6	14	32	50	82
Atomic mass	12.01	28.09	72.60	118.71	207.2
Covalent radius for M(II) state	77	118	122	140	146
Ionic radius (M^{4+})(pm)	—	40	53	69	78
Ionic radius (M^{2+}) (pm)	—	—	73	118	119
Ionisation enthalpy (M^+) (I) $(kJ\ mol^{-1})$	1086	786	761	708	715
(II)	2352	1577	1537	1411	1450
(III)	4620	3228	3300	2942	3081
(IV)	6220	4354	4409	3929	4082

Electronegativity (Pauling scale)	2.5	1.8	1.8	1.8	1.9
Density (g cm^{-3}) at 293 K	3.51 (for diamond) 2.21 (for graphite)	2.34	5.32	7.26	11.34
Melting point (K)	4373	1693	1218	505	600
Boiling point (K)	–	3550	3123	2896	2024
Electrical resistivity (ohm cm)	10^{14}–10^{16}	50	50	10^{-5}	2×10^{-5}

(i) Atomic radii : On moving down the group the atomic radii of group 14 elements go on increasing as the atomic number increases, but from silicon and onwards, Ge, Sn and Pb due to intervening of d and f - orbitals in electronic configuration and because of the ineffective shielding effect the atomic radii increases gradually.

(ii) Ionisation enthalpy : On moving down in the group 14 as the atomic number increases, the order of change one notices in ionisation enthalpy is **C > Si > Ge > Sn < Pb.** From C to Sn as the atomic number increases the atomic size also increases and hence the ionisation enthalpy decreases but instead of decreasing the ionisation enthalpy of Pb slightly increases because of the intervening of d and f- both types of orbitals in electronic configuration of Pb. So the force of attraction towards the nucleus increases due to poor shielding effect of that orbital and hence, ionisation enthalpy decreases.

(iii) Eletropositivity (Metallic character) : On moving down the group 14 the eletropositivity increases, so the carbon behaves totally as non-metal. Silicon is essentially a non-metal and Germanium is metalloid (having pronounced metallic character) while tin and lead are typical metals. Elements of group 14 are less eletropositive, hence, the metallic character observed is less.

(iv) Eletronegativity : The elements of group 14 are more eletronegative than elements of group 13. The electrongativity decreases as the atomic number increases due to increase in the atomic size. But it remains almost same from Si to Pb.

(v) Melting points and Boiling points : The melting points and boiling points of group 14 elements are much higher than those of group 13 elements, because elements of group 14 form four covalent bonds, hence there exists a strong binding between the atoms. Therefore the melting points and boiling points are higher. The intermolecular forces decrease as the atomic number increases in group 14 and therefore, melting point and boiling point also decrease.

(vi) Density : On moving down in the elements of group 14, that means from carbon to lead, regular increase in density is seen because there is a greater increase in atomic mass than increase in atomic size, so the density increases.

(vii) Catenation : Group 14 elements show catenation property in the order **C > > Si > Ge ≈ Sn > > Pb.** Because the atomic size of carbon is less and eletronegativity is higher, further the C – C bond enthalpy is also very high, so it indicates maximum catenation properties at the same time remarkable decrease in silicon.

(viii) Allotropy : Elements of group 14 show allotropy. Carbon has number of allotropic forms out of which diamond, graphite and fullerene are the crystalline forms of carbon. Tin has two allotropes, **white tin or β–tin.** It gets stable at room temparature whereas **grey tin or α–tin** remains unstable, and it can be obtained from β–tin at 286 K temperature.

white tin $(\beta - \text{tin}) \xrightleftharpoons{286\ K}$ grey tin $(\alpha - \text{tin})$

Oxidation states and trends in chemical reactivity : Group 14 elements have outermost valence shell electronic configuration $ns^2\ np^2$ and hence, these elements have common oxidation state +4. Now due to intervening of d and f-orbitals in Ge, Sn and Pb the inert pair effect becomes more and more prominent so they all show oxidation state +2 with +4 and the stability of +2 oxidation state increases in order, which can be given as Ge < Sn < Pb. Thus, the divalent state of lead is more prominent. The trends in chemical reactivity are given below :

(i) Simple M^{4+} ions in this group are not known.

(ii) Except carbon the other elements of the group form compounds with co-ordination number higher than 4, like e.g.$[SiF_5]^-$, $[SiF_6]^{2-}$, $[PbCl_6]^{2-}$.

(iii) In divalent state, stable compounds of MX_2 type for carbon and silicon are rare. The stability of divalent state increases in the order **Ge < Sn < Pb.**

(iv) Tendency of catenation decreases in the order as **C >> Si > Ge ≈ Sn > Pb.**

(v) Ability to form $p\pi - p\pi$ bonds with element itself and ability to form such bond with other elements like dinitrogen and dioxygen decreases from carbon to lead. So, CO_2 is a gas but silica is a solid.

(vi) Si, Ge, Sn, and Pb form MX_4 type tetrahedral and covalently bonded compounds. The ionic character and thermal stability of halides decreases with increasing atomic number of halogen and they are hydrolysed by water, e.g.

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$$

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl$$
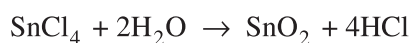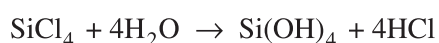
Ge, Sn and Pb also form MX_2 type halides. The stability of dihalides increases in order

$CX_2 < < SiX_2 < < GeX_2 < < SnX_2 < PbX_2$

The divalent state becomes more stable on moving down the group. $Sn(II)Cl_2$ is obtained by dissolving Sn in con. HCl. On cooling this solution, $Sn(II)Cl_2$ crystallises in form of $SnCl_2 \cdot 2H_2O$. Anhydrous $SnCl_2$ acts as a reducing agent in acidic solution.

$$2Fe^{3+} + Sn^{2+} \rightarrow Sn^{4+} + 2Fe^{2+}$$
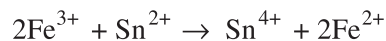
Pb(II) halides are obtained by adding halide ions into a soluble lead salts.

$$Pb^{2+} + 2X^- \rightarrow PbX_2 \ \left(\text{where X = F, Cl, Br, I}\right)$$
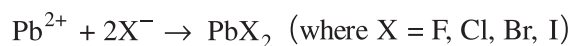
PbI_2 is yellow, other halides are colourless and sparingly soluble in water.

(vii) Si, Ge, Sn and Pb form MO_2 type oxides. In silica, silicon and oxygen atoms combine by covalent bond and form infinite three dimensional network of four oxygen atoms. In SiO_2 each Si atom is covalenty bonded to four oxygen atoms. In SiO_2 Si atom combines with oxygen atoms tetrahedrally.

Crystalline silicon dioxide occurs in **quartz, cristobalite and tridymite minerals.** Quartz is used as a **piezoelectric crystal, crystal oscillator** and **in transducers.** Silica gel is obtained by acidification of sodium silicate. When this gel is dehydrated, the **obtained silica gel is extensively used in chromatography and for the drying of other subtances,** and therefore, it acts as a drying agent.

GeO_2, SnO_2 and PbO_2 are solid and exist in several modifications. **SiO_2 is acidic but GeO_2 and SnO_2 are amphoteric while PbO_2 is basic.** Sn(IV) oxide is prepared by heating Sn and O_2 or reaction of Sn with con HNO_3. SnO_2 is used in polishing powder and in manufacturing of glass and pottery. PbO_2 is prepared by reaction of Pb_3O_4 with dil HNO_3.

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

PbO_2 is a strong oxidising agent and liberates O_2 when treated with acids. Sn and Pb

both form MO type stable oxides. SnO is obtained by heating tin oxalate.

$$SnC_2O_4 \xrightarrow{\Delta} SnO + CO + CO_2$$

PbO exists in red, orange and yellow colour depending upon the method of preparation. It can be prepared by heating lead carbonate. On heating PbO with air in a reverbatory furnace at 773 K temperature gives red Pb_3O_4. It is a combination mixture of $2(PbO) \cdot (PbO_2)$.

Anomalous behaviour of carbon : Carbon differs from the other members of its group, because the atomic size of carbon is small and has higher electronegativity. The ionisation enthalpy of carbon is high and also lacks d-orbital in its electronic configuration. Due to following characteristics, it differs from the other members of its group.

(i) Carbon forms only four covalent bonds while other elements have d or d and f-orbitals. So they can form more covalent bonds. (5 or 6)

(ii) Carbon atom forms single bond. Moreover, double or triple bond with the other carbon atoms and some other atoms like O,N and S which are small in size and have high eletronegativity forms $C = O$, $C = S$, $C = N$, $C \equiv N$ with $p\pi - p\pi$ bonding. If the atomic size of some other atoms are very big then overlapping of $p\pi - p\pi$ orbital does not remain effective.

(iii) The trend of catenation in carbon is maximum due to its high value of carbon-carbon single bond enthalpy $(348 \text{ kJ mol}^{-1})$. So it forms number of organic compounds having chain and cyclic structure while in other elements, this trend goes on decreasing.

(iv) Carbon forms only $p\pi - p\pi$ type bonding while other elements form $p\pi - p\pi$ and also $d\pi - p\pi$ type of bonding.

5.6 Carbon Catenation

The carbon atom has tendency to link with another carbon atom by covalent bond and forms chain or cyclic structure of carbon which is called catenation. This trend is observed due to small size and high eletronegativity of carbon atom. Tendency of catenation depends upon the bond enthalpy of covalent bond between two carbon atoms; higher the bond enthapy more is the tendency of catenation. The bond enthalpy of $C - C$ is 348 kJ mol^{-1} which is the highest than the other elements in its group so it forms a number of chain and cyclic structure compounds due to catenation and $p\pi - p\pi$ bond fomation the carbon exhibits different allotropes.

Allotropes : Due to catenation in carbon and $p\pi - p\pi$ bond formation, it exhibits many allotropes. The diamond and graphite are the crystalline allotropes. In 1985, H.W.Kroto, R.E.Smalley and R. I. Curl discovered the third crystalline allotrope fullerene. Coal wood charcoal, animal charcoal lamp black, coke, gas carbon etc are amorphous allotropes of carbon. The structure and properties of crystalline allotropes are given below :

(i) Diamond : Due to **sp^3 hydridisation** in carbon, it combines with other four carbon atoms by single covalent bond. The bonded four carbons are arranged towards the corner of the tetrahedron as shown in Fig. 5.4. Each carbon atom, due to sp^3 hybridisation joins with other four carbon atoms by single covalent bond and forms three dimensional network structure. The distance between two carbon atoms is **154 pm.** All the carbon atoms are bound to each other by covalent bonding and these bonds are very strong. So diamond is extremely hard solid substance.

154 pm
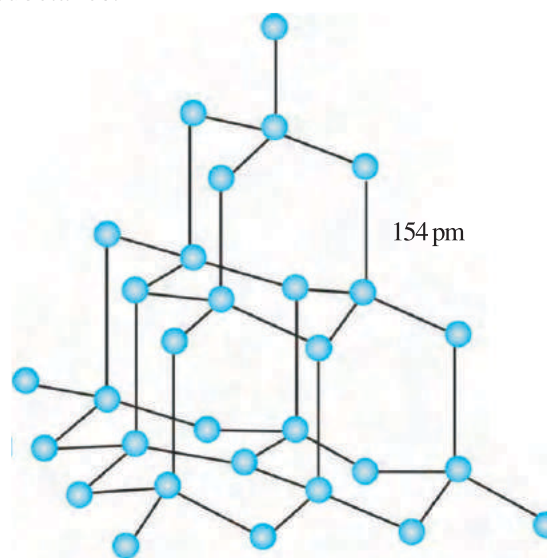
Fig 5.4 Diamond

(ii) Graphite : As the result of **sp^2** hybridisation in carbon atom, it combines with other

three carbon atoms and as a result hexagonal layer structure is formed as shown in Figure 5.5. The distance between two carbon atoms is 141.5 pm and distance between two layers is 340 pm and have weak van der Waals attractive forces between the two layers. Due to weak van der Waals forces the graphite is soft.
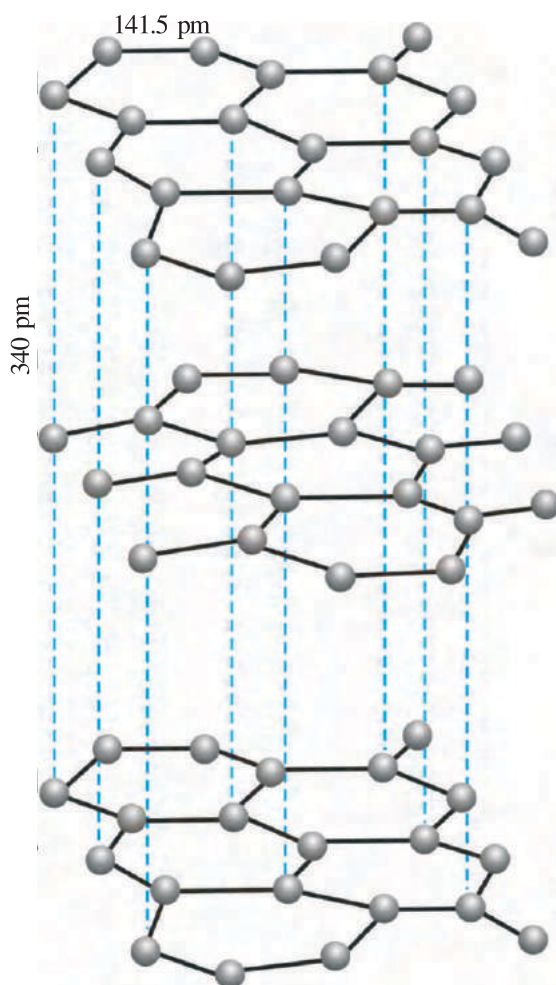
Fig 5.5 Graphite

(iii) Fullerene : The crystalline form of carbon is made up of **porous cage** like molecules. It possesses C_{2n} structure. The two important members are having number of carbon atoms C_{60} and C_{70}. Crystalline fullerene was first prepared by evoparation of graphite using lasers but presently preparation involves the heating of graphite in an electric arc in the presence of an inert gas such as He or Ne, that gives sooty material on condensation, mainly C_{60} with small quantity of C_{70} and traces of other fullerene,

consisting of even number of carbon atom upto 350 or above. As shown in Figure 5.6 the C_{60} molecule has shape like **soccer ball** and also called Buckminister Fullerene as given in Figure 5.6.
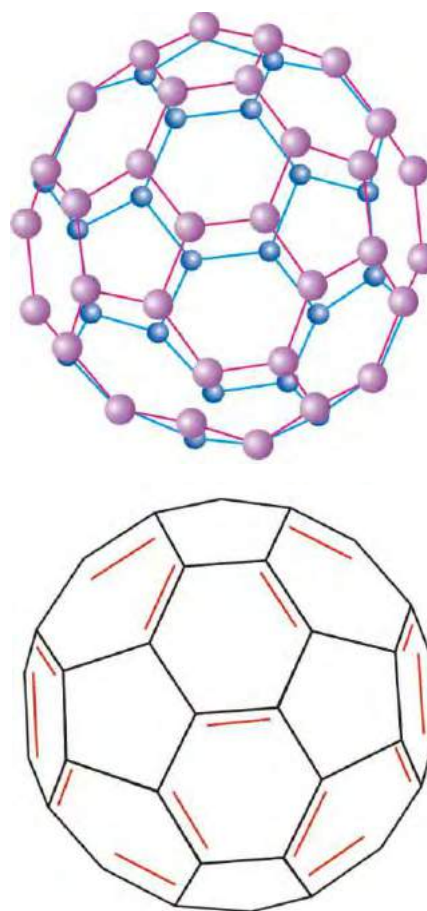
Fig 5.6 Fullerene

The shape of fullerence resembles to shape of football. The special shape of fullerene is also called **bucky ball.** It contains twelve rings having five carbon atoms and twenty rings having six carbon atoms. The ring structure having six carbon atoms is fused to both types of ring, while the ring structure having five carbon atoms is fused only to six membered ring. All the carbon atoms in Fullerene are equivalent and they undergo **sp^2 hybridisation.** So each carbon atom combines with other three carbon atoms with σ−bond. The remaining electron forms π−bond and hence, the π−bond electron gets delocalised in molecular orbital which gives aromatic character in fullerene. In fullerene the carbon-carbon single and double bonds with distance 143.5 pm and 138.3 pm are there respectively. **C_{60} and C_{70} fullerene are soluble**

in toluene solvent and give purple and orange-red coloured solution. Fullerenes are the only pure forms of carbon because they have no dangling bond so possess smooth structure.

Physical Properties of Carbon :

(i)   Carbon has a number of allotropes from which diamond, graphite and fullerene are crystalline, and different types of coal, coke, gas carbon are the amorphous allotropes.

(ii)   Diamond is hard whereas graphite is soft.

(iii)   Diamond is insulator while graphite is good condutor of electricity.

(iv)   Fullerene is the crystalline synthesized form of carbon. It has cage like structure.

(v)   Diamond and graphite have network structure while fullerene has molecular structure.

(vi)   Diamond and graphite are insoluble in liquid solvent, while fullerence is soluble in suitable solvent (benzene).

(vii)   Charcoal is porous, hence, it possesses the adsorption property.

Chemical Properties (Chemical reactions)

(i)   All the allotropic forms of carbon burn in air and form CO or CO_2. If the proportion of O_2 is limited, then CO is formed and if the proportion of O_2 is more, then CO_2 is formed. This combustion reaction is exothermic reaction.

$$2C + O_2 \rightarrow 2CO + Energy$$

$$C + O_2 \rightarrow CO_2 + Energy$$
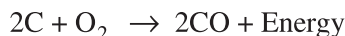
(ii)   **Reduction properties :** Carbon is a strong reducing agent. It reduces many metallic oxides and form corresponding metals. During reduction, sulphide is obtained from metal sulphate.

$$ZnO + C \rightarrow Zn + CO$$

$$PbO + C \rightarrow Pb + CO$$

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

$$BaSO_4 + 4C \rightarrow BaS + 4CO$$

$$PbSO_4 + 4C \rightarrow PbS + 4CO$$
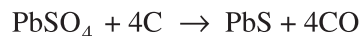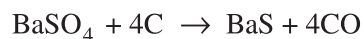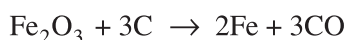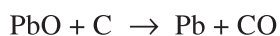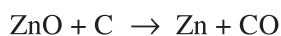
On passing water vapour over red hot coke H_2 gas can be evolved.

$$C + H_2O \rightarrow CO + H_2$$
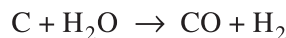
(iii)   **Reaction with other elements :** Passing vapour of sulphur over the red hot carbon gives CS_2.

$$C + 2S \rightarrow CS_2 \text{ (carbon disulphide)}$$
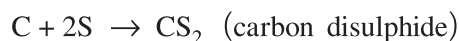
When an electric spark is struck between carbon electrodes in the presence of H_2, acetylene is formed.

$$2C + H_2 \xrightarrow{\text{Electric spark}} C_2H_2 \text{ (Acetylene)}$$
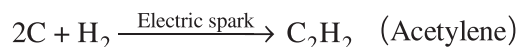
When carbon is heated with beryllium, it forms beryllium carbide.

$$2Be + C \xrightarrow{\Delta} Be_2C \text{ (Beryllium carbide)}$$

(iv)   **Reaction with acid :** When charcoal is heated with hot and dil HNO_3, it slowly dissolves and gives brown substance which is known as artificial tannin. When carbon reacts with con. HNO_3 it gets oxidised and forms CO_2

$$C + 4HNO_3 \rightarrow CO_2 + 4NO_2 + 2H_2O$$

Carbon reacts with hot con. H_2SO_4, it gets oxidised to CO_2 and H_2SO_4 is reduced to SO_2 and a small quantity of mellitic acid (Beneze hexacarboxylic acid) is also formed.

$$C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$$

$$12C + 9H_2SO_4 \rightarrow \underset{\text{Mellitic acid}}{C_6(COOH)_6} + 6H_2O + 9SO_2$$

Uses of some important compounds of carbon :

(1) Halides of carbon : The reaction of carbon with halogen forms carbon tetrahalides. CF_4 is a gaseous, CCl_4 is liquid while CBr_4 and CI_4 are solids. Its order of stability is $CF_4 > CCl_4 > CBr_4 > CI_4$

Uses :

(i) CCl_4 is used as a solvent and **fire extinguisher.**

(ii) CF_2Cl_2, which is known as **Freon,** was earlier used in refrigerator as a coolant.

(iii) CCl_4 is used as medicine for hookworm in intenstine.

(2) Carbon disulphide : (CS_2) :

Uses :

(i) It is used in the manufacture of Viscose Yarn.

(ii) It is used as an insecticide for curing infected seeds.

(iii) It is used in vulcanisation of rubber.

(iv) It is used as solvent in the manufacture of varnishes and match-sticks.

(v) It is used in the manufacture of carbon tetrachloride

(3) Carbide Compounds : The compounds of carbon with high electropositive elements are known as carbide compounds. e.g. SiC, Fe_3C, CaC_2, WC, Al_4C_3, Be_4C

Uses :

(i) SiC, which is known as **carborandum,** is very hard, so used as **refractory** and **abrassive for** sharpening and grinding metals and other substances.

(ii) WC is used for making tools and mould, for making coins etc.

(iii) CaC_2 is used for preparing acetylene and it is used for **welding** and in manufacturing of number of organic compounds such as ethyl alcohol, acetic acid etc.

(iv) Be_4C is very hard and is used as a shield against radioactive radiation.

(4) Oxides of carbon : Carbon can burn in air or O_2 and gives carbon monoxide (CO) and carbon dioxide (CO_2).

(i) Carbon Monoxide (CO) :

Preparation :

(i) Carbon monoxide is prepared by incomplete combustion of carbon or carbon containing compounds in a limited supply of O_2

$$C + \frac{1}{2}O_2 \xrightarrow{\Delta} CO$$
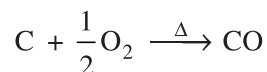
Incomplete combustion of petrol and diesel produces CO.

(ii) CO is prepared by the reduction of oxides of heavy metals with carbon.

$$ZnO + C \rightarrow Zn + CO$$

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$
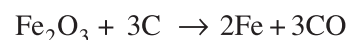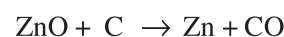
(iii) Pure CO can be prepared in a laboratory on small scale by heating formic acid (HCOOH) with con H_2SO_4 at about 373 K to 413 K temperature. Here, H_2SO_4 acts as a dehydrating agent.

$$HCOOH \xrightarrow[\text{Con.} H_2SO_4]{373\,K-413\,K} CO + H_2O$$
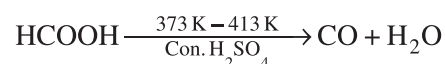
(iv) On commercial scale CO is prepared by passing water vapour at 473 K to 1273 K temperature over hot coke and produce mixture of CO and H_2 which is known as watergas or synthesis gas.

$$C_{(s)} + H_2O_{(g)} \xrightarrow{473\,K-1273\,K} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{Water gas}}$$
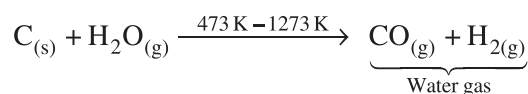
Instead of water vapour if air is used then it produces mixture of CO and N_2 which is known as producer gas.

$$2C_{(s)} + O_{2(g)} + 4N_{2(g)} \xrightarrow{1273\,K} \underbrace{2CO_{(g)} + 4N_{2(g)}}_{\text{Producer gas}}$$
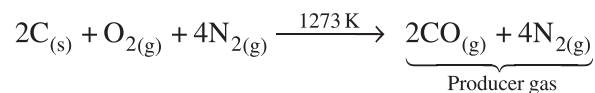
Properties :

(i) Carbon monoxide is colourless and odourless gas, and it is sparingly soluble in water.

(ii) It is highly toxic in nature because it forms stable (nearly 300 times) complex with haemoglobin present in blood and stops the oxygen carrying capacity of the blood, hence it causes death.

(iii) CO on combustion gives pale blue flame

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 + Heat$$
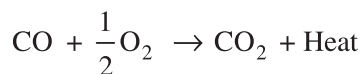
(iv) Reducing character : It reacts with many metal oxides and reduces to corresponding metals e.g.

$$ZnO + CO \rightarrow Zn + CO_2$$

$$CuO + CO \rightarrow Cu + CO_2$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$
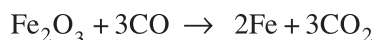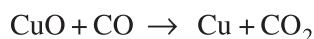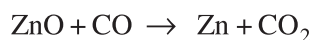
(v) Formation of metal carbonyl character : CO combines as ligand with many transitional metals, such as Ni, Fe, Co etc and form metal carbonyl complex compounds. e.g.
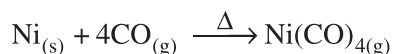
$$Ni + 4CO \xrightarrow{333\ K - 343\ K} [Ni(CO)_4]$$
Nickel tetracarbonyl

$$Fe + 5CO \rightarrow [Fe(CO)_5]$$
Iron pentacarbonyl
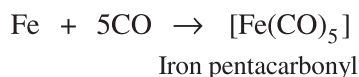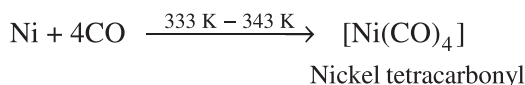
Uses :

(i) CO is useful for extraction of some metals from their oxides. For example, used in blast furnace.

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$
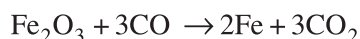
(ii) CO is used to prepare tetracarbonyl nickel in **Mond's carbonyl process** to obtain pure nickel metal from impure nickel metal.

$$Ni_{(s)} + 4CO_{(g)} \xrightarrow{\Delta} Ni(CO)_{4(g)}$$

(iii) In industrial field CO is used as a fuel in the form of water gas and producer gas.

(iv) It is used in manufacturing of methyl alcohol and formic acid.

(v) It is used in manufacturing of **magnetic tapes** (Iron carbonyl) for tape recorder.

(ii) Carbon Dioxide (CO_2) :

Preparation :

(i) Carbon dioxide is prepared by burning carbon, hydrocarbon like CH_4 or carbon monoxide in excess of air.

$$C + O_2 \rightarrow CO_2$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$2CO + O_2 \rightarrow 2CO_2$$
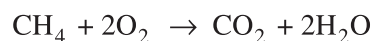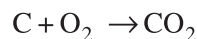
(ii) In laboratory, CO_2 is obtained by reaction of $CaCO_3$ with dil HCl

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

(iii) On industrial scale, CO_2 is obatined as a by-product during manufacturing of lime and manufacturing of ethyl alcohol.

$$CaCO_3 \xrightarrow[1600\ K]{\Delta} \underset{Lime}{CaO} + CO_2$$

$$C_6H_{12}O_6 \xrightarrow[enzyme]{Zymase} 2C_2H_5OH + 2CO_2$$
Ethyl alchol
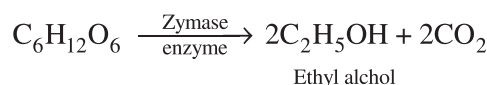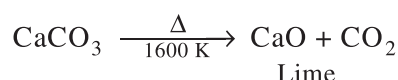
Properties :

(i) It is colourless, odourless gas and about 1.5 times heavier than air.

(ii) It is not poisonous but it does not support life of animal and human being but they die in its presence due to lack of O_2 gas.

(iii) At room temperature and 50 to 60 atm. pressure CO_2 gas can be liquefied, when liquid CO_2 is allowed to evaporate rapidly i.e. expands rapidly, it is converted into solid which is known as dry ice.

(iv) CO_2 gas is neither combustible nor supporter of combustion. However, in its presence certain active metals such as Na, K, Mg etc. continue to burn.

$$2Mg + CO_2 \rightarrow 2MgO + C$$

(v) CO_2 turns blue litmus paper red so it is acidic in nature.

(vi) It is sparingly soluble in water but when dissolved in water, **carbonic acid (soda water (H_2CO_3)** can be obtained which is dibasic acid and it dissociates in two stages.

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3^+O$$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3^+O$$
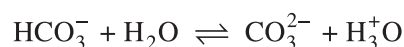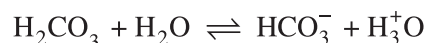
(vii) On passing CO_2 through lime water it turns milky due to formation of insoluble $CaCO_3$ and on passing it in excess milkiness disappears due to formation of soluble calcium hydrogencarbonate (calcium bicarbonate)

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
Lime water   Calcium carbonate

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$
Calcium hydrogen-
carbonate
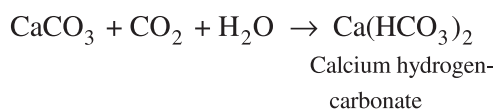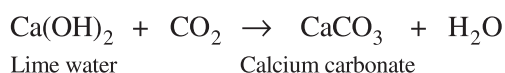
(viii) In the presence of sunlight and chlorophyll of green plants, CO_2 reacts with water to form glucose. This reaction is called photosynthesis.

$$6CO_2 + 6H_2O \xrightarrow[\substack{\text{In presence of}\\ \text{chlorophyll}}]{hv} C_6H_{12}O_6 + 6O_2$$
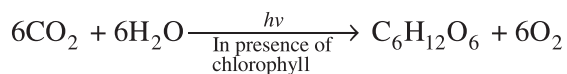
Uses :

(i) Mixture of ether and solid CO_2 creates low temperature upto 165 K, hence it is used in liquefying other gases and **act as a coolant in cold storage.**

(ii) CO_2 is neither combustible nor supporter of combustion. Therefore it is used as a fire extinguisher.

(iii) CO_2 is used in preparation of soft drinks and soda water.

(iv) CO_2 used in manufacturing of washing soda (Solvay's Process).

(v) Dry ice is used in curing of local burns and in hospital for surgical operation of sores.

(vi) During artificial respiration for the victims of CO poisoning it is used in form of **carbogen $\left(95\% \; O_2 + 5\% \; CO_2 \text{ mixture known as carbogen}\right).$**

(vii) CO_2 is used for the purification of cane sugar juice in manufacturing of sugar.

(viii) CO_2 is used in photosynthesis by green plants.

(ix) To control the $pH(7.26$ to $7.42)$ of blood CO_2 gas is used in **carbonic acid buffer system $\left(H_2CO_3 + HCO_3^-\right).$**

(x) Large amount of CO_2 is used in production of fertiliser like urea.

Important Compounds of Silicon :

(1) Silicon hydrides : Hydride compounds of silicon have general formula Si_nH_{2n+2}. The value of bond enthalpy for silicon-silicon is 297 $kJmol^{-1}$ hence, catenation character is observed in it so it forms limited hydride compounds Si_nH_{2n+2} where n = 1 to 8. This compound is also known as **silane.** The stability of silanes are less compared to hydrides of carbon, hence, they have more reduction power.

(2) Silicon dioxide : (Silica) SiO_2 : It is a solid substance having three diamensional structure. A silicon atom combines with four oxygen atoms by covalent bonding. Thus, SiO_2 does not exist as a single molecule but the arrangement of number of atoms form a giant crystal. More than 22 allotropic structures are known in which some are crystalline like quartz, tridimite, crystobelite etc., while amorphous like silica gel and kieselgur. SiO_2 is acidic, hence, it dissolves in liquid alkali or alkali carbonate to form silicate compounds.
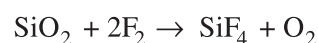
At high temperature SiO_2 reacts with NaOH to form Na_2SiO_3.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$
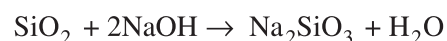
SiO_2 react with HF and gives SiF_4

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$
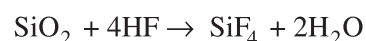
SiO_2 reacts with halogen (only F_2) and SiF_4 is obtained and O_2 is liberated.

$$SiO_2 + 2F_2 \rightarrow SiF_4 + O_2$$

Uses of Silica :

(i) It is used as a **Piezoeletrical crystal, crystal oscillators** and as transducer.

(ii) It is used in laboratory glassware and preparation of optical components such as lens and prisms.

(iii) Used in sample cell for U.V. spectrophotometers.

(iv) Used as a drying agent in form of silica gel and also in material for adsorption in chromatography.

(v) Used as catalyst

(vi) Used in water filteration plants in form of Kieselghur

(3) Silicon tetrachloride ($SiCl_4$) : Reaction of silicon with chlorine on heating gives $SiCl_4$

$$Si + 2Cl_2 \xrightarrow{\Delta} SiCl_4$$
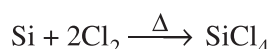
In silicon tetrachloride silicon has sp^3 hybridisation and so it is tetrahedral in shape and forms covalent bond with chlorine atom. Hydrolysis of $SiCl_4$ give **silicic acid** (H_4SiO_4)

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$$
$$\text{Silicic acid}$$
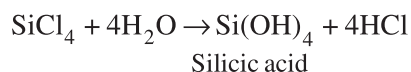
The mechanism for hydrolysis of $SiCl_4$ are in two steps as given below :

(i) In the first step the oxygen atom of H_2O molecules donates pair of electron to empty d-orbital of silicon in $SiCl_4$ and forms co-ordination covalent bond.
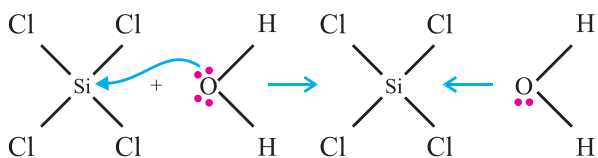
(ii) In second step as the HCl molecule is removed, the chlorine atom of $SiCl_4$ is substituted and finally silicic acid is obtained.
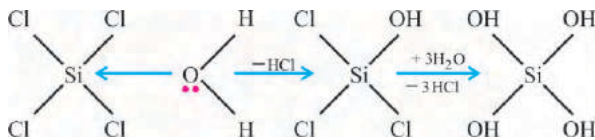
Silicic acid

Silicones : Silicones are synthetic materials containing Si − O − Si bond linkage. These compounds are polymeric substances containing R_2SiO repeating unit. They have general formula $(R_2SiO)_n$ where R is alkyl or aryl group. Its empirical formula R_2SiO is similiar to that of ketone of organic compound, so they are called **silicones.**

Preparation : Methyl chloride reacts with silicon in the presence of copper powder as a catalyst at 570 K temperature, dimethyl chlorosilane is obtained and its hydrolysis is followed by condensation polymerisation that gives silicone.

$$2CH_3Cl + Si \xrightarrow[\text{570 K}]{\substack{\text{Powder}\\\text{of Cu}}} (CH_3)_2SiCl_2 \xrightarrow[\substack{2H_2O\\-2HCl}]{\text{Hydrolysis}} (CH_3)_2Si(OH)_2$$
$$\substack{\text{Dimethyl}\\\text{chloro silane}} \qquad\qquad \substack{\text{Dimethyl}\\\text{Silanol}}$$
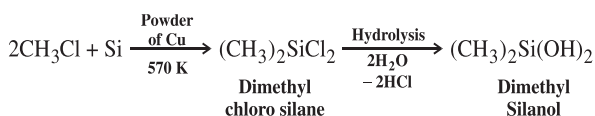
The length of this polymer chain can be controlled by $(CH_3)_3 SiCl$
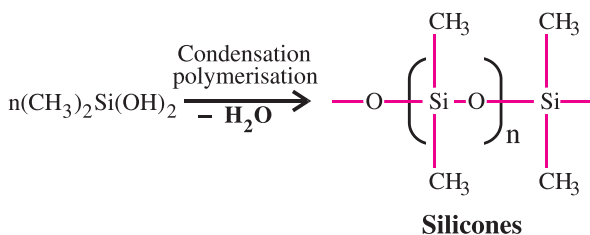
Silicones

Properties :

(i) Short chain silicones are oily, liquid, medium chain behave as viscous oil jellies and greases and those with very long chain behave as **rubbery elastomers** and resins

(ii) Silicones resist the organic reagent, oxidation and thermal decomposition. Hence, they are chemically inert.

(iii) Silicones are heat resistant and electric insulator substances; more over, possess the character of water repellent.

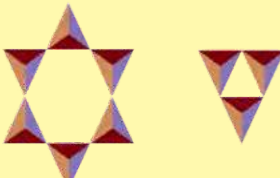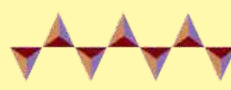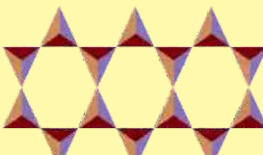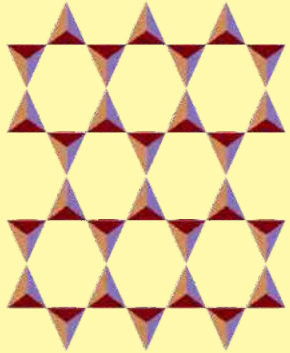### Uses :

(i) For making water-proof paper, wool, textiles, wood. etc they are coated with a thin film of silicones.

(ii) Silicones are used as sealants and electri-cal insulators.

(iii) Used as lubricant at high and low temperatures.

(iv) Used as surgical implants.

(v) Used as antifoaming agents in cosmetics

General Information and Structure of Silicates : Approximately 95% of the earth crust consists of silicates and silica. Silicate compounds contain independent SiO_4^{4-} or such type of ions joined to form combined silicate ions and their charges are being balanced by cations such as Na^+, K^+, Mg^{2+}, Ca^{2+}. The basic structural building block in silicates is the SiO_4^{4-} having tetrahedral structure.

Types of silicates : In the structure of silicates depending upon the number of corner $(0, 1, 2, 3, 4)$ of the SiO_4^{4-} tetrahedron shared with other tetrahedrons and based on that they are classified which are indicated in Table 5.7. In a three dimensional structure of SiO_2, Si^{4+} is partially substituted by Al^{3+} which gives alumi-nosilicate called feldspar. In aluminosilicate the SiO_4^{4-} and AlO_4^{5-} tetrahedrons join with each other in a simple way to form three dimensional networks known as zeolites.

Table 5.7 Classification of silicates

No. of corner of SiO_4^{4-}	Structural arrangement	Type	Anion unit	Examples
0		Orthsilicate	SiO_4^{4-}	Zircon $(ZrSiO_4)$, Forsterite (Mg_2SiO_4)
1		Pyrosilicate	$Si_2O_7^{6-}$	Thortveitite $Sc_2(Si_2O_7)$, Hemimorphite $Zn_2Si_2O_7$ $Zn(OH)_2 \cdot H_4O$
2		Cyclic silicate	$Si_3O_9^{6-}$	Wollastonite $Ca_3Si_3O_9$
		Ring silicate	$Si_6O_{18}^{12-}$	Beryl $Be_3Al_2Si_6O_{18}$
		Chain silicate	$(SiO_3^{2-})_n$	Spodumene $LiAl(SiO_3)_2$
		(a) Linear silicate	**OR** $(SiO_3)_n^{2n-}$	Diopside $CaMg(SiO_3)_2$
		(b) Cross link Chain	$(Si_4O_{11}^{6-})_n$	Tri-molyte $Ca_2Mg_5[Si_8O_{22}](OH)_2$

| 3 | | Sheet silicate | $(Si_2O_5)_n^{2n-}$ OR $(Si_2O_5^{2-})_n$ | Stearite $Mg_3[Si_4O_{10}](OH)_2$ Muscovite $KAl_2[Si_3AlO_{10}](OH)_2$ |
| 4 | | Three dimensional | SiO_2 | Feldspar, Zeolite, (alumino-silicate) different types of silica (quartz, trydimite cristobalite) |

Uses of zeolite : Zeolite has a network of cavities linked by channels. In these channels only small molecules can enter, hence, zeolite is used as a molecular sieve for separating small molecules from big molecules; zeolite is used as a catalyst (shape-selective catalyst). One important calayst of zeolite is ZSM-5. It is used in petrochemicals. It converts alcohol directly into gasoline (petrol) by dehydration and the mixture of hydrocarbons is formed.

SUMMARY

The elements (except He atom) having outermost valence shell electronic configuration $ns^2\, np^1$ to $ns^2\, np^6$ are called p-block elements. Since p-orbital can accommodate six maximum electrons, six groups 13 to 18 are there in p-block elements. We shall study group 13 and 14 i.e. Boron and carbon group elements in this unit. Generally in a row or period electronegativity, ionisation enthalpy and oxidising power are increasing as the atomic number increases while in group it decreases as the atomic number increases. Generally, in group, covalent radius, van der Waals radius and metallic character increases as the atomic number increases. It is a characteristic of the p-block elements that metal, non-metal and metalloid are included in the same group.

The group 13 includes elements, Boron, Aluminium, Gallium, Indium and Thalium. Aluminium is the third most abundant element found in earth's crust. The important ores of aluminium are bauxite and cryolite. Variation in some properties of group 13 elements are like atomic radii and ionic radii, ionisation enthalpy, metallic character, electronegativity, melting point and boiling point, density, character as reducing and nature of compound are observed in elements of boron group i.e. Group 13 elements having electronic configuration $ns^2\, np^1$. Hence, they possess +3 oxidation state and their stability goes on decreasing as the atomic number increases. These elements also possess +1 oxidation state and the stability goes on increasing as the atomic number increases.

The chemical reactivity of group 13 elements are as given below. Group 13 elements do not combine directly with hydrogen but they combine indirectly to form hydride compounds. Boron forms a number of hydrides having molecular formula $B_n H_{n+4}$ and $B_n H_{n+6}$ which are known as boranes. The other elements of this group form

polymeric hydrides. Group 13 elements form MX_3 type trihalides, where X = F, Cl, Br and I are unknown. $AlCl_3$ exists in dimer form. The group 13 elements form oxides and hydroxides having fomula M_2O_3 and $M(OH)_3$ respectively. As the atomic number of elements goes on increasing, the acidic character of oxide and hydroxide goes on dcereasing. Elements of this group form octahedral complexes. Aluminium sulphate reacts and forms double salts with sulphate of NH_4^+ and alkali metal ions having fomula $M_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ or $MAl(SO_4)_2 \cdot 12H_2O$ where M = Na^+, K^+, Rb^+ and NH_4^+. The first element (Boron) of group 13 shows anomalous behaviour. Boron is chemically less reactive and almost inert with normal chemical reagents at normal temperature but reacts with strong oxidising agents and with some typical reagents like non-metal, acid, alkali and metals. Some important compounds of boron are borax powder, boric acid and boron hydride. The properties and uses of aluminium are as given in the text. Aluminium reacts with acid and base so it is amphoteric in nature.

The group 14 includes elements carbon, silicon, germanium, tin and lead. The first element of this group is carbon, so it is also known as carbon group elements. Carbon shows catenation property due to its small size, high electronegativity and very high carbon-carbon bond energy. Due to typical characteristic of catenation it forms number of compounds which are studied in organic chemistry. It also forms compounds with metals and non-metals. Group 14 elements have variation in properties like atomic radii, ionisation enthalpy electropositive character, electronegativity, melting points and boiling points, density, catenation and allotropy. The oxidation state of group 14 elements are +2 and +4. The trends in chemical reactivity are as given in the text. The carbon shows anomalous behaviour. The crystalline allotropes of carbon are diamond, graphite and fullerenes. The physical properties and chemical properties are as given in the text. Some important compounds of carbon are halides of carbon, carbon disulphide, carbide compounds, carbon monoxide and carbon dioxide, and the method of preparation and uses are as given in the text. The important compounds of silicon are silicon hydrides having general formula Si_nH_{2n+2}. The value of bond enthalpy for silicon-silicon is 297 kJmol^{-1} hence catenation character is observed in silicon and it forms limited hydride compounds, having formula Si_nH_{2n+2} where n = 1 to 8, and these compounds are also known as silanes. The stability of silane compounds are less compared to hydrides of carbon and hence reducing power is more. Silicon also forms silicon dioxide known as silica and more than 22 allotropic structures are known in which some are crystalline and some are amorphous. Silica is acidic and hence it dissolves in liquid alkali or alkali carbonate to form silicate compounds. Silicon reacts with only F_2 and form SiF_4 while reacts with Cl_2 and form $SiCl_4$. The hydrolysis of $SiCl_4$ gives silicic acid and the mechanism for hydrolysis are in two steps. The silicones are synthetic materials containing $Si - O - Si$ bond linkage. These compounds are polymeric substances containing R_2SiO reapeating unit. The general formula is $(R_2SiO)_n$, where R is methyl or phenyl group. The empirical formula is R_2SiO which is similar to that of organic compound, ketone, so it is called silicone. The prepartion, properties and uses are as given in the text.

Approximately 95% of earth's crust consists of silicates and silica compounds, containing independent SiO_4^{4-} having tetrahedral structure. The types of silicates depending upon the number of corners (0, 1, 2, 3 and 4) of the SiO_4^{4-} tetrahedron are shared with other tetrahedrons and based on that they are classified as given in the text. In a three dimensional structure of SiO_2, its Si^{4+} partially substituted by Al^{3+} gives alumino-silicate are called feldspar and zeolites. In zeolites the SiO_4^{4-} and AlO_4^{5-}. tetrahedron joined together in simple way to form three dimensional network. The uses of silicates are as a molecular sieves and shape selectives catalyst. One important catalyst of silicate is ZSM-5 used in petrochemical industry which converts alcohol directly into gasoline.

EXERCISE

1.   **Select the proper choice from the given multiple choices :**

(1)   What is the general electronic configuration for valence orbital of p-block elements ?

(A) $ns^2\ np^1$ (B) $ns^2\ np^6$ (C) $ns^2\ np^{1-6}$ (D) $ns^2\ np^{1-5}$

(2)   Which is the correct order of ionisation enthapy of group 13 elements ?

(A) B > Al > Ga > In > Tl   (B) B < Al < Ga < In < Tl

(C) B > Al < Ga > In < Tl   (D) B > Al > Ga < In < Tl

(3)   What is the general formula for boron hydride ?

(A) B_nH_{2n+4} (B) B_nH_{n+6} (C) B_nH_{2n+6} (D) $B_{2n}H_{n+6}$

(4)   Mention the colour of borax bead when it comes in contact with Cr^{3+} ion solution ?

(A) Brown   (B) Blue   (C) Pink   (D) Green

(5)   Which substance is known as inorganic benzene ?

(A) Boron   (B) Diborane   (C) Hexaborane   (D) Borazine

(6)   Which element has second order in abundance in earth's crust ?

(A) Carbon   (B) Germanium   (C) Silicon   (D) Aluminium

(7)   Which halide is colourless ?

(A) $PbCl_2$ (B) $PbBr_2$ (C) PbF_2 (D) All

(8)   Which substance is used to stop the radioactive rays ?

(A) Be_4C (B) WC   (C) CaC_2 (D) Al_4C_3

(9)   Which mixture is known as producer gas ?

(A) $CO + N_2$ (B) $CO + H_2$

(C) $CO + H_2O$ (D) $N_2 + O_2$

(10) Which substance is obtained on the hydrolysis of $SiCl_4$?

    (A) SiO_2 (B) SiH_4 (C) Na_4SiO_4 (D) H_4SiO_4

(11) What type of silicate is the talc ?

    (A) ring   (B) branch   (C) pyro   (D) sheet

(12) Give use of ZSM-5 ?

    (A) isomerism in petrol   (B) direct gasoline from alcohol

    (C) preparation of hydrocarbons   (D) all

(13) Which compound is more stable ?

    (A) CF_4 (B) CI_4 (C) CCl_4 (D) CBr_4

(14) What is observed when excess of CO_2 is passed in lime water ?

    (A) Lime water becomes milky

    (B) Milky colour of lime water disappears

    (C) O_2 gas is produced in lime water

    (D) $CaCO_3$ is obtained in lime water

(15) Which proportion is correct for boron isomers ?

    (A) ^{10}B 20%   (B) ^{11}B 20%   (C) ^{11}B 40%   (D) ^{10}B 80%

2.   **Write the answers of the following question in short :**

(1) Which groups are known as p-block elements ?

(2) Write the names of elements of group 13 ?

(3) Give the name of ore of indium.

(4) Write the increasing order of atomic radii of group 13 elements.

(5) State the oxidation states of gallium.

(6) Which hydrides of group 13 elements are in polymeric form ?

(7) Hydroxides of which elements of group 13 are amphoteric ?

(8) Give three forms of borax.

(9) State the effect of heat on boric acid.

(10) Draw structure of diborane.

(11) Write equation for reaction of Al with dil HCl.

(12) What is catenation ?

(13) Give the names of elements of group-14.

(14) Write allotropes of tin.

(15) Write the order of stability of dihalides of carbon group elements.

(16) Write uses of SnO_2.

(17) Which substance was earlier used as a coolant in refrigerators ?

(18) Write uses of tungsten carbide.

(19) Write equation for production of pure CO.

(20) What is carbogen ?

(21) Write uses of silica gel.

(22) Which ions are present in aluminosilicate ?

(23) Write uses of ZSM-5

(24) Give the equation for reaction of con HNO_3 with carbon.

(25) Mention the general and empirical formula of silicones

3.   **Write the answers of the following questions :**

(1)   Why the first ionisation enthapy of In is less Tl ?

(2)   Why does the boron form covalent bond instead of ionic bond ?

(3)   Why does the stability of +3 oxidation state goes on decreasing as the atomic number increases in group 13 ?

(4)   Explain the double salts with suitable example.

(5)   Write the equation of reaction B with H_2SO_4 and NaOH.

(6)   Explain the equation of preparation of borax from boric acid.

(7)   Write the uses of boric acid.

(8)   Explain metallic character of elements of group 14.

(9)   Write uses of silica.

(10) Write the anomalous behaviour of carbon.

(11) Expalin the properties of carbon as strong reducing agent.

(12) Write uses of CS_2.

(13) Give the equation for preparation of producer gas and water gas.

(14) Write properties of CO.

(15) Write uses of CO_2.

(16) Give the equation for preparation of silicon hydride.

(17) Write equations for preparation of silicones.

(18) Write uses of silicones.

(19) Write uses of zeolites.

(20) What is aluminosilicate ? Explain.

(21) Which is the pure form of carbon ? Why ?

(22) Write the equation for preparation of borax bead.

(23) Write uses of borax powder.

(24) Draw structure of Al_2Cl_6 and write uses of $AlCl_3$.

4. **Write the answers of the following questions in detail :**

(1) Explain the chemical reactivity of group 13 elements.

(2) Explain the preparation and properties of boric acid.

(3) Write the uses of boron and its compounds.

(4) Explain the chemical properties of carbon.

(5) Write the preparation and properties of CO.

(6) Write the properties and uses of CO_2.

(7) Explain the preparation of silicon tetrachloride and its hydrolysis.

(8) Write short notes :

(1) Silicones   (2) Silicate compounds

Hydrocarbons

6.1 Introduction

Simple organic compounds in which only carbon and hydrogen atoms are present, are called Hydrocarbons. Hydrocarbons are very important compounds in our daily life. Hydrocarbons are obtained from natural sources such as plants and animals. The main sources of hydrocarbons in nature are petroleum, natural gas, coal etc. Hydrocarbon compounds also include petrol, diesel, LPG, CNG etc. Hydrocarbons can be used to manufacture different types of polymers, dyes, paints, drugs etc. Therefore, it is necessary to study them for better understanding and the importance of hydrocarbon in our daily life.

6.2 Hydrocarbons

Hydrocarbons are considered as the simplest compounds in organic chemistry, as only carbon and hydrogen atoms are present in them. Hydrocarbons are obtained from natural sources such as coal, natural gas and petroleum.

6.2.1 Classification of Hydrocarbons :

Different types of organic compounds can be obtained by replacing the hydrogen atom of hydrocarbon by appropriate functional group.

There are four main types of hydrocarbons based on the different types of bonds between carbon-carbon atoms in them. They are as follows : (i) Alkane compounds (ii) Alkene compounds (iii) Alkyne compounds and (iv) Arene compounds.

(i) Alkanes are saturated hydrocarbons. Alkanes contain single bond between carbon-carbon atoms and carbon-hydrogen atoms. Alkanes are acyclic and cyclic compounds.

(ii) Alkenes are unsaturated hydrocarbons. Alkenes contain atleast one carbon-carbon double bond. Like alkanes, alkenes also contain acyclic and cyclic compounds.

(iii) Alkynes are unsaturated hydrocarbons. Alkynes contain atleast one carbon-carbon triple bond. Alkynes mainly contain acyclic compounds.

(iv) Arene compounds are special type of unsaturated hydrocarbons. Arenes contain characteristic carbon-carbon double-bond. Arene compounds are mainly cyclic compounds.

6.2.2 Classification of Carbon and Hydrogen atoms in hydrocarbons :

Each carbon and hydrogen of a hydrocarbon is classified based on the number of other carbon atoms attached to them.
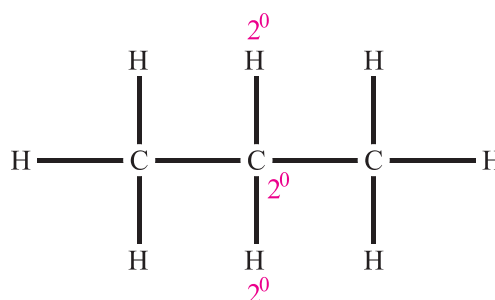
If a carbon atom is attached to only one carbon atom, it is called primary (1^0) carbon. Hydrogen attached with this primary carbon is called primary (1^0) hydrogen.
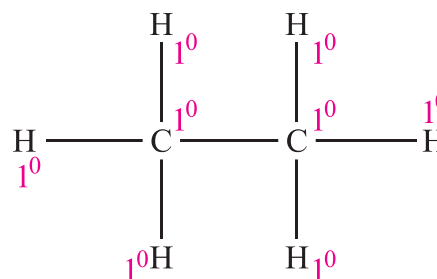
Ethane

In the above example, both the carbon atoms are primary (1^0) carbon, and also all the hydrogen atoms linked to them are primary hydrogen.
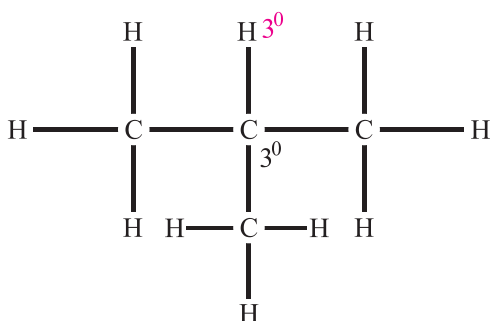
If one carbon atom is attached to two other carbon atoms then that carbon is known as secondary (2^0) carbon. The hydrogen atoms linked to this (2^0) secondary carbon are called secondary (2^0) hydrogen.
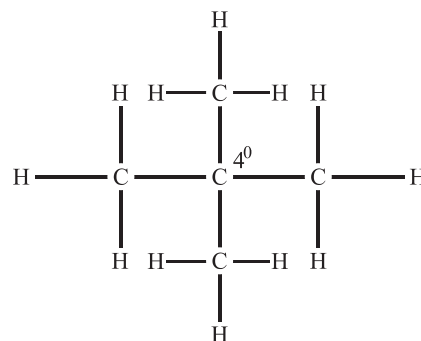

Propane

In the above example, the central carbon is attached with two other carbon atoms, hence, it is called secondary (2^0) carbon, and the two hydrogen atoms attached to it are also secondary (2^0) hydrogens.

If one carbon atom is attached to three other carbon atoms, then, that carbon is known as tertiary (3^0) carbon and the hydrogen attached to that carbon is called tertiary (3^0) hydrogen.

2 Methyl Propane

Dimethyl propare

In the above example the tertiary (3^0) carbon is attached with three other carbon atoms and the three hydrogens attached to it are tertiary (3^0) hydrogens.

If a carbon atom is attached to four other carbon atoms it is called quarternary (4^0)
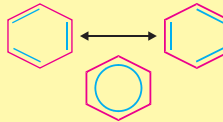
carbon. The four carbons complete its tertravalency, and hence, no hydrogen can be attached to it. As a result, quarternary (4^0) hydrogen is not possible.

The classification of hydrocarbons is given in Table 6.1.

Table 6.1 Classification of Hydrocarbons

Hydrocarbon	Type	Characteristic	General Formula	Bond	Shape	Example	Structure
Alkane	Acyclic	Saturated	C_nH_{2n+2}	C − C	Three Dimensional	Methane	CH_4
						Ethane	CH_3CH_3
						Propane	$CH_3CH_2CH_3$
	Cyclic	Saturated	C_nH_{2n}	C − C	Planar Three Dimensional	Cyclopropane	
						Cyclobutane	
Alkene	Acyclic	Unsaturated	$C_n H_{2n}$	C = C C − C	Planar	Ethene Propene	$CH_2 = CH_2$ $CH_2 = CH-CH_3$
	Cyclic	Unsaturated	C_nH_{2n-2}	C = C C − C	Planar	Cyclopropene	
						Cyclobutene	

Alkyne	Acyclic	Unsaturated	$C_n H_{2n-2}$	$C \equiv C$ $C - C$	Linear	Ethyne Propyne	$CH \equiv CH$ $CH \equiv C-CH_3$
Arene	Cyclic	Characteristic Unsaturated	$C_n H_{2n-6}$	$C - C$ and $C = C$	Planar	Benzene	

6.3 Alkane Compounds

Alkane compounds are saturated hydrocarbons. The hydrocarbons which contains single bond between carbon-carbon are called alkanes. The general formula for alkanes is $C_nH_{2n + 2}$, where n = number of carbon atoms.

In alkanes sp^3 hybrid orbitals of carbon and 1s orbitals of four hydrogen atoms form tetrahedral structure of hydrocarbon. In tetrahedral structure of alkane $C - C$ and $C - H$ possesses a $\sigma-$bond. The bond lengths of $C - C$ is 154 pm and $C - H$ bond length is 112 pm. All $H - C - H$ bond angles are of $109^0 28'$. The shape of methane molecule is represented in Figure 6.1.
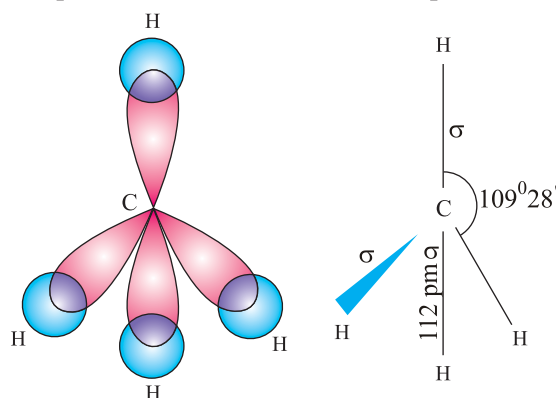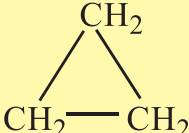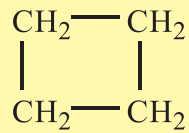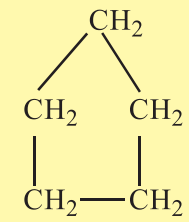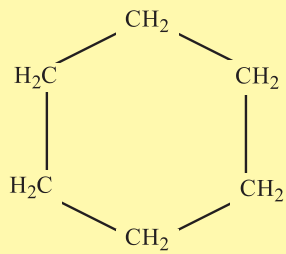
Figure 6.1 Shape of methane molecule

6.3.1 IUPAC Nomenclature of Alkanes and Cyclo-alkanes : The structural formula and IUPAC names of alkanes and cycloalkanes are given in Table 6.2.

Table 6.2 IUPAC Nomenclature

Structural formula	IUPAC name
CH_4	Methane
$CH_3 \ CH_3$	Ethane
$CH_3 \ CH_2 \ CH_3$	Propane
$CH_3 \ CH_2 \ CH_2 \ CH_3$	Butane
$CH_3 \ CH_2 \ CH_2 \ CH_2 \ CH_3$	Pentane
$CH_3 \ CH_2 \ CH_2 \ CH_2 \ CH_2 \ CH_3$	Hexane
$CH_3 \ CH_2 \ CH_2 \ CH_2 \ CH_2 \ CH_2 \ CH_3$ or $CH_3-(CH_2)_5-CH_3$	Heptane

$CH_3-(CH_2)_6-CH_3$	Octane
$CH_3-(CH_2)_7-CH_3$	Nonane
$CH_3-(CH_2)_8-CH_3$	Decane
	Cyclopropane
	Cyclobutane
	Cyclopentane
	Cyclohexane

## 6.3.2 Isomerism and Nomenclature in Alkanes :

The compounds having same molecular formula but different physical and chemical properties are called isomers and this phenomenon is called isomerism. Compounds which have same molecular formula, but their structural formulas are different, are called structural isomers.

The study of isomerism can be done very well in alkane chains. In the first three hydrocarbons methane, ethane and propane isomerism is not observed. Isomers are observed in the successive members having more than three carbon atoms.

In common nomenclature method, all the isomers of alkane have same fundamental name,

e.g., both the isomers having C_4H_{10} moleculer formula are known as butane, but the name of each isomer is separated by its prefix. The prefix is known according to the branch in the molecule.

(1) Prefix 'n' is used for such alkanes in which all the carbon atoms are combined in same long chain. Here, n-means normal, e.g.,
CH_3 CH_2 CH_2 CH_3 (n−butane)

(2) Prefix 'iso' is used in such alkanes in which an alkyl group like methyl group $(-CH_3)$ is attached to carbon second from last carbon. e.g.

prefix 'iso'
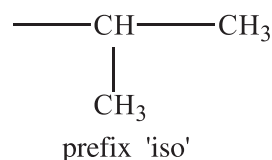
(3) Prefix 'neo' is used in such alkanes in which two alkyl groups like methyl groups are combined with the carbon second from left of the long chain of carbon. Prefix 'neo' applicable to pentane and nonane like alkanes.

prefix 'neo'
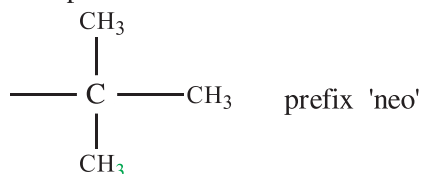
This type of nomenclature is convenient for simple hydrocarbons, but for more complex hydrocarbons IUPAC nomenclature is more convenient. You have studied IUPAC nomenclature of alkane compounds in Semester-1. In the following Table 6.3 some alkanes, structural formula of their isomers, IUPAC name, common name, boiling points and melting points are given :

Table 6.3 Structural formula of alkanes, IUPAC Name, Common Name, Melting Point and Boling Point
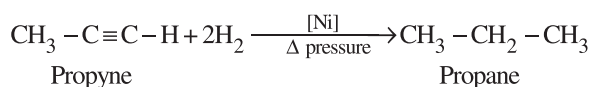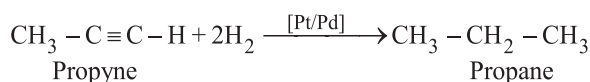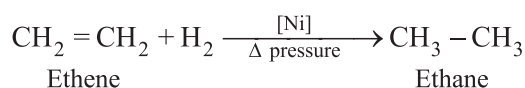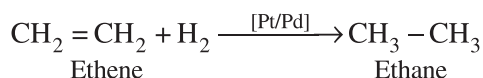
No.	Molecular formula	Structural formula	IUPAC Name	Common Name	Melting point (K)	Boiling point (K)
1	CH_4	CH_4	Methane	Methane	90.5	111.0
2	C_2H_6	CH_3-CH_3	Ethane	Ethane	101.0	184.0
3	C_3H_8	$CH_3-CH_2-CH_3$	Propane	Propane	85.3	231.0
4	C_4H_{10}	$CH_3-(CH_2)_2-CH_3$	Butane	n-Butane	134.6	272.0
			2 Methyl propane	Iso-butane	114.7	261.0
5	C_5H_{12}	$CH_3-(CH_2)_3-CH_3$	Pentane	n-pentane	143.3	309.1
			2 Methyl butane	Iso-pentane	113.1	301.0
			2, 2-Dimethyl propane	Neo-pentane	265.4	282.5
6	C_6H_{14}	$CH_3-(CH_2)_4-CH_3$	Hexane	n-Hexane	178.5	342.0
			2 Methyl pentane	Iso-hexane	113.0	301.0
			3 Methyl pentane	–	155.0	336.0
			2,2 Dimethyl butane	Neo-hexane	175.0	323.0
			2,3 Dimethyl butane	–	144.0	331.0

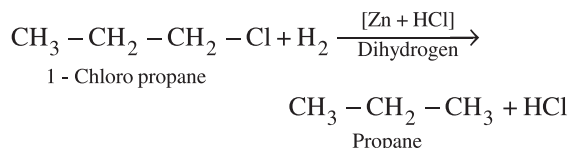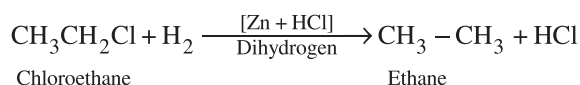| 7 | C_7H_{16} | $CH_3-(CH_2)_5-CH_3$ | Heptane | n-Heptane | 182.4 | 371.4 |
8	C_8H_{18}	$CH_3-(CH_2)_6-CH_3$	Octane	n-octane	216.2	398.7
9	C_9H_{20}	$CH_3-(CH_2)_7-CH_3$	Nonane	n-nonane	222.0	423.8
10	$C_{10}H_{22}$	$CH_3-(CH_2)_8-CH_3$	Decane	n-decane	243.3	447.1

6.3.3 Preparation of alkane compounds :

(1) From unsaturated hydrocarbons : Alkane compounds are obtained by addition reaction of unsaturated hydrocarbons like alkene and alkyne compounds with dihydrogen in presence of catalyst like Pt or Pd at normal temperature. This reaction is known as hydrogenation. If this reaction is carried out in presence of Ni catalyst, it requires high temperatures and pressure.
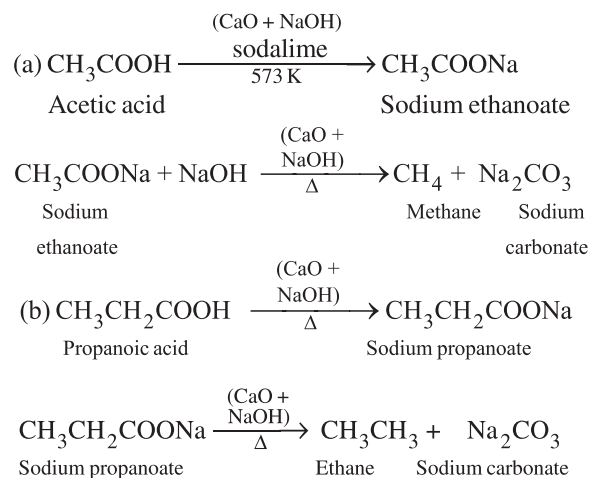
$$CH_2=CH_2 + H_2 \xrightarrow{[Pt/Pd]} CH_3-CH_3$$
Ethene .... Ethane

$$CH_2=CH_2 + H_2 \xrightarrow[\Delta\ pressure]{[Ni]} CH_3-CH_3$$
Ethene .... Ethane

$$CH_3-C\equiv C-H + 2H_2 \xrightarrow{[Pt/Pd]} CH_3-CH_2-CH_3$$
Propyne .... Propane

$$CH_3-C\equiv C-H + 2H_2 \xrightarrow[\Delta\ pressure]{[Ni]} CH_3-CH_2-CH_3$$
Propyne .... Propane

(2) From alkyl halide : Alkane is obtained by reduction reaction of alkyl halide in presence of Zn and HCl

$$CH_3CH_2Cl + H_2 \xrightarrow[Dihydrogen]{[Zn+HCl]} CH_3-CH_3 + HCl$$
Chloroethane .... Ethane

$$CH_3-CH_2-CH_2-Cl + H_2 \xrightarrow[Dihydrogen]{[Zn+HCl]}$$
1 - Chloro propane
$$CH_3-CH_2-CH_3 + HCl$$
Propane

(3) From carboxylic acids : Sodium salts of carboxylic acid are first obtained by reaction of carboxylic acid with sodalime (solid NaOH + CaO). When these sodium salts are allowed to react with sodalime at high temperature, they give alkanes containing one carbon less than the carbon atoms in original carboxylic acid.

This reaction is known as decarboxylation reaction because carbon dioxide is released from carboxylic acid during this process.

$$(a)\ CH_3COOH \xrightarrow[573\ K]{sodalime\ (CaO+NaOH)} CH_3COONa$$
Acetic acid .... Sodium ethanoate

$$CH_3COONa + NaOH \xrightarrow[\Delta]{(CaO+NaOH)} CH_4 + Na_2CO_3$$
Sodium ethanoate .... Methane ..... Sodium carbonate

$$(b)\ CH_3CH_2COOH \xrightarrow[\Delta]{(CaO+NaOH)} CH_3CH_2COONa$$
Propanoic acid .... Sodium propanoate

$$CH_3CH_2COONa \xrightarrow[\Delta]{(CaO+NaOH)} CH_3CH_3 + Na_2CO_3$$
Sodium propanoate ..... Ethane ..... Sodium carbonate

6.3.4 Properties of Alkane Compounds :

(1) Physical Properties : Alkanes have covalent nature of $C-C$ and $C-H$ bonds. Alkanes are non-polar molecules because of less difference in electronegativities of carbon and hydrogen atoms.

Due to non-polar character, alkane compounds create weak intermolecular attraction (van der Waals force) between two molecules. Because of the weak intermolecular attraction forces in alkane, C_1 to C_4 carbon containing alkane compounds are in gaseous form. C_5 to C_{17} carbon containing alkane compounds are in liquid form and alkanes containing C_{18} or more carbon atoms are in solid form at normal temperature (298 K). Due to non-polar nature, alkanes are insoluble in polar solvent like water. The intermolecular attraction forces increase with increase in carbon atom in the alkane series.

It is observed that alkanes having high molecular masses possess high boiling point. e.g.

CH_4 (110.0 K)

CH_3CH_3 (184.0 K)

$CH_3CH_2CH_3$ (231.0 K)
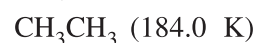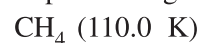
The boiling points of secondary (2^0) and tertiary (3^0) alkanes are less as compared to primary alkanes containing similiar number of carbons.
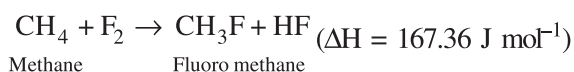
The boiling points of secondary methyl butane (301 K) and tertiary 2-2 dimethyl propane (282.5 K) are less than n-pentane (309 K). The reason for decrease in the boiling points from primary (1^0) to tertiary (3^0) can be given as under. As the branching increases, there occurs a decrease in the contact surface area. Due to the decrease in contact surface area intermolecular forces decrease. Thus, less amount of energy is required to convert liquid into vapour state.

(2) Chemical properties (Chemical reactions) : Alkane compounds are saturated compounds and so give only substitution reactions.

(i) Halogenation : At very high temperature or in presence of ultraviolet radiation of sunlight, alkane reacts with halogen to form alkyl halide. This phenomenon is called halogenation. The order of reactivity of halogens for halogenation reaction is as follows.
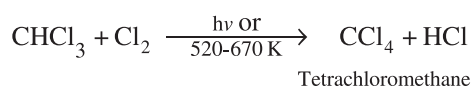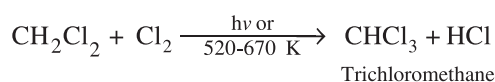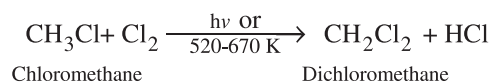
$$F_2 > Cl_2 > Br_2 > I_2$$
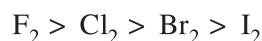
As fluorine molecule is highly active, according to free radical mechanism, this reaction does not need a catalyst.

$$\underset{\text{Methane}}{CH_4} + F_2 \rightarrow \underset{\text{Fluoro methane}}{CH_3F} + HF \; (\Delta H = 167.36 \text{ J mol}^{-1})$$

(a) Chlorination : In chlorination of alkane, in presence of sunlight or high temperature $(573 - 673 \text{ K})$ alkanes react with chlorine Cl_2, e.g. in presence of uv radiation or at 573 K methane reacts with chlorine and chloro methane is obtained.

$$CH_4 + Cl_2 \xrightarrow[573\ K]{h\nu\ or} \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$
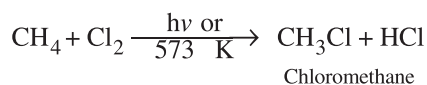
As the reaction proceeds continuously the substitution of remaining three hydrogen by chlorine takes place and, finally, tetrachloromethane is obtained.
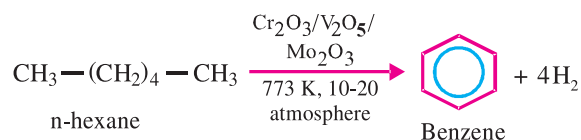
$$\underset{\text{Chloromethane}}{CH_3Cl} + Cl_2 \xrightarrow[520\text{-}670\ K]{h\nu\ or} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[520\text{-}670\ K]{h\nu\ or} \underset{\text{Trichloromethane}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow[520\text{-}670\ K]{h\nu\ or} \underset{\text{Tetrachloromethane}}{CCl_4} + HCl$$

(b) Bromination : Bromine reacts with alkane which is similiar to chlorination reaction but it is slow.

(c) Iodination : Alkane with iodine gives reversible reaction.

$$CH_4 + I_2 \rightleftharpoons \underset{\text{Iodomethane}}{CH_3I} + HI$$
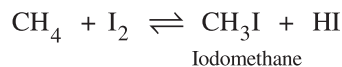
(ii) Cyclization : When normal alkane having 6 or more carbon atoms is heated at 773 K temperature and 10-20 atmosphere pressure in the presence of catalyst get converted to benzene and its derivatives are obtained. This reaction is known as cyclization or dehydrogenation.

e.g. n-hexane at 773 K temperature and 10-20 atmosphere pressure in the presence of V_2O_5 or Cr_2O_3 or Mo_2O_3 as catalyst, dehydrogenation takes place and benzene is formed.

$$\underset{\text{n-hexane}}{CH_3-(CH_2)_4-CH_3} \xrightarrow[\substack{773\ K,\ 10\text{-}20 \\ \text{atmosphere}}]{\substack{Cr_2O_3/V_2O_5/ \\ Mo_2O_3}} \underset{\text{Benzene}}{\bigcirc} + 4H_2$$

(iii) Reaction with water (vapour) : Reaction of alkane in presence of Ni catalyst with water vapour at higher temperature, dihydrogen gas is released. This process is used in industries to obtain dihydrogen gas. Likewise, reaction of methane with water vapour in presence of Ni catalyst at higher temperature, a mixture of CO and H_2 called water gas is obtained.

$$\underset{\text{Methane}}{CH_4} + H_2O_{(g)} \xrightarrow[\Delta]{[Ni]} CO + 3H_2$$
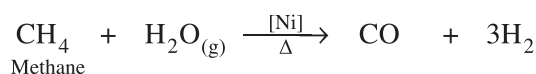
6.4 Alkene Compounds

Alkene compounds are unsaturated hydrocarbons i.e. hydrocarbons in which atleast one double bond between two carbon atoms is present. The general formula of alkene is C_nH_{2n}. Ethene is the first member of this group. There is sp^2 hybridization between the two carbon atoms in ethene. Three hybrid orbitals are formed by sp^2 hybridization and form three $\sigma-$ bond. The orbitals which do not take part in the hybridisation overlap to form one π bond. Ethene has total four C$-$H $\sigma-$ bond. The bond length of each C$-$H bond is 110 pm and bond length of C$=$C is 134 pm while bond angle of H$-$C$-$H is $116^06'$ and bond angle of C$-$C$-$H is $121^07'$. The shape of ethene molecule is triangular planar, which is represented in Figure 6.2.
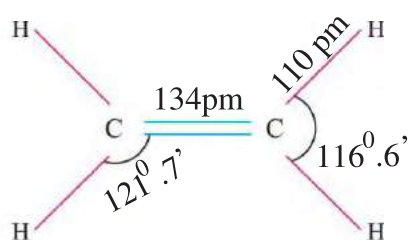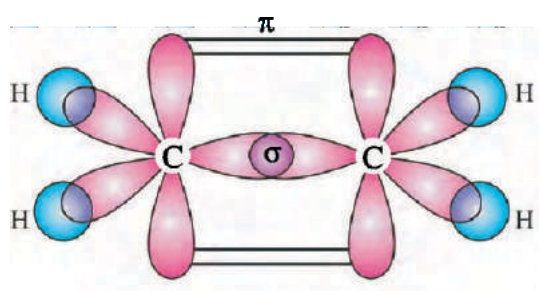
H – C – H bond angle 116⁰6'

H – C – C bond angle 121⁰7'

C = C bond length 134 pm

C – H bond length 110 pm

Fig. 6.2 Shape of Ethene

6.4.1 IUPAC Nomenclature and Isomerism in alkene :

(1) For the IUPAC nomenclature of alkene, the longest branch containing $-C=C-$ is selected.

(2) The order to number carbon is decided by the longest branch containing $-C=C-$ double bond which must have atleast an order.

(3) The 'ane' suffix is removed from the main name of alkane and 'ene' suffix is attached to it, viz. 'ane' suffix removed from the butane and add 'ene' suffix attached to it will make **but + ene = butene.** If the number of same substituted group is 2, 3 or 4 then the suffix di, tri and tetra are put respectively before its name on the basis of above rules IUPAC nomenclature of alkene is given in Table 6.4.

Table 6.4

Structural formula	IUPAC Name
$CH_2=CH_2$	Ethene
$CH_3-CH=CH_2$	Propene
$CH_3-CH_2-CH=CH_2$	But-1-ene
$CH_3-CH=CH-CH_3$	But-2-ene
$CH_2=\overset{\underset{\mid}{CH_3}}{C}-CH_3$	2,Methyl prop-1 ene
$CH_2=CH-\overset{\underset{\mid}{CH_3}}{CH}-CH_3$	3,Methyl but-1 ene
$CH_2=CH-CH=CH_2$	Buta-1, 3-diene
$(CH_3)_2-CH-CH=CH-CH=CH$ ... H_3C-CH ... C_2H_5	2, 7-dimethyl-Nona-3,5-diene
	Deca-1,3,5,9-tetraene
H_3C-CH_2 ... C_2H_5 ... $H_3C-CH-CH=C-CH_2-CH-CH_3$ ... CH_3	4-Ethyl-2, 6-dimethyloct 4-ene
$CH_3-CH=C(CH_2CH_2CH_3)_2$	3-(n-propyl) hex-2-ene

Isomerism in Alkene : Alkene compounds give two types of isomerism : (i) Structural isomerism (ii) Geometrical isomerism

(i) Structural isomerism : The alkene compounds containing two or three carbon atoms do not show structural isomerism, but the alkene compounds containing four or more carbon atoms show structural isomerism.

For example, the alkene having molecular formula C_4H_8 shows structural isomerism and the isomers can be shown as under :

Molecular formula	Structural formula	IUPAC name
C_4H_8	(i) $CH_2=CH-CH_2-CH_3$	But-1-ene
	(ii) $CH_3-CH=CH-CH_3$	But-2-ene
	(iii) $CH_2=\overset{\underset{\mid}{CH_3}}{C}-CH_3$	2,Methyl prop-1 ene

(ii) Geometrica.l isomerism : Although some alkene compounds have same structural formula and molecular formula, their functional group and/or spatial arrangement of atoms is in different directions. Here, due to the presence of $- C = C -$ the molecular structure is planar. This type of isomerism is known as geometrical isomerism.

Usually, geometrical isomers are known as cis and trans isomers. For example,
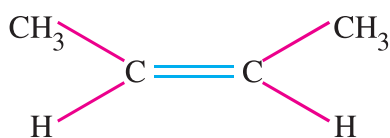
Cis But - 2 - ene

Trans But - 2 - ene

In cis isomer, two carbon atoms having double bonds are attached to the similar atom or group of atoms present on same side of $C = C$. While in trans isomer, similar groups are found in diagonal position of $C = C$ If double bond containing carbons have same functional groups on same side, it does not show geometrical isomerism. The polarity in cis and trans isomers is as under.
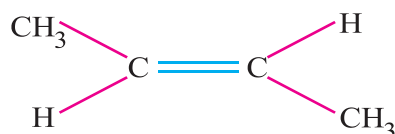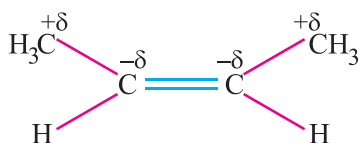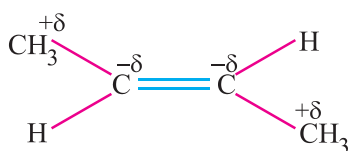

Cis But - 2 - ene

(μ = 0.33 D)

Trans But - 2 - ene

(μ = 0.0 D)

From the above figure, it becomes clear that cis isomer is polar while trans isomer is non-polar, because in trans isomer both methyl groups are in opposite derections due to which resulting value of dipole moment is zero.

6.4.2 Preparation of alkene compounds :

(i) From alkyne : Alkene is obtained by the addition reaction of alkyne with H_2 gas in presence of mixture of palladium (Pd) and charcoal as catalyst. This catalyst mixture of palladium and charcoal is known as 'Lindlars' catalyst. Thus, addition of hydrogen in group is called hydrogenation reaction.

$$CH \equiv CH + H_2 \xrightarrow[\substack{Lindlar's \\ catalyst}]{[Pd + C]} CH_2 = CH_2$$

Ethyne   Ethene

$$CH_3 - C \equiv CH + H_2 \xrightarrow[\substack{Lindlar's \\ catalyst}]{[Pd + C]} CH_3 - CH = CH_2$$

Propyne   Propene
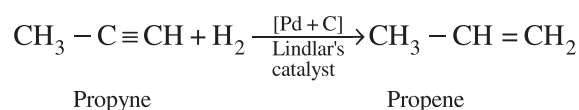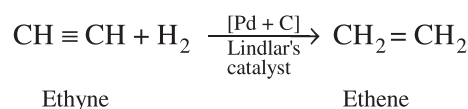
(ii) From alkyl halide : Alkene is obtained by reacting with potassium hydroxide dissolved in ethanol. (ethanolic KOH) with alkyl chloride at higher temperature. During this reaction, removal of halogen from α-carbon and hydrogen from β-carbon of alkyl halide takes place. Because of this, the reaction is known as β-elimination or dehydrohalogenation reaction.

$$CH_3CH_2Cl \xrightarrow[]{\substack{Ethanolic \\ KOH}} CH_2 = CH_2 + KCl + H_2O$$

Ethyl chloride   Ethene
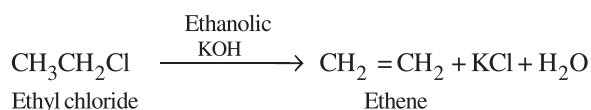
(iii) From vicinal dihalide (From dihalogen alkane) : Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as vicinal dihalides. Vicinal dihalides on treatment with zinc metal gives a molecule of ZnX_2 $(X = halogen)$ and forms an alkene. This reaction is known as dehalogenation.

1, 2 dibromo ethane   ethene

1, 2 dibromo propane   propene
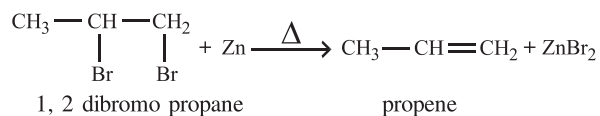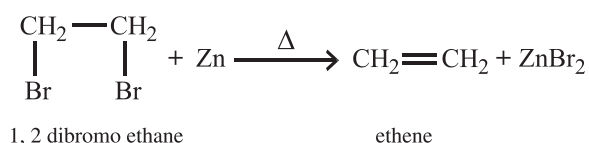
(iv) From alcohol : Alkene is obtained by reacting alcohol with conc H_2SO_4 at 443 K temperature. During this process water molecule is released. This process is called dehydration. It is also known as acidic dehydration of alcohols.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[443\ K]{[\text{conc. } H_2SO_4]} \underset{\text{Ethene}}{CH_2 = CH_2} + H_2O$$
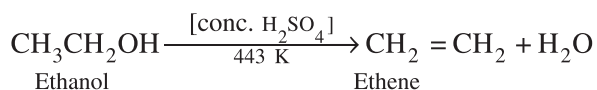
6.4.3 Properties of alkene compounds :

(1) Physical properties of alkenes :

(i) Variation is observed in physical properties of alkene due to polar nature. Isomerism is also observed in alkene.

(ii) Alkene containing two, three or four carbon atoms are in gaseous form, C_5 to C_{18} members are in liquid form and those with more number of carbons are obtained in solid form.

(iii) Ethene is colourless gas with a fruity sweet smell.

(iv) Except ethene all other alkenes are odourless and tasteless.

(v) Except ethene all alkenes are insoluble in polar solvent like water, but soluble in non-polar organic solvents like petrol, benzene, ether and carbon tetrachloride.

(vi) Alkenes have lower melting points and boiling points than alkanes, and these increase with the increase in the molecular mass.

(vii) The boiling points of isomers having linear chain are higher than those of alkenes having branched chain.

IUPAC name structural formula, boiling points and melting points of some alkenes are given in the Table 6.5 :

Table 6.5

The IUPAC Name, structural formula, melting and boiling points of alkenes

IUPAC Name	Structural formula	Melting point K	Boiling point K
Ethene	$CH_2=CH_2$	104	171
Propene	$CH_2=CH-CH_3$	–	225
But-1-ene	$CH_2=CH-CH_2-CH_3$	–	266.5
Pent-1-ene	$CH_2=CH(CH_2)_2-CH_3$	–	303
Hex-1-ene	$CH_2=CH(CH_2)_3-CH_3$	135	336.5
Hept-1-ene	$CH_2=CH(CH_2)_4-CH_3$	154	366.0
Oct-1-ene	$CH_2=CH(CH_2)_5-CH_3$	169	395.5
2-Methyl but-2-ene	$CH_3-CH=C(CH_3)_2$	150	313.0
2, 3 –Dimethyl but-2-ene	$(CH_3)_2C=C(CH_3)_2$	199	346

(ii) Chemical properties of alkene (chemical reactions) : $- C = C -$ present in alkene has weak π-bond which breaks easily and electrons of π-bond are released. In alkene with $- C = C -$; π-bond of carbon breaks and the addition of atom or functional group (group of atoms) of reactants on carbon atom takes place. This addition reaction is known as electrophilic addition reaction.

(1) Reaction with halogen acid : Alkyl halide is obtained by the reaction of alkene with halogen acid. This is known as hydrohalogenation reaction.

Reaction of symmetrical alkene is as under

$$\underset{\text{Ethene}}{CH_2 = CH_2} + HCl \longrightarrow \underset{\substack{| \\ Cl \\ \text{Chloro ethane}}}{CH_3 - CH_2}$$
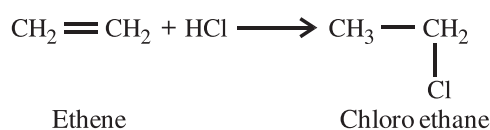
(a) Reaction of asymmetrical alkene (CH₃–CH=CH₂) with halogen acid and Markovnikov Rule :

$$CH_3—CH = CH_2 + HCl$$

Propene

I → $CH_3—CH—CH_3$ | Cl **2-Chloropropane**

II → $CH_3—CH_2—CH_2Cl$ **1-Chloropropane**
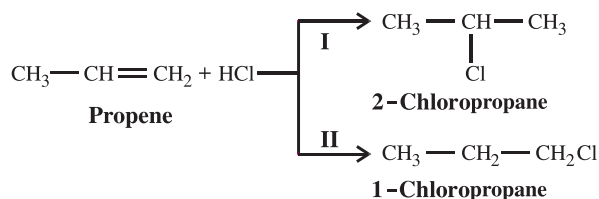
Here, by the reaction of propene with hydrochloric acid, two products I and II are obtained. It is necessary to know the Markovnikov rule to understand the stability of products obtained.

In 1869, Russian scientist Markovnikov proposed the rule as under :

"In the addition reaction of compounds having asymmetric ethylinic double bond the electronegative part of asymmetric reagent attaches with the ethylinic carbon having less number of hydrogens." This principle is better understood by the following reaction mechanism :

Reaction Mechanism : Initially, electrophilic H^+ ion of hydrochloric acid (HCl) is attached with carbon containing ethylinic double bond and forms carbocation as under.

$$CH_3—CH = CH_2 + H—Cl$$

↓ H^+

$CH_3—\overset{+}{C}H—CH_3 + Cl^-$
stable
(Secondary Carbocation) 2⁰

$CH_3—CH_2—\overset{+}{C}H_2 + Cl^-$
unstable
(Primary Carbocation)1⁰

Primary carbocation is less stable than secondary carbocation. Due to this Cl^- ion of HCl attaches rapidly to the carbon of secondary carbocation. When carbon has positive charge in its molecule, it is called carbocation.

$CH_3—\overset{+}{C}H—CH_3 + Cl^- \longrightarrow CH_3—CH—CH_3$ | Cl
2-Chloro propane

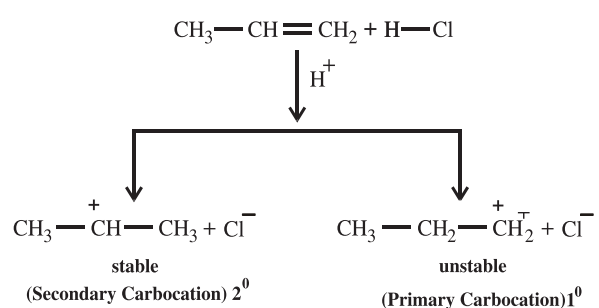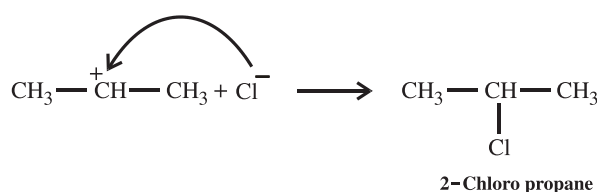Thus, Cl^- ion attaches to the ethylinic carbon containing less hydrogen. The product obtained is stable, as a result, the product is 2-chloro propane.

(b) Reaction of asymmetric alkene with halogen acid and peroxide effect :
If the reaction occurs between asymmetric alkene with halogen acid like HBr in presence of hydrogen peroxide then the product obtained is against the Markovnikov's rule. HCl and HI do not show this type of reaction. Only HBr shows this reaction.

In 1933, M.S Kharsh and F. R. Mayo studied this reaction mechanism which is known as Kharsh effect, peroxide effect or anti-Markovnikov rule. e.g.

$$CH_3—CH = CH_2 + HBr \xrightarrow[\text{(C}_6\text{H}_5\text{CO)}_2\text{O}_2]{\text{(Benzoyl peroxide)}} CH_3—CH_2—CH_2—Br$$

Propene   **1- Bromo propane**
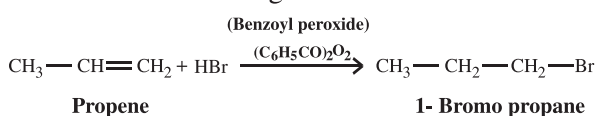
According to peroxide effect, free radical addition reaction mechnism is shown as under. Free radical is obtained by the homolytic covalent bond fission.

(i)

$$C_6H_5—\overset{O}{\overset{\|}{C}}—O—O—\overset{O}{\overset{\|}{C}}—C_6H_5 \longrightarrow 2C_6H_5—\overset{O}{\overset{\|}{C}}—\overset{..}{\overset{..}{O}}{}\cdot$$

↓

$2\dot{C}_6H_5 + 2CO_2$
Free radicals

(ii)

$$\dot{C}_6H_5 + H—Br \rightarrow C_6H_6 + \dot{B}r$$
Free radical   Free radical

(iii)

$$CH_3—CH = CH_2 + \dot{B}r$$

↓

$CH_3—\overset{\cdot}{C}H—CH_2$ | Br
(Unstable intermediate)
(Primary free radical)

$CH_3—\overset{\cdot}{C}H—CH_2—Br$
(Stable intermediate)
(Secondary free radical)

(iv)

$$CH_3—\overset{\cdot}{C}H—CH_2Br + H—Br \longrightarrow$$

$$CH_3—CH_2—CH_2—Br + \dot{B}r$$
Main product   **1 Bromo propane**   **Free radical**

(v)

CH$_3$—CH—$\overset{\bullet}{C}$H$_2$ + H—Br
      |
      Br
Intermediate product

$\downarrow$

CH$_3$—CH—CH$_3$ + $\overset{\bullet}{B}$r
      | **Free radical**
      Br

2- Bromo propane
(Secondary product)

(2) Reaction with dihydrogen : At normal temperature alkane is obtained by addition reaction of alkene with dihydrogen in presence of catalyst like Pt or Pd. This reaction is called hydrogenation. If this reaction is carried out in presence of Ni catalyst, then higher temperature and pressure are required.

$$CH_2 = CH_2 + H_2 \xrightarrow{Pt/Pd} CH_3 - CH_3$$
      Ethene   Ethane

$$CH_2 = CH_2 + H_2 \xrightarrow[\Delta,\ pressure]{Ni} CH_3 - CH_3$$
      Ethene   Ethane
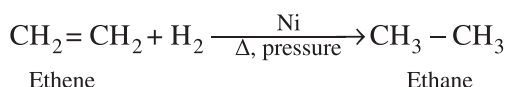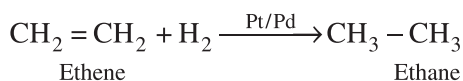
(3) Reaction with halogen : By the addition of halogen to alkene, π bond of ethylinic double bond breaks and the addition of halogen molecule takes place to form dihalogenated alkane.

$$CH_2 = CH_2 + Cl_2 \longrightarrow CH_2 - CH_2$$
                                         | |
                                         Cl   Cl

Ethene   **1, 2 Dichloro ethane**

6.5 Alkyne Compounds

Like alkenes, alkynes are also unsaturated hydrocarbons. The hydrocarbons, in which there is at least one triple bond between two carbon atoms, are called alkyne compounds. General formula of alkynes is C_nH_{2n-2}.

Acetylene (ethyne) is the first member of the alkyne series in which two carbon atoms are attached by one triple bond and possess sp hydbridisation. Thus, ethyne molecule has bond angle of 180^0 and is a linear molecule. Bond length between C—H bond is 106 pm and between C ≡ C bond, bond length is 120 pm as represented in Fig. 6.3.

C–H bond length 106 pm

C ≡ C bond length 120 pm

bond angle 180^0
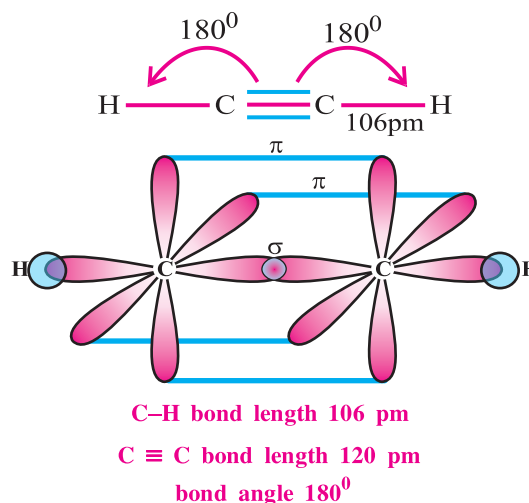
Fig. 6.3 Shape of ethyne molecule

6.5.1 IUPAC Nomenclature of alkyne Compounds and Isomerism : In IUPAC nomenclature of alkynes, 'ane' suffix of alkanes is removed from the name and 'yne' suffix is attached to it. (Except suffix all the other rules are the same as those for alkanes and alkenes), e.g. Ethane $\rightarrow$ Ethyne.
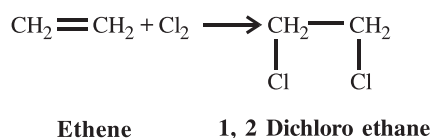
In the following Table 6.6, IUPAC nomenclatures of various alkyne compounds are given :

Table 6.6

Structural formula	IUPAC Name
CH≡CH	Ethyne
H$_3$C–C≡CH	Propyne
H$_3$C–CH$_2$–C≡CH	But-1-yne
H$_3$C–C≡C–CH$_3$	But-2-yne
H$_3$C—CH—C≡CH 　　　| 　　　CH$_3$	3-Methyl but-1-yne
CH$_3$—C≡C—CH—CH$_3$ 　　　　　　　| 　　　　　　　CH$_3$	4-methyl pent-2-yne
CH$_3$ 　　　　| CH≡C—C—CH$_3$ 　　　　| 　　　　CH$_3$	3,3 Dimethyl but-1-yne

Isomerism of Alkyne compounds : The carbon containing compounds having same molecular formula but different structural formulae are called structural isomers. This phenomenon is known as structural isomerism. Alkyne compounds containing two or three carbon atoms having same structural formula do not give structural isomers. Structural isomers of alkynes containing four carbon atoms are given in Table 6.7.

Table 6.7

The Molecular formula, structural formula and IUPAC Name of Alkyne

Molecular formula	Isomer (Structural formula)	IUPAC Name
C_4H_6	(i) $CH_3-CH_2-C{\equiv}CH$	But-1-yne
	(ii) $CH_3-C{\equiv}C-CH_3$	But-2-yne
C_5H_8	(i) $CH{\equiv}C-CH_2-CH_2-CH_3$	Pent-1-yne
	(ii) $CH_3-C{\equiv}C-CH_2-CH_3$	Pent-2-yne
	(iii) $CH_3-CH-C{\equiv}CH$ $\quad\quad\quad |$ $\quad\quad\quad CH_3$	3 Methyl but-1-yne

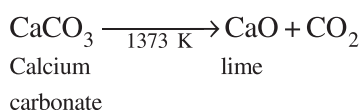**6.5.2 Preparation of Alkyne Compounds :**

(i) From calcium carbide : Ethyne is prepared by the industrial process in which carbide reacts with water. Initially, calcium carbonate is heated at higher temparature from which calcium oxide (lime) is obtained by decomposition.

$$CaCO_3 \xrightarrow{1373\ K} CaO + CO_2$$
Calcium   lime
carbonate

Now heating calcium oxide with coke, calcium carbide and carbon monoxide are obtained.

$$CaO + 3C \xrightarrow{2273\ K} CaC_2 + CO$$
Calcium   Calcium
oxide   carbide
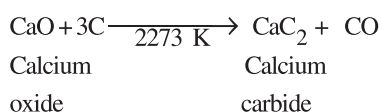
By reaction of calcium carbide with water ethyne is obtained as follows.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + CH{\equiv}CH$$
Calcium   Calcium   Ethyne
carbide   hydroxide
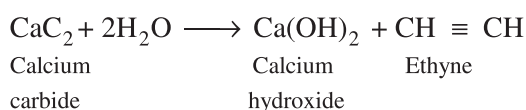
(ii) From vicinal dihalides : Alkenyl halide is obtained by reaction of vicinal dihalide with alcoholic potassium hydroxide reaction and this alkenyl halide on reaction with sodamide $(NaNH_2)$ gives alkyne. This reaction is called dehydro-halogenation.

$$\underset{\text{1, 2 Dibromoethane}}{\overset{\displaystyle CH_2-CH_2}{\underset{\displaystyle Br\quad Br}{|\quad\ |}}} + KOH \xrightarrow[\substack{-KBr\\-H_2O}]{[Alcohol]} \underset{\substack{Bromo\\ethene}}{CH_2{=}CH} \ \underset{Br}{|}$$

$$\xrightarrow[\substack{-NaBr\\-NH_3}]{Na^+NH_2^-}$$

$$CH{\equiv}CH$$
Ethyne
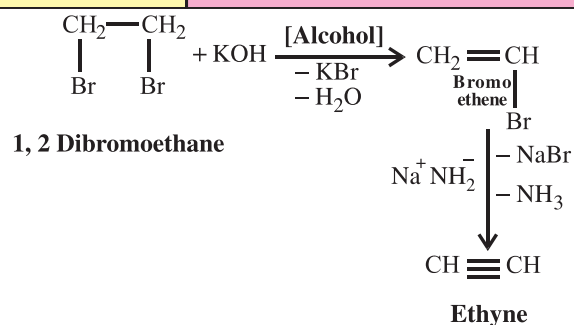
6.5.3 Properties of Alkyne Compounds :

(1) Physical properties :

(i) The first three members of alkyne series are in gaseous form, then after upto C_8 are in liquid form and alkyne containing more than 8 carbons are obtained in solid form.

(ii) All alkyne compounds are colourless. The smell of ethyne is specific. Except ethyne all alkynes are odorless.

(iii) Alkynes are weak polar compounds.

(iv) Alkynes are lighter than water, and are insoluble in polar solvents like water. They are soluble in non-polar organic solvents like ether, carbon tetrachloride, benzene.

(v) With the increase in molecular mass of alkynes, melting point, boiling point, and density also increase.

In the following Table 6.8 the melting points and boiling points of some alkyne compounds are given.

Table 6.8
The IUPAC Name, Structural formula melting point and boiling point of alkyne Compounds

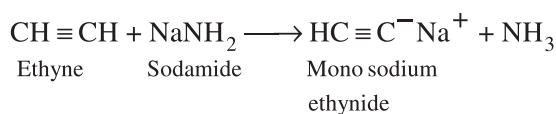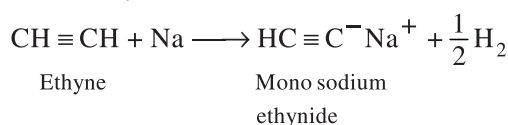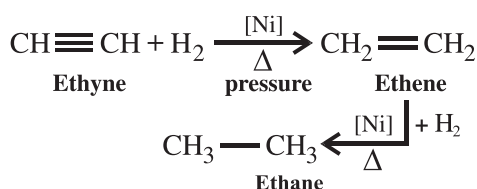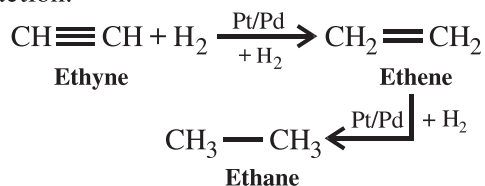| Alkyne	Structural formula	Melting point (K)	Boiling point (K)
Ethyne	$HC\equiv CH$	192.2	189
Propyne	$HC\equiv C-CH_3$	170.3	249.8
But-1-yne	$HC\equiv C-CH_2-CH_3$	147.3	281.1
But-2-yne	$H_3C-C\equiv C-CH_3$	240.7	300.0
Pent-1-yne	$HC\equiv CCH_2CH_2CH_3$	167.3	313.2
Pent-2-yne	$H_3CC\equiv C-CH_2-CH_3$	163.7	329.1
Hex-1-yne	$HC\equiv CCH_2CH_2CH_2CH_3$	141.1	344.3
Hex-2-yne	$H_3CC\equiv CCH_2CH_2CH_3$	183.5	357.5
Hex-3-yne	$H_3CCH_2C\equiv C-CH_2-CH_3$	169.5	354.4
Hept-1-yne	$HC\equiv CCH_2CH_2CH_2CH_2CH_3$	192.1	372.7

(2) Chemical Properties (Chemical Reactions) of Alkynes :

(i) Acidic properties of Alkynes : Only ethyne possesses acidic properties. Ethyne is a weak acid, it reacts with strong base like sodium or sodamide to give mono sodium ethynide (sodium acetylide)

$$CH\equiv CH + Na \longrightarrow HC\equiv C^-Na^+ + \frac{1}{2}H_2$$

Ethyne   Mono sodium ethynide

$$CH\equiv CH + NaNH_2 \longrightarrow HC\equiv C^-Na^+ + NH_3$$

Ethyne   Sodamide   Mono sodium ethynide

(ii) Addition Reaction (Electrophilic addition reaction with dihydrogen) :
Alkyne on heating with dihydrogen reacts in presence of catalysts like Pt, Pd or Ni and gives alkene by addition reaction, which further on reacting with more hydrogen gives alkane by addition reaction. This realtion is known as hydrogenation reaction.

$$CH\equiv CH + H_2 \xrightarrow[+H_2]{Pt/Pd} CH_2 = CH_2$$

Ethyne   **Ethene**

$$CH_3 - CH_3 \xleftarrow[]{Pt/Pd \mid +H_2}$$

Ethane

$$CH\equiv CH + H_2 \xrightarrow[\Delta\ pressure]{[Ni]} CH_2 = CH_2$$

Ethyne   **Ethene**

$$CH_3 - CH_3 \xleftarrow[\Delta]{[Ni] \mid +H_2}$$

Ethane

With dihalogen : When alkyne reacts with dihalogen the π-bond breaks and alkenyl dihalide is formed. Further reacting with more dihalogen, this gives tetrahalo alkane by addition reaction. This reaction is known as halogenation reaction.

$$CH_3-C\equiv CH + Br_2 \longrightarrow CH_3-\underset{\underset{Br}{|}}{C}=\underset{\underset{Br}{|}}{CH}$$

Propyne   **Dibromine**   **1,2-Dibromo propene**

$$\Big\downarrow Br_2$$

$$CH_3-\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{C}}-\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{CH}}$$

1, 1, 2, 2 Tetra bromo propane
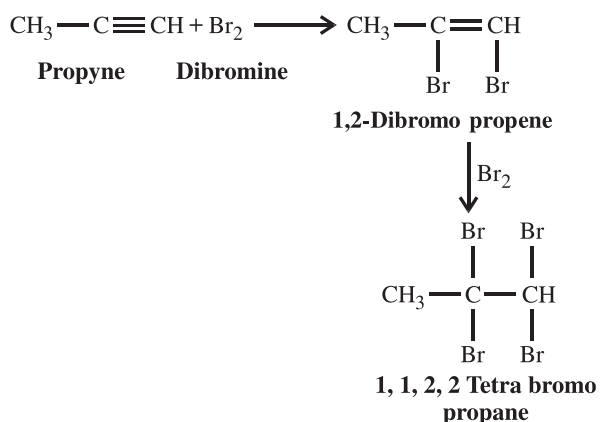
With hydrogenhalide : By addition reaction of alkyne with hydrogen halides like HCl, HBr, HI, it gives alkene halide. On reacting with more hydrogen halide, this gives dihalide of alkane. This reaction is known as hydro-halogenation.

$$CH\equiv CH + HBr \longrightarrow CH_2 = CHBr$$

Ethyne   **Bromo ethene**

$$\Big\downarrow HBr$$

$$CH_3 - \underset{\underset{Br}{|}}{CH} - Br$$

1,1-Dibromo ethane
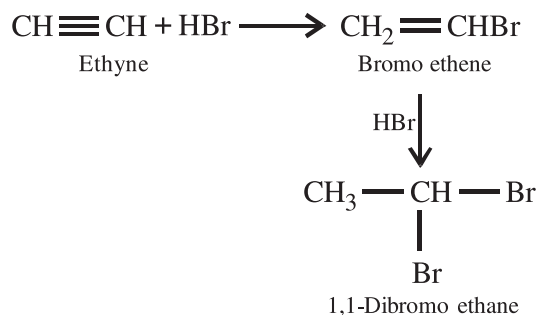
With water : Alkyne does not react with water at normal temparature, but in presence of mercuric sulphate and dilute sulphuric acid at 333 K temperature it gives carbonyl compounds.

$$CH \equiv CH + H_2O \xrightarrow[\substack{\text{dil. } H_2SO_4 \\ \text{333 K}}]{HgSO_4} CH_2 = CH$$

Ethyne

$$CH_3 - \underset{\underset{O}{\|}}{C} - H \xleftarrow{\text{Rearrangement}} \underset{\text{Ethene-1-ol}}{OH}$$

Ethanal
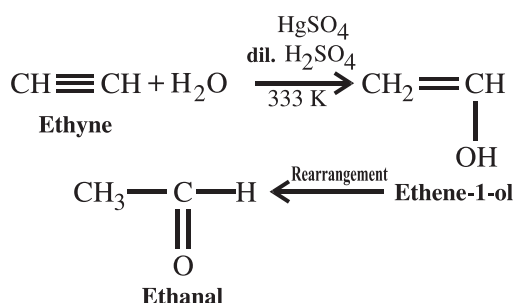
Polymerisation : The reaction of ethyne with HCl and HCN gives vinyl chloride and vinyl cyanide (acrylonitrile) respectively. A large number molecules of vinyl chloride join with each other by chemical bond forming large molecule of polyvinyl chloride polymer. This reaction is known as polymerisation. In the same way polyacrylonitrile is obtained from vinyl cyanide.

$$CH \equiv CH + HCl \xrightarrow{HgCl_2} CH_2 = CHCl$$
Ethyne Vinyl chloride

$$n(CH_2 = CHCl) \xrightarrow{\text{Polymerisation}} \left[CH_2 - \underset{\underset{Cl}{|}}{CH} \right]_n$$
Viniyl chloride

Polyvinyl chloride (PVC)

$$CH \equiv CH + HCN \longrightarrow CH_2 = CHCN$$
Ethyne Vinyl cyanide

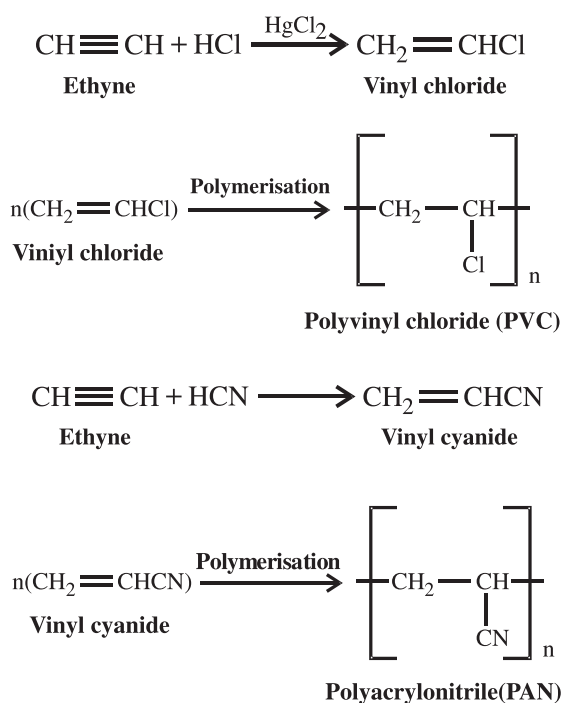$$n(CH_2 = CHCN) \xrightarrow{\text{Polymerisation}} \left[CH_2 - \underset{\underset{CN}{|}}{CH} \right]_n$$
Vinyl cyanide

Polyacrylonitrile(PAN)

6.6 Aromatic Hydrocarbons

Aromatic hydrocarbons are also known as arene compounds.

Most of these compounds possess characteristic fragrance (aroma) due to which they are known as aromatic compounds, for example, the components of organic compounds

present in bitter almond, clove, bishop's seed etc, have specific smell (aroma) in the essential oils alvailable from them and so they are called aromatic compounds. Organic compounds contaning carbon and hydrogen showing aromatic characteristics are called Aromatic Hydrocarbons. The first member of aromatic hydrocarbons is benzene, other members of aromatic hydro-carbon forming homologous series have general formula C_nH_{2n-6m} where m = number of rings in cyclic structure. Cyclic hydrocarbons contain-ing benzene ring are known as benzenoids and when cyclic hydrocarbons do not contain ben-zene ring they are known as non-benzenoids. Some examples of aromatic hydrocarbons are given below in Figure 6.4.
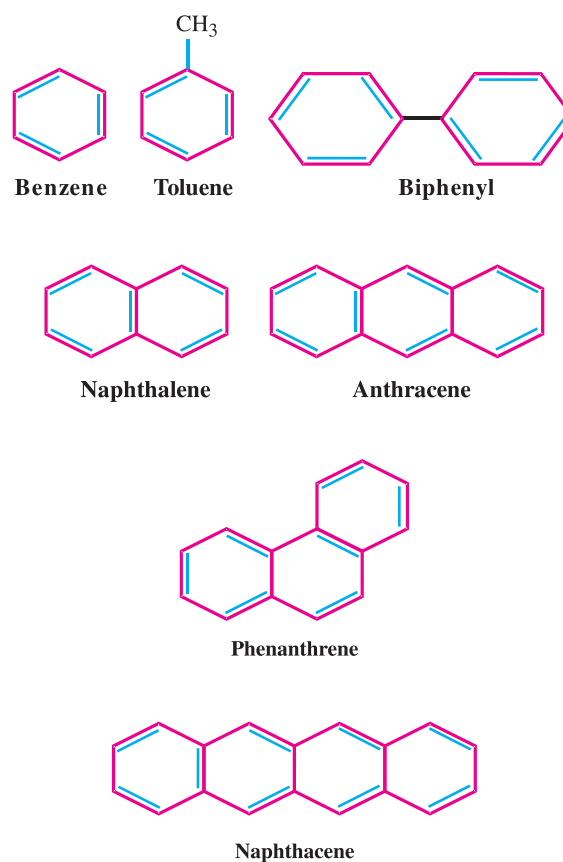
Fig 6.4 Aromatic Hydrocarbon Compounds
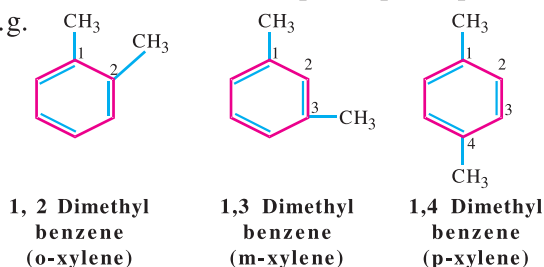
6.6.1 Nomenclature and Isomerism :

Benzene contains 6 carbon and 6 hydrogen atoms which are identical and thus does not have isomers. When any carbon of benzene substitutes its hydrogen it gives monosubstituted benzene it also does not have any isomer. In the IUPAC nomenclature of monosubstituted benzene, the displaced group is indicated, and then word benzene is expressed. e.g.

Chloro-   Nitrobenzene   Methyl-   Ethyl
benzene   benzene   benzene
                         (Toluene)
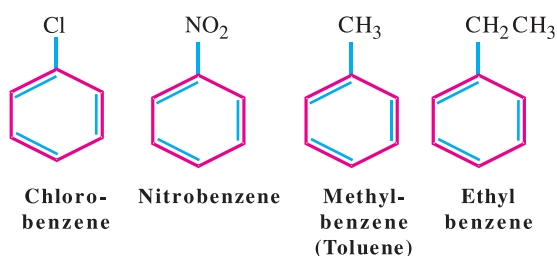
When two hydrogens of two carbon atoms in benzene are substituted, then the obtained disubstituted benzenes have three isomers.e.g. ortho, meta and para. If the substituted groups on carbon in benzene are on 1-2 position, 1-3 position and 1-4 position, then their nomenclatures are indicated by the prefixes ortho(o), meta (m) and para (p) respectively. e.g.

1, 2 Dimethyl   1,3 Dimethyl   1,4 Dimethyl
benzene   benzene   benzene
(o-xylene)   (m-xylene)   (p-xylene)

For the nomenclature of benzene, with the substitution of more than two positions, the reactivity of substituted groups on carbon are taken into consideration and numbering of carbon in benzene is done as 1,2,3... The remaining groups are indicated by considering the alphabetical order.

2, 4, 6 Trinitromethylbenzene

2, 4, 6 Trinitro toluene (TNT)
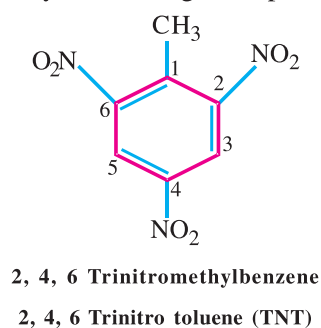
6.6.2 Structure of Benzene :

The scientist Michael Faraday for the first-time obtained benzene from illuminating gases, in 1825. In 1845, the scientist August Hofmann obtained benzene from coaltar. Destructive distillation of coal gives coal gas, coaltar and coke. Coaltar has large amount of aromatic hydrocarbons, Destructive distillation of coaltar gives toluene, xylene, naphthalene etc. whereas the alkanes can be obtained as a result of fractional distillation of petroleum. When heated in presence of catalyst at higher pressure benzene, xylene, toluene can be obtained.

Structure of benzene based on chemical properties : From the qualitative and quantitative analysis of benzene, ratio of carbon and hydrogen atoms is found to be 1:1. Thus, the empirical formula is found to be CH and empirical formula weight = 13. Molecular mass of benzene is 78 gmol^{-1}, hence, the molecular formula of benzene is confirmed as C_6H_6.

Structure of benzene is proved by the following chemical reactions :

(i) On reacting one mole of benzene with three moles of dihydrogen at high temperature and pressure in presence of Ni catalyst, cyclohexane is obtained.

$$C_6H_6 + 3H_2 \xrightarrow[\substack{(High\\temperature\\or\ pressure)}]{[Ni]}$$

Benzene   Cyclohexane
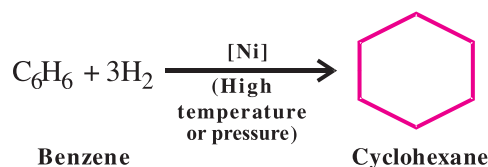
(ii) In reaction with one mole of benzene with three moles of chlorine in presence of ultraviolet light, hexachloro cyclohexane is obtained.

$$C_6H_6 + 3Cl_2 \xrightarrow[\substack{ultraviolet\\light}]{h\nu}$$

Hexachloro
cyclohexane
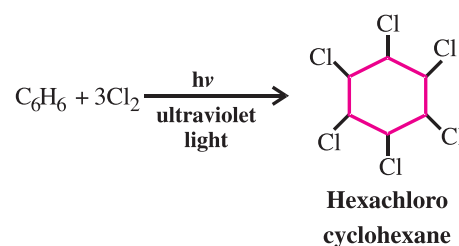
(iii) On reacting one mole of benzene with three moles of ozone, unstable benzene triozonide is obtained. On hydrolysis in presence of zinc it gives three moles of glyoxal.

$$C_6H_6 + 3O_3 \longrightarrow C_6H_6(O_3)_3 \xrightarrow[Zn + 3H_2O]{Hydrolysis} 3\left|\substack{CHO\\ \\CHO}\right. + 3H_2O_2$$

Benzene   Glyoxal
triozonide
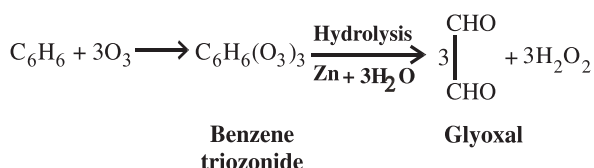
From the above reactions (i), (ii) and (iii), it can be proved that benzene contains hexagonal cyclic structure and in the ring three single bond between C — C and three double bond between C = C are present alternately.

In 1865, scientist August Kekule suggested the following structure of benzene :
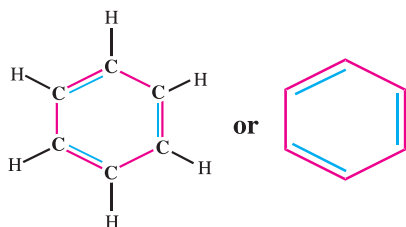
According to Kekule's proposed benzene structure, the following reactions show that it has two structures :

(i) On reacting one mole of benzene with one mole of bromine in presence of FeBr$_3$ catalyst, one isomer bromobenzene is obtained by substitution reaction. As the rate of the reaction is slow, higher temperature is necessary.

$$C_6H_6 + Br_2 \xrightarrow[\Delta]{[FeBr_3]} C_6H_5Br + HBr$$
$$\text{Bromobenzene}$$

From the above reaction, it can be proved that 6 carbons and 6 hydrogens of benzene are equivalent in position and in reactivity.

(ii) On second substitution of benzene with bromine in presence of FeBr$_3$ catalyst, a mixture of o, p-isomers of dibromobenzene in different proportions are obtained.

$$C_6H_5Br + Br_2 \xrightarrow[\Delta]{[FeBr_3]} C_6H_4Br_2 + HBr$$
$$\text{Bromobenzene} \qquad \text{Dibromobenzene}$$
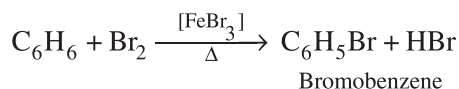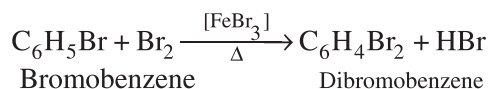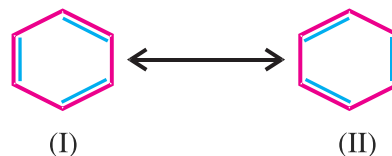
From the above reaction it can be said that during second substitution 6 carbon atoms of benzene are not equivalent. From this result, Kekule gave following structures of benzene in which three double bonds are arranged alternately and these bonds continuously and very rapidly

interconvert so that they resonate between structures (I) and (II).

The structures proposed by Kekule do not resemble with the chemical properties. In fact three double bonds are present in benzene, but it gives substitution reaction like saturated alkane. In normal conditions, like alkenes benzene dose not react with bromine water and cold KMnO$_4$ to give addition reaction. Further, polymerisation does not occur in benzene. Hence, it can be said that although benzene contains three double bonds, it possesses stability.

Stability and Resonance structure of benzene : On the basis of the chemical properties and stability of benzene, Kelkule gave two resonating structures A and B for benzene. So that the intermediate position, structure C is represented. Position of alternate double bond is different.
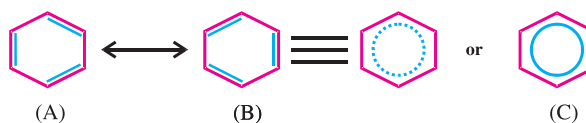
Structure of Benzene based on the physical properties : After 70 years Lewis in 1937 represented Kekule structure of benzene which was based on the information obtained about covalent bonding of organic compound and the electronic configuration of their atom. This can be shown in Fig 6.5.

(A)   **Fig. 6.5 Electronic configuration of benzene**   (B)

Benzene has 6 carbon atoms containing sp^2 hybridisation. Any of its σ-bond between C – C and C – H remain in one single plane. Bond angle between C – C – C and C – C – 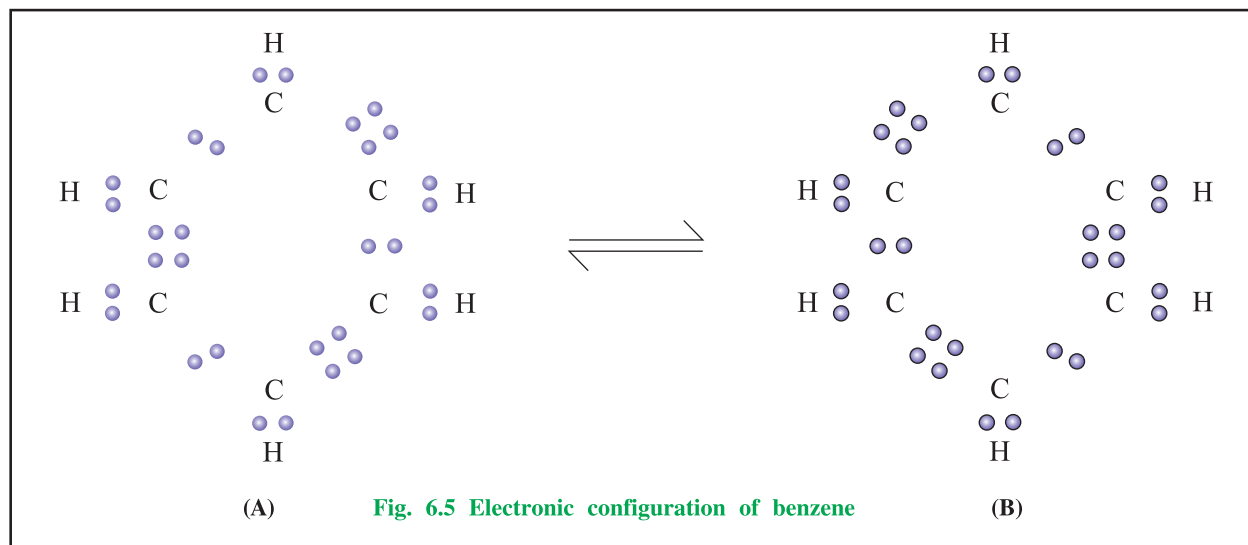H is 120^0. Further more every p_z orbital on each carbon will remain perpendicular to the plane of molecule which is represented in Fig. 6.6 (i). Those p_z orbitals which do not take part in hybridization remain perpendicular from the main axis and form π-bond by sharing electrons. As a result structure of benzene is obtained in which alternate double bond is present. This supports the two structures (A) and (B) of benzene proposed by Kekule.
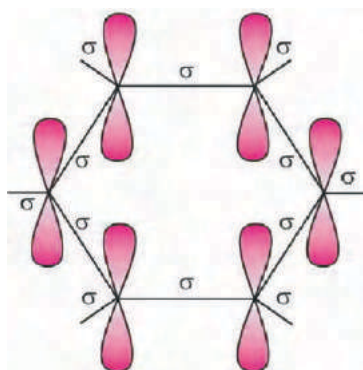
Fig. 6.6 (i)
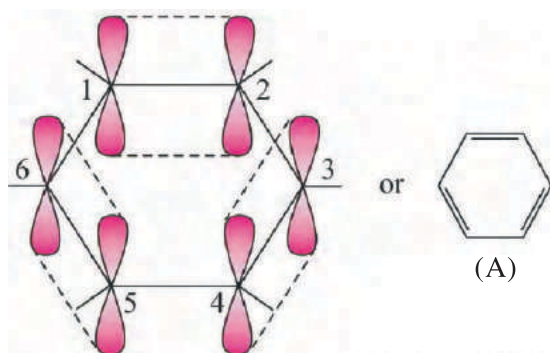
Fig. 6.6 (ii-a)
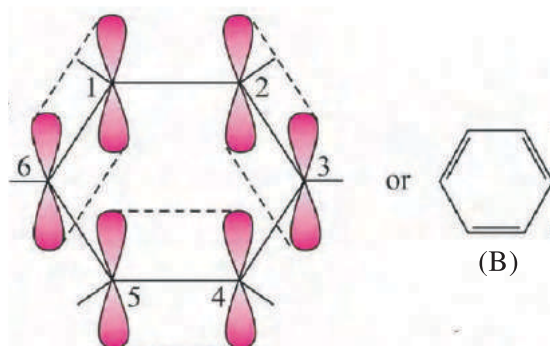
Fig. 6.6 (ii-b)

By the X-ray analysis of benzene, it was found that each C – C bond length is 139 pm. The bond length of – C – C – single bond in alkane is 154 pm and bond length of – C = C– double bond in alkene is 134 pm. Bond length 139 pm in benzene shows its intermediate value. This phenomenon represents the resonance between structures A and B of benzene that means inter- conversion phenomenon is continuous and very rapid. Based upon the resonance, it can be said that the structure of benzene should be between A and B.

Resonating structures of benzene can be further proved by their resonating energy. Cyclohexene, containing one double bond has hydrogenation enthalphy 119.66 k $Jmol^{-1}$. There-fore, benzene having three double bond should have hydrogenation enthalpy of $119.66 \times 3 = 358.98$ k J mol^{-1}. But the experimental hydrogenation enthalpy of benzene is 208.36 k $Jmol^{-1}$. Thus, benzene has $358.98 - 208.36 = 150.62$ k $Jmol^{-1}$ enthalpy less than expected. This 150.62 k $Jmol^{-1}$ value is known as resonance energy of benzene. This resonance energy indicates its stability and also less chemical reactivity. This is known as aromaticity or aromatic character.

Aromatic character of benzene is based on the following facts : (i) Resonance bond energy 150.63 k J mol^{-1} of benzene (ii) sp^2 hybridisation of carbon in benzene (iii) Continuous transfor-mation of the three π-bonds among 6 carbons in benzene.

Kekule's represented structure (C) of benzene is known as aromatic or resonance structure. Its ring shape of molecular orbitals and charge clouds (electron clouds) are represented in Figure. 6.7

Fig. 6.7 Ring shape of molecular orbital of benzene

Aromatic Structure :

(i) The aromatic structure of benzene is represented on the basis of the molecular orbital theory.

(ii) This structure is accepted on the basis of information obtained from X-ray spectrum.

(iii) Each carbon atom of benzene possesses sp^2 hybridisation.

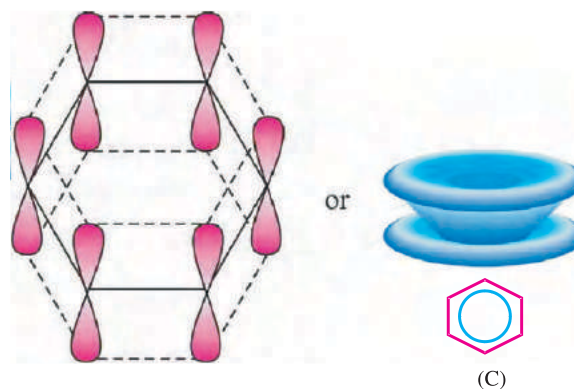(iv) In benzene 6 carbon atoms, 6 hydrogen atoms, 6 (C-C) Carbon-Carbon, σ-bond and 6 (C-H) Carbon-Hydrogen σ-bond lie in a same plane.

(v) In benzene, 6 carbon atoms have perpendicular p_z orbitals. Each p_z contains one π electron. So there are 6π electron which take part in the formation of 3π-bonds.

(vi) The six p_z orbitals overlap with each other and form a huge π–electron cloud above or below the molecular plane, in which 6π electrons revolve over the carbon atom.

(vii) The nature of all the 6 carbon atoms in benzene is the same.

(viii) Bond lengths between all C — C bond in benzene are equal.

(ix) Electron clouds of 6π electrons in benzene support the less potential energy or the presence of resonance energy in it.

6.6.3 Huckel's rule and Aromatization :
In 1931, the scientist Huckel indicated that if the number of π-electrons in planar cyclic compound equals to (4n + 2), then these compounds possess aromatic properties, (aromaticity) where n = number of cyclic structures. According to Huckel's rule, some aromatic cyclic compounds are as under:

Benzene Naphthalene
n = 1 n = 2
πe = 6 πe = 10
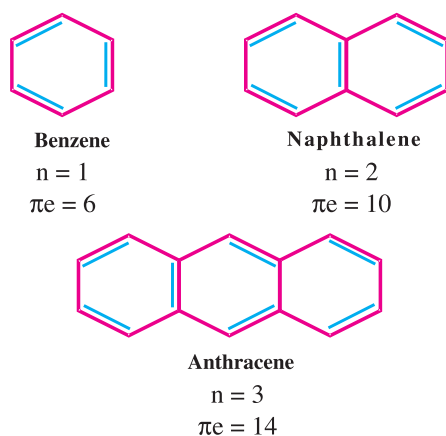
Anthracene
n = 3
πe = 14

Fig 6.8 Aromatic cyclic compounds

In benzene, naphthalene and anthracene, when we put n = 1, 2, 3 then the number of π–electrons we get in benzene is (6) naphthalene (10) and anthracene (14) respectively. This follows Huckel's rule. Hence, on the basis of Huckel's rule, it can be said that cyclic compounds like benzene, naphthalene and anthracene are aromatic compounds.

Characteristics in Aromatic Benzene :

(i) At normal temperature, just like alkanes, benzene resists oxidation with $KMnO_4$ and addition reaction with H_2, Cl_2, Br_2.

(ii) Like alkane, benzene also gives electrophilic substitution reactions like nitration, sulphonation, chlorination, bromination, alkylation, acylation etc. under suitable but vigorous conditions.

(iii) Just like alkenes, benzene also gives reaction with dihydrogen (H_2), dichlorine (Cl_2) and ozone (O_3) in suitable but vigorous reaction conditions.

(iv) Benzene has much more stability than alkene compounds.

(v) Like alkene, benzene does not undergo polymerisation.

(vi) There is only one isomer of monosubstituted benzene but there are three isomers of disubstituted benzene.

(vii) Aromatic or resonating structure is the modern structure of benzene.

(viii) The C — C bond length in benzene is less than C — C bond length of alkane and more than that of C = C double bond in alkene.

(ix) The electron cloud of 6π electrons moves around in ring shape on both the sides of its plane.

(x) Benzene obeys Huckel's rule.

6.6.4 Preparation of Benzene :

(1) From the decarboxylation of aromatic acid : The reaction of benzoic acid with sodalime forms sodium salt of benzoic acid (sodiumbenzoate) which reacts with sodalime at higer temperature to produce benzene.

Benzoic acid → **Sodium benzoate**

(via Soda lime [CaO + NaOH], Δ, $-H_2O$)

Sodium benzoate → **Benzene** $+ Na_2CO_3$

(via [CaO + NaOH], Δ)
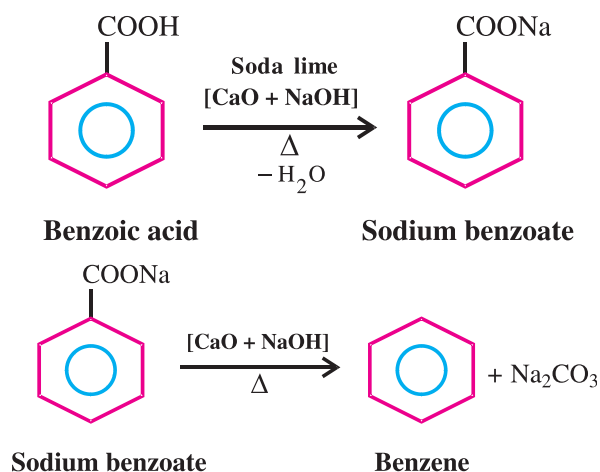
(2) **By the reduction of phenol :** By passing phenol vapours through zinc dust reduction takes place and benzene is obtained.

Phenol $+ Zn$ →(Δ) **Benzene** $+ ZnO$
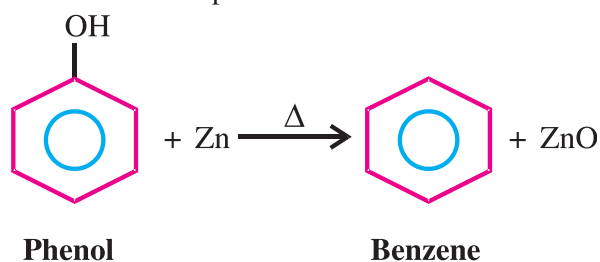
(3) **By cyclic polymerisation :** Ethyne on passing through red hot iron tube, at 873 K temperature benzene is obtained.

Ethyne →(Red hot iron tube, 873 K) **Benzene**

6.6.5 Properties of Benzene :

(1) **Physical properties :**

(i) Benzene has kerosene like odour and is colourless liquid.

(ii) Benzene is non-polar aromatic hydrocarbon.

(iii) Benzene is insoluble in polar solvent like water.

(iv) Benzene is soluble in non-polar organic solvent like carbontetrachloride.

(v) Benzene is a good organic solvent.

(vi) Benzene burns with a sooty flame because it is an aromatic compound.

(vii) Boiling point of benzene is 353 K.

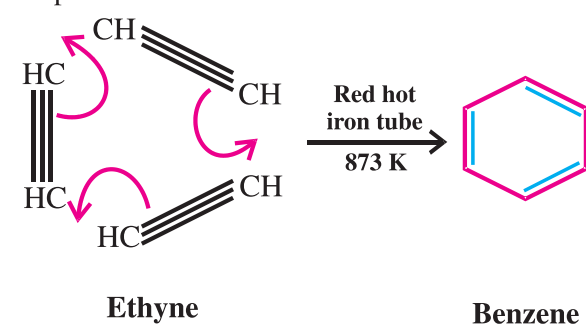(2) **Chemical Properties of Benzene (Chemical Reactions) :** Electrophilic substitution reaction is characteristic of arene compounds. Benzene is aromatic, hence, electrophilic substitution reaction occurs with it. In strong conditions benzene also gives addition and oxidation reactions.

6.6.6 Electrophilic substitution reactions :
The Lewis acid or positively charged ions obtained from the reagents involved in substitution reaction. in presence of catalyst are known as electrophilic ions like $\overset{+}{N}O_2$, $\overset{+}{S}O_3H$ ^+Cl, ^+Br, $^+CH_3$, $CH_3\overset{+}{C}O$ etc. Substitution reactions by these ions are known as nitration, sulphonation, chlorination, bromination, Friedel Crafts alkylation, Friedel-Crafts acylation respectively.

(1) **Nitration of Benzene :** When benzene is heated with the mixture of con. HNO_3 and con. H_2SO_4 at 323-333 K temperature, one hydrogen of benzene is replaced to give nitrobenzene.

$$HNO_3 + H_2SO_4 \rightleftharpoons \overset{+}{N}O_2 + HSO_4^- + H_2O$$
electrophilic reagent

Benzene →(Con. HNO_3 Nitration [con. H_2SO_4] 323-333 K) **Nitrobenzene** $+ H_2O$
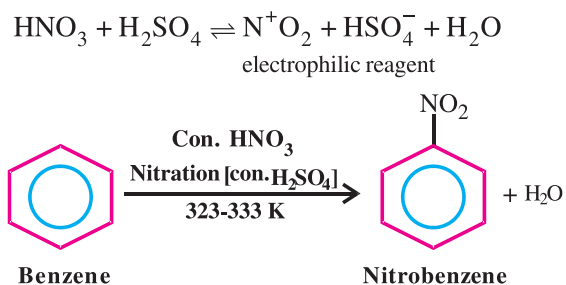
Here, $\overset{+}{N}O_2$ ion attacks as an electrophilic reagent on the carbon of benzene and H^+ is released from that carbon. Hence, nitration is known as electrophilic substitution reaction.

(2) **Sulphonation of Benzene :** A mixture of benzene and fuming H_2SO_4 or oleum $(H_2SO_4 + SO_3)$ when heated at 353 K temperature one hydrogen of benzene is replaced to give benzene sulphonic acid.

$$2H_2SO_4 \rightleftharpoons \overset{+}{S}O_3H + HSO_4^- + H_2O$$
Electrophilic regent

Benzene →(Sulphonation con. $H_2SO_4 + SO_3$ 353 K) **Benzene sulphonic acid** $+ H_2O$
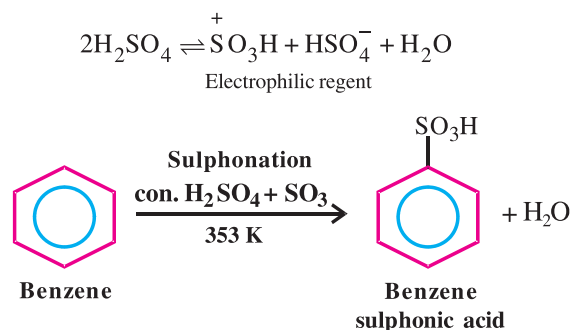
Here, the carbon on which $\overset{+}{S}O_3H$ electrophilic reagent is substituted, liberates proton (H^+) from it. Thus sulphonation is known as an electrophilic substitution reaction.

(3) Chlorination of Benzene (Halogenation) : In the reaction between benzene and chlorine, in presence of anhydrous $FeCl_3$ catalyst at 303-313 K temperature, one hydrogen is replaced to form chlorobenzene.

$$Cl_2 + FeCl_3 \rightleftharpoons Cl^+ + FeCl_4^-$$
<center>Electrophilic reagent</center>

Benzene   Chlorobenzene
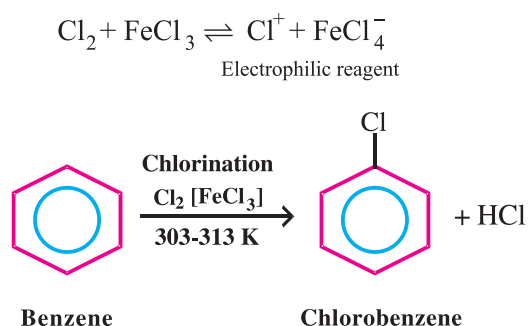
Here, the carbon at which electrophilic ion Cl^+ enters, proton H^+ is liberated from that carbon. Thus, chlorination is known as electrophilic substitution reaction.

(4) Friedel - Crafts Alkylation of Benzene : Scientists Friedel and Crafts invented this reaction in 1877, therefore, it is known as Friedel-Crafts Alkylation reaction

Reaction between benzene and alkyl halide in presence of anhydrous $AlCl_3$ helps to get alkyl benzene. Likewise on heating benzene with, methyl chloride at 353 K temperature one hydrogen is substituted to give methyl benzene (toluene)

$$CH_3Cl + AlCl_3 \rightleftharpoons \overset{+}{C}H_3 + AlCl_4^-$$
<center>electrophilic reagent</center>

Benzene   Methyl benzene (Toluene)

Here, the carbon at which electrophilic ion $^+CH_3$ enters, liberates proton H^+ from that carbon. Thus alkylation is known as electrophilic substitution reaction.

In place of methyl chloride, if ethyl chloride is taken, ethyl benzene is formed as shown below.

Benzene   Ethyl benzene
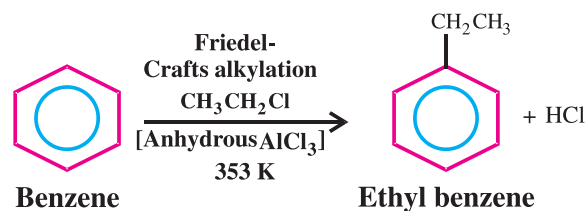
(5) Friedel-Crafts Acylation of Benzene: When benzene is heated with acetyl chloride in presence of anhydrous $AlCl_3$ at 353 K temperature, one of its hydrogen is replaced to give acetophenone.
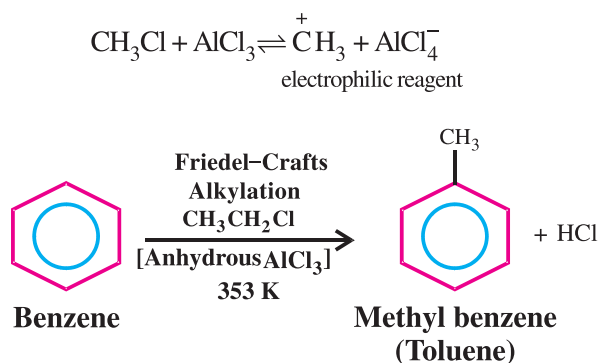
$$CH_3COCl + AlCl_3 \rightleftharpoons CH_3\overset{+}{C}O + AlCl_4^-$$
<center>electrophilic ion</center>

Benzene   Acetophenone
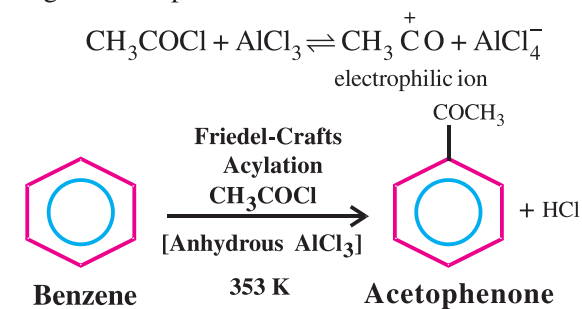
Here, the carbon at which electrophilic ion $CH_3\overset{+}{C}O$ enters, liberates H^+ proton from that carbon. Thus, acylation is also known as electrophilic substitution reaction.

In this reaction, in place of acetyl chloride, if acetic anhydride is taken, then the reaction is as follows :

Benzene   Acetophenone
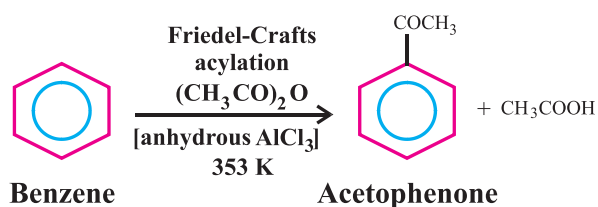
6.6.7 Inductive group and its Directing effect in monosubstituted Benzene : Six carbon atoms of benzene possess equal reactivity. Thus, as seen earlier monosubstituted isomers are not obtained. But when any functional group enters in benzene by first substitution, the obtained reactivity of remaining five carbon atoms are not similar in substituted benzene derivative. When second substitution is carried out on a monosubstituted benzene, the position of second entering functional group depends on monosubstituted derivative and characteristics of first functional group. Thus, the effect of first functional group

already present in monosubstituted benzene decides the place of second entering functional group. It will attach to carbon to which, the group already present in monosubstituted benzene directs the second entering group to become an inductive group. Effect of first functional group is known as directing effect. This directing effect is of two types :

(1) Ortho-Para directing effect : If first functional group present in monosubstituted benzene is $-NH_2$, $-NHR$, $-NR_2$, $-NHCOR$, $-OH$, $-OR$, $-OCOR$, $-R$, and $-X$, (where R = alkyl group : X = F, Cl, Br, I) etc, due to its effect attached to ortho and/or para position it can be represented as 1-2 (ortho) and 1-4 (para) respectively. Usually, functional group containing ortho and para directive effect are to pass on electron towards the phenyl ring and hence they are known as electron donating or positive groups.

In monosubstituted derivative, second substitution occurs at ortho and para position, and therefore, disubstituted derivative will be a mixture of ortho and para isomers.

Likewise, in first substitution reaction of chlorobenzene with excess chlorine, the first entered Cl^- group is ortho-para directive. So the second substituting functional group enters at ortho and para position. As a result, mixture of two isomers 1, 2 dichloro benzene and 1, 4 dichloro benzene are obtained.

Chloro benzene → **1, 2-Dichloro benzene or o - Dichloro benzene** + **1, 4-Dichloro benzene or p - Dichloro benzene**
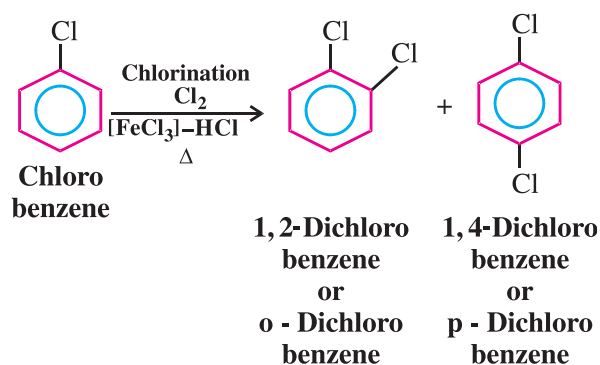
Some other examples of this directive effect are as under :

(1) Bromination of bromobenzene, by second substitution, mixture of 1, 2 dibromobenzene and 1, 4 dibromobenzene are obtained.

Bromo benzene → **1, 2 Dibromo benzene or o - Dibromo benzene** + **1, 4 Dibromo benzene or p - Dibromo benzene**
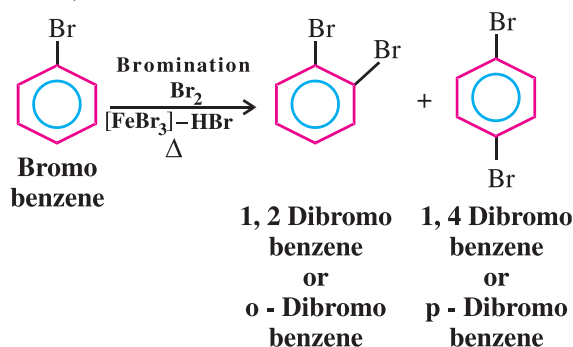
(2) On performing Friedel-Crafts' alkylation in toluene, due to the effect of ortho-para directing methyl group, the second substitution, produces mixture of ortho and para xylene.

Toluene → **1-2 dimethyl benzene or o - xylene** + **1-4 dimethyl benzene or p - xylene**
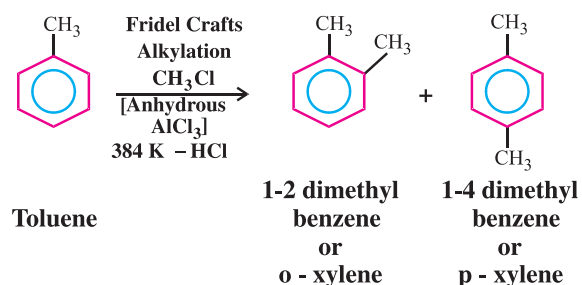
(3) On chlorination of toluene due to the presence of ortho-para directing group in toluene by second substitution, mixture of artho chlorotoluene and para chloro toluene is obtained. Due to the difference in their boiling-points ortho and para isomers are separated by distillation.

Toluene → **1-Chloro 2-methyl benzene (o-Chloro toluene)** + **1-Chloro 4-methyl benzene (p-Chloro toluene)**
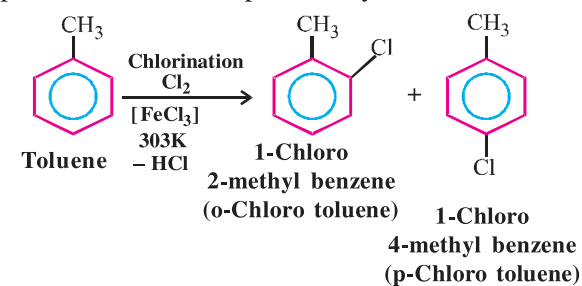
(2) Meta-directing Effect : If the first functional group present in monosubstituted benzene is $-NO_2$, $-CHO$, $-COOH$, $-CN$, $-CCl_3$, $-COR$, $-COOR$, $-SO_3H$ etc., due to the effect of any one of these, the second entering functional group will attach to the meta position. Usually, such types of functional groups are attractive electrons from the phenyl ring towards themselves, hence, they are known as electron attracting or negative groups. In monosubstituted benzene derivatives, second substitution occurs

at meta position, then only one isomer is obtained, for such disubstituted benzene.

E.g. In nitrobenzene nitration takes place at 353-363 K temperature, then second substitution reaction occurs, nitrobenzene obtained from the first substitution due to the presence of meta directing functional group, the second entering-NO_2 functional group enters to the meta position on second substitution. As a result only one isomer metadinitrobenzene is obtained.

Nitrobenzene   **m-dinitro benzene**
or
1-3, dinitrobenzene
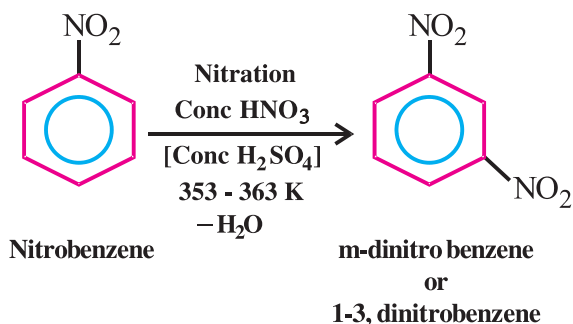
Some examples of meta-directing effects are given below :

(1) Sulphonation of benzene sulphonic acid at 473 K temperature, due to the effect of meta directing $-SO_3H$ group, the newly entering $-SO_3H$ group attaches to the meta position and benzene m-disulphonic acid is obtained.

Benzene sulphonic acid   **Benzene meta disulphonic acid (BDS)**
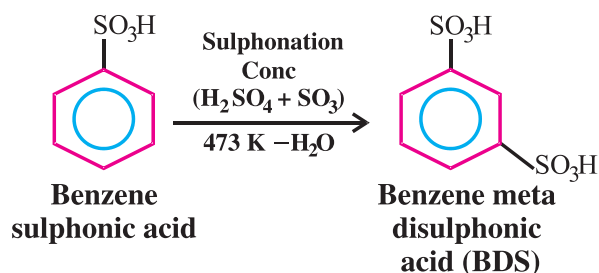
(2) Bromination of benzoic acid in presence of $FeBr_3$ as a catalyst due to the effect of meta directing $-COOH$ group, the newly entering $-Br$ group attaches at m-position and meta bromobenzoic acid is obtained.

Benzoic acid   **Metabromo benzoic acid**

6.6.8 Reactions of functional group :

(1)

Benzene sulphonic acid   **Phenol**

Benzene m-disulphonic acid (BDS)   **Resorcinol**

(2)

Ethyl benzene   **Styrene**

(3)

Toluene   **Benzoic acid**

(4)

Benzaldehyde   **Benzoic acid**
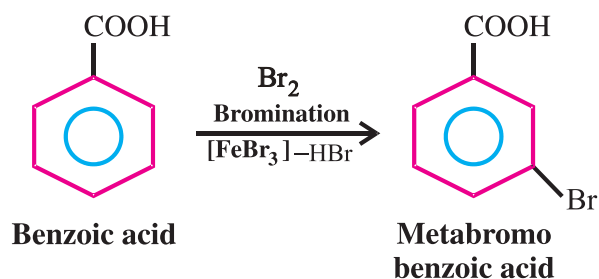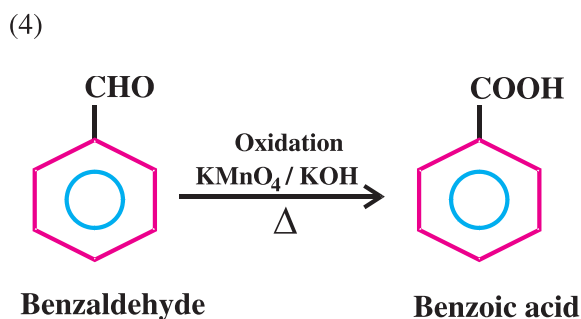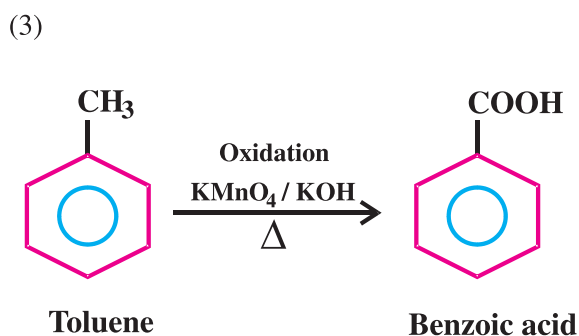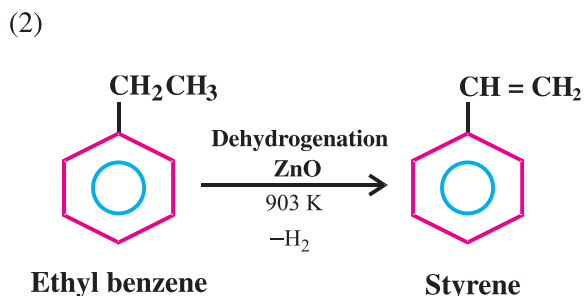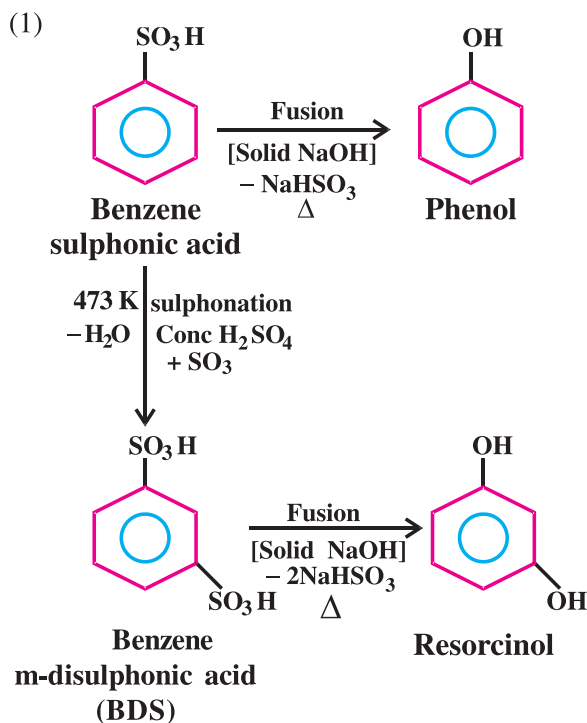
Chemical Reactions of Toluene :

Reactions in the phenyl ring :

(1) Nitration :

CH_3

Toluene

Nitration
Conc HNO_3
[Conc H_2SO_4]
333-343 K
$-H_2O$

CH_3 NO_2

o - Nitro toluene
(ONT)

+

CH_3

NO_2

p - Nitro toluene
(PNT)

Nitration Fuming HNO_3 [Fuming H_2SO_4]
$-H_2O$
384 K

Nitration [Conc H_2SO_4]
Conc HNO_3
353-363 K
$-H_2O$

CH_3
O_2N NO_2

NO_2

**2, 4, 6 - Trinitrotoluene
(TNT)**

Nitration Conc HNO_3
[Conc H_2SO_4] 373 K
$-H_2O$

CH_3 NO_2

NO_2

**2, 4, -Dinitro toluene
(DNT)**

(2) Sulphonation :

CH_3

Toluene

sulphonation
Fuming H_2SO_4
303 K $-H_2O$

CH_3 SO_3H

o-Toluene
sulphonic acid
(OTS)

+

CH_3

SO_3H

p-Toluene
sulphonic acid
(PTS)

$-$ NaHSO$_3$ Solid NaOH
Fusion
Δ

CH_3 OH

**1-Hydroxy 2-methyl
benzene
(o-Cresol)**

Δ
$-$ NaHSO$_3$
Fusion
Solid NaOH

CH_3

OH

**1-Hydroxy 4-methyl
benzene
(p-Cresol)**

(3) Bromination :

CH_3

Toluene

Bromination
$2Br_2$
[FeBr$_3$] 313 K
$-2HBr$

CH_3 Br

**1-Bromo
2-methyl benzene
(o-Bromo toluene)**

+

CH_3

Br

**1-Bromo
4-methyl benzene
(p-Bromo toluene)**

CH_3 Br

Br

**2,4-Dibromo
toluene**

Bromination $2Br_2$
[FeBr$_3$] $-2HBr$
Δ

(4) Alkylation :

Toluene → 1,3-Dimethyl benzene (m-Xylene)

Alkylation CH_3Cl
[BF_3 / HF]
384 K, $-HCl$

(5) Acylation (Friedel-Crafts) :

Toluene → p-Methyl acetophenone

Friedel-Crafts Acylation
CH_3COCl
or
$(CH_3CO)_2O$
[Anhydrous $AlCl_3$]
384 K
$-HCl$ or CH_3COOH

6.6.9 Organic Conversions :

(1) p-Nitrobromobenzene from benzene :

Benzene → Bromobenzene

Bromination(Br_2)
[$FeBr_3$] $-HBr$

Bromobenzene → p-Nitro bromo benzene or Nitro bromobenzene

Nitration
Conc HNO_3
[Conc H_2SO_4]
353 - 363 K,
$-H_2O$
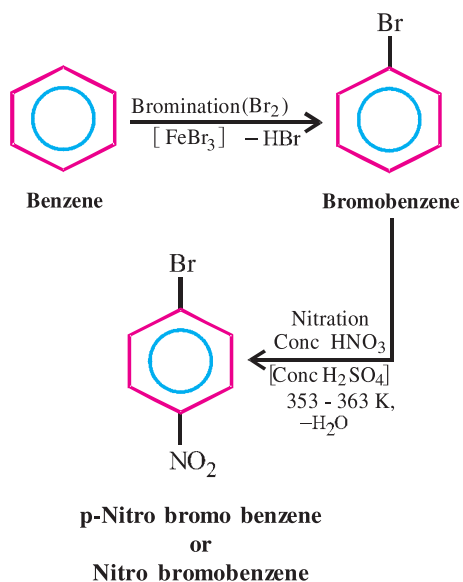
(2) Benzene to Benzaldehyde :

Benzene → Toluene

Friedel Crafts
alkylation
CH_3Cl
[Anhydrous $AlCl_3$]
353 K
$-HCl$

Toluene → Benzaldehyde

Oxidation
CrO_2Cl_2 or
CrO_3/ $(CH_3CO)_2O$
Δ
$-H_2O$

(3) Ethyne to cyclohexane :

$3(HC\equiv CH)$ → Benzene → Cyclohexane

Ethyne

Red hot Fe
873 K

$3H_2$
[Ni] Δ
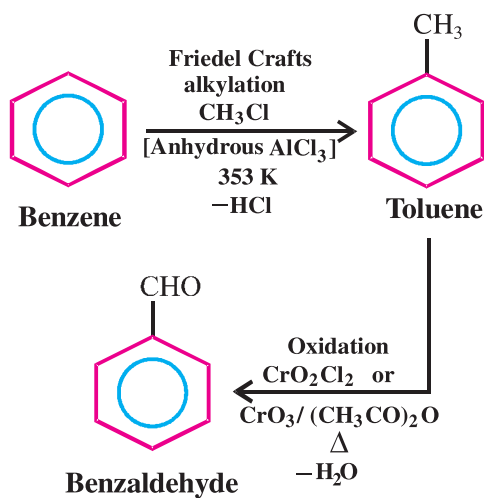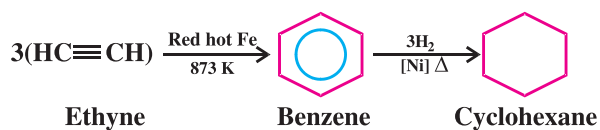
(4) Toluene to Benzaldichloride :

Toluene → Benzylchloride

Chlorination Cl_2
[hv]
384 K $-HCl$

Benzylchloride → Benzaldichloride

Chlorination Cl_2
[hv]
384 K $-HCl$
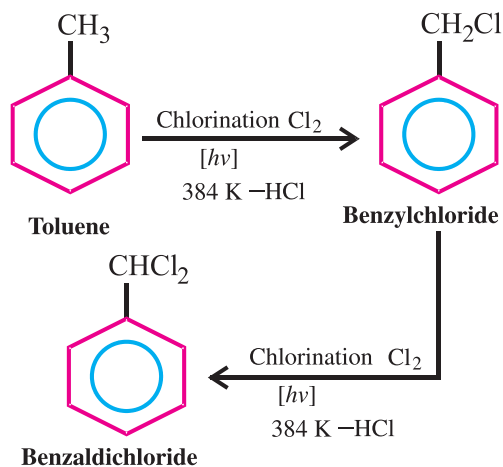
(5) Benzoic acid from Benzal dichloride

Benzal dichloride → Benzotrichloride

Chlorination Cl_2
[hv]
384 K $-HCl$

Benzotrichloride → Benzoic acid

Hydrolysis
Aqueous $Ca(OH)_2$
$+ 2H_2O$
Δ $-3HCl$

or

Benzal dichloride → Benzaldehyde

Hydrolysis - Aqueous
$Ca(OH)_2 + H_2O$
Δ $-2HCl$

Benzaldehyde → Benzoic acid

Oxidation [O]
$KMnO_4$/ KOH
Δ
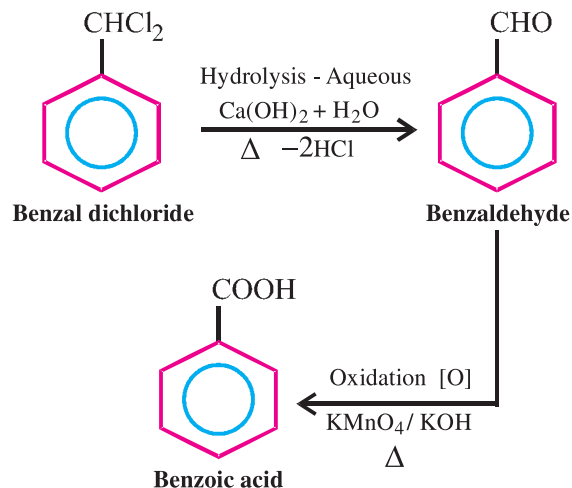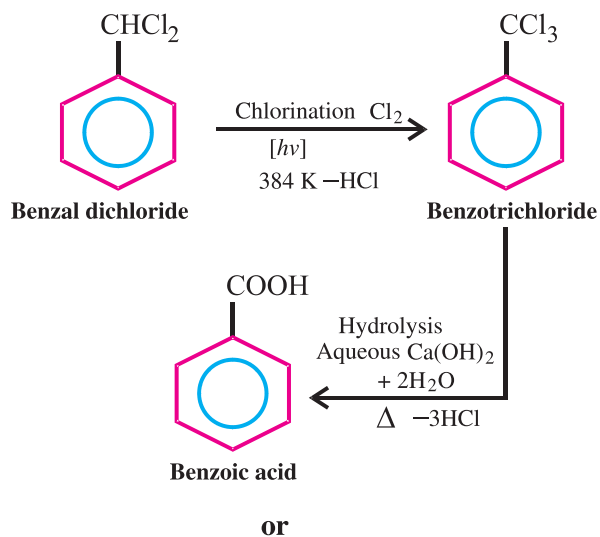
SUMMARY

Hydrocarbons are compounds of carbon and hydrogen. Mostly hydrocarbons are obtained from coal and petroleum, which is a big source for obtaining energy. Petro-chemicals are used as the raw material in the large scale production of important indus-trial products. Hydrocarbons are calssified on the basis of the structure, as straight chain, saturated alkanes, unsaturated alkenes, unsturated alkynes, cyclic aliphatic and cyclic aromatic compounds.

Alkanes can be prepared from unsaturated hydrocarbons, alkyl halide, and carboxylic acid. According to the different number of carbon atoms in alkane, physical state changes due to weak intermolecular forces.

When the number of carbon atom increases in alkane, the molecular weight increases, as a result we can see increase in the boiling points.

In alkane, alkene and alkyne compounds nomenclature is based according to IUPAC system. In hydrocarbon compounds when molecular weights are same, but physical and chemical properties are different, they show isomerism phenomenon.

Alkene compounds are prepared from alkyne, alkylhalide, vicinal dihalide and alcohol. The melting points and boiling points of alkenes are higher compared to alkynes. In 1869 Russian scientist Markovnikov gave rule which is known as Markonikov rule. In 1933 anti-Markovnikov rule was given by M.S Kharsh and F.R.Mayo which is also known as peroxide effect. Alkyne compounds are prepared from calcium carbide and vicinal dihalides. In alkyne compounds, melting points, boiling points and densities increase with the increase in molecular masses, polymerisation of alkyne compounds give polymers like PVC and PAN.

Important reactions of alkanes like free radical formation, substitution, combustion, oxidation and cyclisation, while in alkene and alkyne mainly electrophilic addition reactions are taking place. Benzene is the first member of aromatic hydrocarbon compounds. Benzene and benzanoids possess aromatic characteristic. Kekule represented resonating structure of benzene. Benzene is aromatic and its proof is obtained by Huckel's rule. The concept of planar cyclic compound are clarified by Huckel's law. In 1937 scientist Lewis gave electronic configuration of benzene. By this sp^2 hybridization of carbon in benzene can be understood.

Ortho, meta and para isomer compounds can be easily understood by inductive group in benzene and its directive effects.

Aromatic hydrocarbons give mainly electrophilic substitution reactions and sometimes addition reactions although it is saturated.

EXERCISE

1. **Select the proper choice from the given multiple choices :**

(1) Which is the saturated hydrocarbon from the compounds mentioned below :

(A) Phenyl group (B) Alkane (C) Alkene (D) Alkyne

(2) Which substance has (2^0) secondary carbon ?

(A) Propane (B) n-Butane (C) 2 Methyl propane (D) Methane

(3) What is obtained by reduction reaction of alkyl halide ?

(A) Alcohol (B) Alkene (C) Alkane (D) Cl_2

(4) Which gas is released in decarboxylation reaction ?

(A) CO_2 (B) CO (C) O_2 (D) N_2

(5) Sodalime is a mixture of which substances ?

(A) NaOH, $CaCO_3$ (B) NaOH, CaO

(C) KOH, $Ca(OH)_2$ (D) KOH, CaO

(6) The general formula of alkene is ....

(A) $C_nH_{2n+2}O$ (B) C_nH_{2n} (C) C_nH_{2n+1} (D) C_nH_{2n+2}

(7) Which mixture is used as Lindlar's catalyst ?

(A) Pd + Pt (B) Ni + P (C) Pt + halogen (D) Pt + charcoal

(8) The catalyst used for obtaining carbonyl compound from alkyne with H_2O........

(A) Pt (B) $HgSO_4$ (C) $HgCl_2$ (D) HCN

(9) What is the bond length of C = C in benzene ?

(A) 139 pm (B) 133 pm (C) 154 pm (D) 111 pm

(10) The value of resonance energy in benzene ....

(A) 119.66 kJ (B) 208.36 kJ (C) 150.63 kJ (D) 358.99 kJ

(11) Which is the electrophilic ion in nitration reaction of benzene ?

(A) SO_3H^+ (B) NO_2^- (C) NO_2^+ (D) HNO_3

(12) From the following which is the formula of toluene ?

(A) CH_3 (B) OH   (C) NH_2 (D) COOH
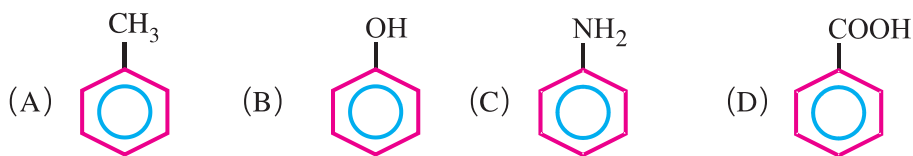
(13) What is the number of σ-bonds and π-bonds in benzene ?

(A) Six σ and 3π   (B) Six σ and 1π

(C) Eight σ and 3π   (D) Twelve σ and 3π

(14) Which catalyst is used in bromination of toluene ?

(A) $FeBr_3$ (B) $FeSO_4$ (C) $FeCl_3$ (D) $AlBr_3$

(15) The general formula of arene compounds is ....

(A) C_nH_{2n-6} (B) C_nH_{2n-3m} (C) C_nH_{2n+6m} (D) C_nH_{2n-6m}

2.   Answer the following questions in brief :

(1) Give IUPAC names and structural formulas of the following :

Neopentane, Isobutane, Formaldehyde, n-Butane, Benzyl chloride, TNT

(2) Give IUPAC names of the compounds having following structural formulae :

(i) $CH_3 - CH = C (CH_3)_2$

(ii)

(iii) CH_3 —OH

(iv) $H_3C - C ≡ C - CH_2 - CH_3$
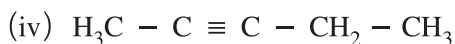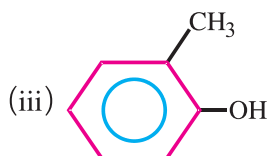
(3) Why quarternary hydrogen is not possible in alkane ?

(4) Moving from primary to tertiary alkane the boiling point decreases. Why ?

(5) What is called dehydrohalogenation reaction ?

(6) Give only equation for the preparation of PVC.

(7) Give the structural formulae and the names of the aromatic compounds containing three rings.

(8) What is the resonance energy ?

(9) What is called electrophilic ion ? Give example.

(10) Give only equation of Friedel-Crafts alkylation reaction in benzene ?

(11) Which functional groups are responsible for meta directing effect ?

(12) Give the structure of benzene suggested by Kekule ?

(13) Give the electronic configuration of benzene given by Lewis ?

(14) Mention Huckel's rule of aromatization.

3. **Write answers to the following questions :**

(1) Give the following organic conversions :

(i) Ethyne from 1, 2 dibromoethane

(ii) Ethanoic acid from chloroethane

(iii) 1 – Bromo propane from propyne

(iv) 4 Nitro 1-bromobenzene (p – Nitrobromobenzene) from benzene

(v) 4 Nitro 4- methylbenzene (p – Nitrotoluene) from benzene

(vi) 1, 3 Dimethyl benzene (m-Xylene) from benzene

(vii) Phenol from benzene

(2) Who discovered benzene and when ?

(3) Explain the classification of aliphatic hydrocarbons giving the suitable examples.

(4) Give the preparation reaction of alkane from alkyl halide.

(5) Mention the difference between physical state and boiling point of alkane due to increase in number of carbon atoms.

(6) Give formation of benzene by reduction of phenol

(7) Explain the reaction mechanism of asymmetric alkene with HCl according to Markovnikov rule.

(8) Prove the acidic properties of alkynes.

(9) Explain the addition reactions in alkynes.

(10) Discuss the physical properties of alkynes.

4.   **Answer the following questions in detail :**

(1)   Write a note on preparation of alkyne compounds.

(2)   What is aromaticity ? Give its details.

(3)   Explain the structure of benzene based on its chemical reactions.

(4)   Discuss the mechanism of nitration, halogenation and sulphonation of benzene.

(5)   Write a note on directing effect of second substitution in benzene.

(6)   Explain the ortho-para and meta directive effect in toluene giving two examples of each.

(7)   Explain the modern structure of benzene based on its physical properties.

(8)   Explain the structure of aromatic benzene according to molecular orbital theory.

(9)   Nitration of bromobenzene gives 2-Bromo, 1-nitrobenzene and 4-Bromo-1-nitrobenzene but bromination of nitrobenzene gives 3-Bromo-1-Nitrobenzene benzene. Why ?

(10)   Why polymerisation of benzene is not possible even when it possesses double bonds ?

●

Environmental Chemistry

7.1 Introduction

As we know that environment means everything which exists around us. The aggregation of social, biological, physical and chemical factors existing around us is called environment. Environmental chemistry means scientific study of chemical and biochemical processes occurring in environment. Thus, **the study of the sources, reactions, transport, effects and fates of chemical species in the air, soil and water environment and the effect of human activity on these is called environmental chemistry.** Environmental chemistry is an interdisciplinary science that includes disciplines like atmospheric, aquatic, soil and analytical chemistry. Analytical chemistry includes study of different methods and techniques used for analysis of chemical compounds.

The incidents and changes occurring in environment creates a number of questions like why do our eyes suffer irritation when we pass through specific areas ? Why the temperature of earth is increasing ? What is the reason for erosion of historical buildings ? Why does soil become dry ? What type of water is safe for drinking ? Why does a person working in a factory become deaf earlier than a normal one ? To answer these questions, we have to take help of environmental chemistry. It gives importance to the study of air, water, soil and noise pollution. In this unit we will discuss mainly the causes and the effects of air, water and soil pollution and also the remedies for its removal and how to control it.

7.2 Environmental Pollution

The pollution of environment is called environmental pollution. This pollution occurs due to harmful wastes produced by natural and

human activities. The substances which produce or spread the pollution are known as pollutants. Pollutants are found in solid, liquid or gaseous forms. Different time durations are required for natural degradation of pollutants. **Pollutants which degrade rapidly are known as rapidly degradable pollutants.** e.g. discarded vegetables naturally degrade within 7-10 days. **Pollutants which degrade slowly are known as slowly degradable pollutants.** e.g. agricultural wastes require 3 to 5 months for their natural degradation. For this reason, the farmers remove dungheaps maximum twice in a year. **Some pollutants remain for decades in their original form without degradation. They are known as non-degradable pollutants. e.g.** dichlordiphenyltrichloroethane (DDT), plastic materials, heavy metals, radioactive wastes etc. These compounds are not degraded naturally so it is difficult to remove them from the environment. These pollutants are proved to be more harmful to living beings. As we know that our environment consists of lithosphere (soil), hydrosphere (water) and atomsphere (air, gas), so, study of environmental pollution requires to know pollution that occurs in these three spheres. We will study them sequentially in this unit.

7.3   Atmospheric Pollution

The gaseous coverage surrounding the earth is known as atmosphere which is extended upto 500 km above sea level. **The lowest region of atmosphere is called troposphere in which all living beings including human beings reside.** It is extended upto 10 km above sea level. **The region which is above the troposphere and between 10 to 50 km from the sea level is known as stratosphere.** Dinitrogen (N_2), dioxygen (O_2), carbon dioxide (CO_2), water vapour (H_2O) and argon (Ar) are present in troposphere. Dintrogen (N_2), dioxygen (O_2) and ozone (O_3) are present in stratosphere. Troposphere and stratosphere greatly affect the biosphere of earth due to which study of pollution, in these two regions, is very important for the

study of pollution in environment. So we will study the air pollution in troposphere and stratosphere.

7.3.1   Tropospheric   Pollution   :
Tropospheric pollution occurs due to the presence of undesirable solid or gaseous particles in the air. The gaseous pollutants - SO_x, NO_x, CO, CO_2, H_2S, O_3, hydrocarbons and particulate pollutants dust, mist, fumes, smoke and smog are to a great extent present in the troposphere.

7.3.1.1   Gaseous Air Pollutants :

(1) Oxides of sulphur (SO_x) : When sulphur containing fossil fuel is burnt, then oxides of sulphur are produced. Sulphur dioxide is the most common gaseous species which is poisonous to both animals and plants. Even low concentration of sulphur dioxide causes respiratory diseases like asthma, swelling and irritation of respiratory tract in human beings. Sulphur dioxide also causes irritation to eyes and turn them into reddish and tearful. High concentration of sulphur dioxide leads to stiffness of flower buds which eventually fall off from plants. The oxidation of sulphur dioxide without catalyst is slow, but the particulate matter present in polluted air acts as catalyst and converts sulphur dioxide into sulphur trioxide.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$
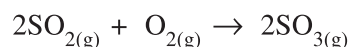
This reaction can also be possible in presence of oxidising agents like ozone and hydrogen peroxide.

$$SO_{2(g)} + O_{3(g)} \rightarrow SO_{3(g)} + O_{2(g)}$$

$$SO_{2(g)} + H_2O_{2(l)} \rightarrow H_2SO_{4(aq)}$$
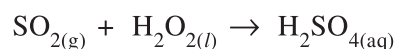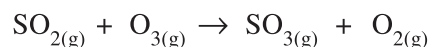
(2) Oxides of Nitrogen (NO_x) : Nitrous oxide (N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2) are present greatly in atmosphere as oxides of nitrogen. Generally these oxides of nitrogen are known as NO_x. We know that dioxygen (21%) and dinitrogen (78%) are the main constituents of air. In specific conditions, they react with each other and form oxides of nitrogen. NO_2 is oxidised to NO_3^- which, when

enters into soil, acts as a fertilizer. In an automobile engine, when fossil fuel is burnt at high temperature, then significant quantities of nitric oxide and nitrogen dioxide are produced due to the combination of dinitrogen and dioxygen.

$$N_{2(g)} + O_{2(g)} \xrightarrow{1483 \text{ K}} 2NO_{(g)}$$
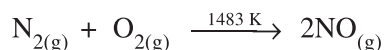
NO reacts instantly with dioxygen to give NO_2

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$
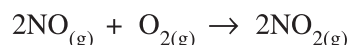
In stratosphere the rate of production of NO_2 becomes faster when nitric oxide reacts with ozone.

$$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$$
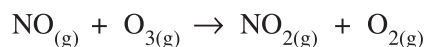
Thus, forest fires, vehicle smokes, mineral oil, coal and natural gas burning, smokes generated by supersonic jet etc. are the sources of NO_x. In heavy traffic and congested areas, the irritant red-hazy environment is produced due to oxides of nitrogen. Higher concentration of NO_2 damage the leaves of plants and decrease the rate of photosynthesis. NO_2 is lung irritant. It causes an acute respiratory diseases in children. It is highly toxic to living tissues. Moreover, it is also harmful to metals and textile fibres.

(3) Hydrocarbons : The compounds of hydrogen and carbon only are called hydrocarbons. The hydrocarbons such as 3, 4- benzpyrene are present in smoke which is produced from incomplete combustion of fuel of vehicles and smoking of cigarettes. They are carcinogens, which means they cause cancer. They break the tissues of plant. Moreover, causes shedding of leaves, flowers and twigs. Benzene is also a carcinogen.

Benzene

3, 4- Benzpyrene

(4) Oxides of Carbon :

(i) Carbon monoxide (CO) : Carbon monoxide is the most severe air pollutant. It is colourless, odourless and highly poisonous gas. It is being produced from incomplete combustion of carbon.

$$2C_{(s)} + O_{2(g)} \xrightarrow{\text{Incomplete Combustion}} 2CO_{(g)}$$
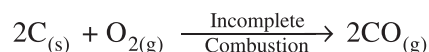
Carbon monoxide is present as a major constituent in smoke produced by vehicles. Moreover, it is also produced by incomplete combustion of firewood, coal and petroleum products. The number of vehicles in the world is increasing day-by-day and so higher and higher CO is released from these vehicles due to inadequate polluti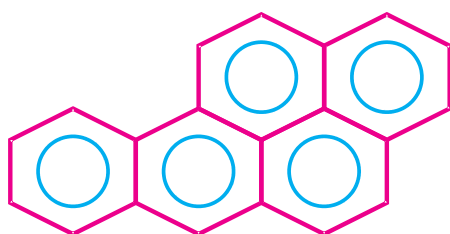on control equipments and lack of their regular service. Carbon monoxide enters into our body and binds with haemoglobin to form carboxyhaemoglobin complex, which is about 300 times more stable than the oxygen-haemoglobin complex. When the concentration of carboxyhaemoglobin reaches to about 3 to 4 % in blood, the oxygen carrying capacity of blood reduces. It causes headache, weak eyesight and cardiovascular disorder. Carbon monoxide gas produced during smoking enters our body through lungs and causes harmful effects. Due to this people are advised not to smoke. **That is why on cigarette cases the statutory warning-"Smoking Kills" is printed.** Smoking by pregnant woman results in increased level of CO in her blood which may increase the possibility of premature birth, spontaneous abortion and a deformed baby.

(ii) Carbon dioxide (CO₂) : CO_2 is natural constituent of air which is necessary for every vegetation. Its level in normal atmosphere is 0.03 %. Carbon dioxide is released by respiration, by burning of fossil fules for energy and by decomposition of limestone during the manufacturing of cement. So the level of carbon dioxide increases in the atmosphere. Plants use the carbon dioxide from the atmosphere for the photosynthesis. In this manner plants decrease the level of carbon dioxide in atmosphere. But due to increased use of fossil fuel and

deforestation, by growing human population to satisfy their greed, CO_2 level is increasing in atmosphere. The increased amount of carbon dioxide is responsible for global warming. Pollution effect due to gaseous pollutants in troposphere results in increased temperature of earth and also causes acid rains. Now, we will study in detail the effects of gaseous pollutants.

Global Warming and Green House Effect : The simple meaning of green house is 'plant growing house'. Plants can be grown at expected temperature in glass houses made from insulated walls and transparent ceiling. During day time the sunlight passes through transparent ceiling and transfer heat to soil, vegetation and other materials. The surplus absorbed heat by these constituents is reflected during night, but due to decreased penetration ability of this heat, it cannot escape from the walls or ceiling of glass house. So this heat stays in plant growing house and results in warm environment. Due to this, summer plant can grow in greenhouse when the temperature of outside environment is quite low. Nature also has such wonderful arrangement to keep the earth warm. In 1882, French Mathematician Jean Fourier, first of all, compared the environment of earth with green house. Later on, in 1886, Swedish chemist Swante Arrhenius and American scientist Chamberlin explained that greenhouse and atmosphere of earth are working in the same way. This means that sun rays enter but do not escape. **This process of warming of the earth is known as Greenhouse effect or Global Warming and the gases actively involved in it are called Greenhouse gases.** Carbon dioxide, methane, ozone, chlorofluorocarbons (CFCs), nitrous oxide and water vapour present in atmosphere act as greenhouse gases. Actually these greenhouse gases act as blanket of earth. In absence of greenhouse effect the temperature of earth would be $30\,^0C$ lesser than the present temperature. Can we imagine how a living being can sustain in this coolest environment ?
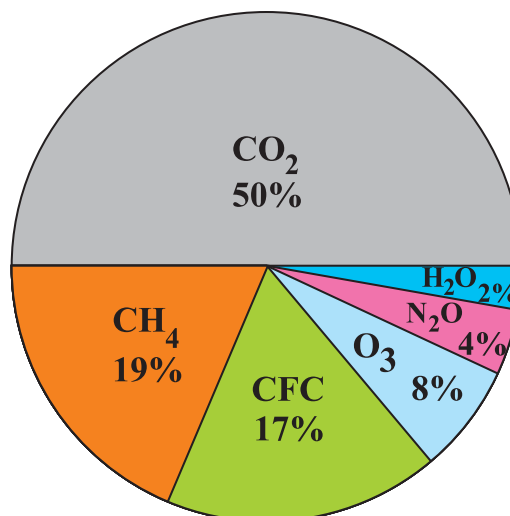
Fig. 7.1 Contribution of green house gases in global warming

Fig 7.1 shows the contribution of green house gases like CO_2, CH_4, CFC, O_3, N_2O and H_2O is 50%, 19%, 17%, 8%, 4% and 2% respectively in global warming. United Nations Intergovernmental Panel on Climate Change has given the word **'Global Warming Potential' (GWP)** for heat retaining capacity of green house gases. The GWP based sequence of green house gases is as

$$\overset{10000\ times}{CFC} \quad > \quad \overset{150\ times}{N_2O} \quad > \quad \overset{25\ times}{CH_4} \quad > \quad CO_2$$

This suggests that methane is 25 times stronger than carbon dioxide; nitrous oxide is 150 times stronger than methane and chlorofluorocarbon is 10,000 times stronger than nitrous oxide in terms of Global Warming Potential. In other words, compared to carbon dioxide, methane has 25 times, nitrous oxide has 3800 times and chlorofluorocarbon has 380 lakh times stronger Global Warming Potential.

If the amount of carbon dioxide in atmosphere is increased from 0.03 %, then, due to disturbance in balance of natural greenhouse, the temperature of earth will be increased. Digestion of dung heap, paper, kitchen waste and organic materials, in absence of oxygen, produce methane. Generally, chlorofluorocarbons are used in aerosols, foam plastic cup, refrigerator, airconditioner, production of electronic circuits,

oil paints and foams used in fire extinguisher that ultimately enter into atmosphere. Burning of coal and petroleum products at higher temperature in power plants and automobiles release nitrous oxide. Moreover, this gas also enters into atmosphere by use of nitrogen containing fertilizers. In this manner, the increasing amount of green house gases in atmosphere results in increased temperature of earth. This will result in increased water level of sea due to melting of ice on the poles; increase in frequency and intensity of floods in rivers and damages to the areas of sea shores and also erosion of soil. Increase in average temperature of earth may increase the possibilities of contagious diseases and also diseases like malaria, dengue and yellow fever. That is why it is essential to think about the remedies to control the increasing temperature of earth.

Remedies to Control the Increasing Temperature of Earth :

(i) To protect forests and grow more trees, because trees utilize carbon dioxide for photosynthesis and release oxygen. According to one estimate photosynthesis utilizes 2200 crore tons of CO_2 annually from atmosphere and releases 1600 crore tons of oxygen.

(ii) To take proper care of vehicles we should insist on regular service to keep engine in good condition.

(iii) Renewable energy sources should be used more. Complete dependence on coal and petroleum products should be reduced.

(iv) To control the amount of NO_x in atmosphere use of chemical fertilizers should be stopped or reduced and to opt for organic farming.

(v) Devices or instruments free from chloro-fluorocarbons should be used.

(vi) To stop the release of methane gas in atmosphere. We have to increase efforts in the direction towards production of biogas and best fertilizer from agricultural wastes and excreta of animals by avoiding the preparation of heap in open ground.

Acid Rain : As we know, the pH of rain water is about 5.6 because water reacts with CO_2 of atmosphere and produces carbonic acid (H_2CO_3).

$$H_2O_{(l)} + CO_{2(g)} \rightleftharpoons H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)}$$
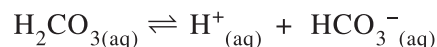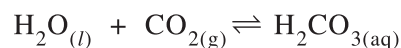
When the pH of rain water becomes lower than 5.6 then it is called acid rain. SO_2 and NO_2 released from burning of fossil fuels like coal and petroleum products in power plants and from combustion of petrol and diesel in vehicles, react with moisture of air and are converted into sulphuric acid and nitric acid. These acidic clouds move with wind and under suitable condition it rains.

$$2SO_{2(g)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2H_2SO_{4(aq)}$$

$$4NO_{2(g)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 4HNO_{3(aq)}$$

The acid rain in water reservoirs like rivers, ponds adversely affect fish, micro organisms and plants, in aquatic world. Acid rain has proved harmful to agriculture because this water results in increased erosion of nutrients essential for plant growth. Large amount of acidic rain decreases soil fertility. The buildings made up of stones and metals are affected adversely due to acid rain. Taj Mahal, the historical monu-ment of our country is also being affected by acid rain. The harmful gases released from nearby refineries are responsible for this. Implementation of Clean Air Law against industries producing SO_x and NO_x, may protect from the adverse effect of acid rain.

7.3.1.2 Particulate Pollutants :
Particulate pollutants are the minute solid particles or liquid droplets in air. They are present in vehicle exhausts, smoke particles from fires, dust, ash from units generating electricity and industries. Particulate pollutants can be classified in two types viable and non-viable. Bacteria, fungi and

algae etc. microorganisms spread in atmosphere are viable particulate pollutants. Non-viable pollutants are classified on the basis of their characteristics and size.

(1) Smoke : It is solid or mixture of solid and liquid produced during burning of organic materials. e.g. smoke from bidi-cigarette, smoke produced by burning of fossil fuels, dried leaves and garbage.

(2) Dust : It is a fine solid particle (more than 1 μ (micron) in diameter, $1\mu = 1$ micro meter $= 10^{-6}$ meter). These particles are produced by crushing or grinding of solid materials. Sand from sand blasting, sawdust from wood works and fly ash from industries are examples of such pollutants.

(3) Mist : Natural spray of liquid produced by condensation of vapours present in air, is called mist e.g. sulphuric acid mist. Furthermore, herbicides and insecticides produce mist after spreading in the air.

(4) Fumes : They are produced by condensation of vapour released during distillation, boiling and some other chemical reactions of organic solvents, metals and oxides of metals.

Spreading of smoke, dust, mist and fumes through air causes a great danger to human health. Effect of particulate pollutants is based on size of particles. Particulates of one micron (10^{-6} meter) size reaches easily to lungs and causes diseases related to lungs. Particulates having the size more than 5 microns lodge in nasal passage and harm human health.

Smog : Smog is a word derived from combination of smoke and fog which are common air pollutants present in urban areas. Smog can be divided into two parts.

(1) Classical Smog : Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and sulphur dioxide gas. Chemically it is a reducing mixture so it is called the **reducing smog.** In nineteenth century, classical smog was found in heavily populated industrial cities such as London and other cities in England. In these cities high sulphur coal was used as the energy sources both at domestic places and in the industries. At that time, the smoke produced was released near the ground level due to unawareness about pollution control. Due to this, the smog episodes were frequent in these cities depending on prolonged periods of climatic conditions. In 1952, such severe smog remained for several weeks in London. More than 4000 people died due to inhalation of the smog. As this classical smog was responsible for the accident in London, it is conventionally known as **'London smog'.**

(2) Photochemical Smog : Photochemical smog is produced in warm, dry and sunny climate. It is produced by sunlight on nitrogen oxide and hydrocarbons produced by vehicles and industrial units. Photochemical smog is known as oxidising smog because it possesses high concentration of **oxidising agent**. This type of smog is found frequently in the automobile rich city – Los Angeles of America. So it is known as **'Los Angeles Smog'.**

When fossil fuels are burnt, different types of pollutants are emitted into the troposphere of earth. Out of these, when nitrous oxide and hydrocarbons are present at sufficiently high level then in presence of sunlight a chain reaction occurs between them and NO_2 is produced. This NO_2 is converted into nitric oxide and free oxygen after absorbing the energy from sunlight.

$$NO_{2(g)} \xrightarrow{\ h\nu\ } NO_{(g)} + O_{(g)} \qquad 7.1$$

Due to high reactivity, free oxygen reacts with oxygen gas of air and produces ozone.

$$O_{(g)} + O_{2(g)} \rightleftharpoons O_{3(g)} \qquad 7.2$$
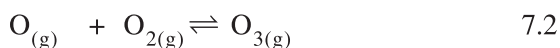
$O_{3(g)}$ formed according to reaction(7.2) reacts rapidly with $NO_{(g)}$ formed according to reaction (7.1) and produces $NO_{2(g)}$ again. It results in hazy atmosphere.

$$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)} \qquad 7.3$$

NO_2 and O_3 are strong oxidising agents. They react with unburnt hydrocarbons present in polluted air and produce formaldehyde, acrolein and peroxyacetylnitrate.

Photochemical smog causes severe effect on health. Ozone and peroxyacetylnitrate create acute irritation in eyes. Ozone and nitric oxide cause irritation in nose and throat. Their high concentration create the health related problems like headache, chest-pain, dryness of throat, cough and difficulty in breathing etc. Photochemical smog damages plant kingdom. The metals, stones, building materials, rubber and painted surface are also affected by erosion. For controlling formation of photochemical smog we must control the formation of NO_2, hydrocarbons, ozone and peroxyacetylnitrate. Mixing of NO_2 and hydrocorbons in atmosphere can be reduced by using catalytic converters in vehicles.

7.3.2 Stratospheric Pollution : Layer of ozone is present in upper region of stratosphere. We know it as 'Ozone Layer'. When ultraviolet radiations reach dioxygen molecule in stratosphere, two free oxygen atoms are produced. This oxygen atoms combine with dioxygen molecule and forms ozone.

$$O_{2(g)} \xrightarrow{\text{uv}} O_{(g)} + O_{(g)}$$

$$O_{(g)} + O_{2(g)} \xrightleftharpoons{\text{uv}} O_{3(g)}$$
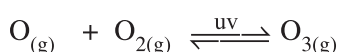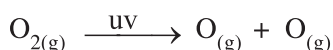
Ozone layer protects all living beings against harmful effect of ultraviolet radiations coming from sunlight. But pollutants produced from some anthropogenic activities deplete this ozone layer. So it becomes important to discuss the reasons for depletion of ozone layer, its effects and remedies for its prevention.

● **Depletion of Ozone Layer :** In September 1980, scientists reported a large hole in ozone layer over Antarctica. 30 % loss in this ozone layer was recorded. Generally, **substances that cause depletion of ozone or make it thinner are abbreviated as ODS (Ozone Depletion Substances).** Scientists have established that one molecule of CFC is capable to destroy one lakh O_3 molecules in the stratosphere. 95 derivatives of chloro or bromo fluorocarbon are known which are familiarly known as ODS. These ODS are greatly used in refrigerator, airconditioner, watercooler and fire extinguishers. 93 countries, including India, have accepted not to use ODS by signing Montreal Protocol on 16th September, 1987. Lately many other countries have also accepted it. To create its awareness in the whole world, United Nations decided to celebrate 16th September of every year as 'Ozone Protection Day' at international level.

Reasons for Depletion of Ozone Layer :

(1) Entering in atmosphere, CFC mixed with gases of atmosphere, reaches in stratosphere. Strong ultraviolet radiations present there, break the CFC molecule and produce chlorine free radical ($\overset{\bullet}{C}l_{(g)}$).

$$CF_2Cl_{2(g)} \xrightarrow{\text{uv}} \overset{\bullet}{C}l_{(g)} + \overset{\bullet}{C}F_2Cl_{(g)}$$
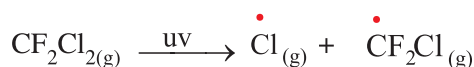
This chlorine free radical reacts with ozone of stratosphere and produces chlorine monoxide free radical and oxygen molecule.

$$\overset{\bullet}{C}l_{(g)} + O_{3(g)} \rightarrow \overset{\bullet}{C}lO_{(g)} + O_{2(g)}$$
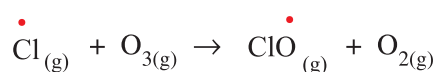
This chlorine monoxide free radical reacts with oxygen atom and produces chlorine free radical.

$$\overset{\bullet}{ClO}_{(g)} + O_{(g)} \rightarrow \overset{\bullet}{Cl}_{(g)} + O_{2(g)}$$
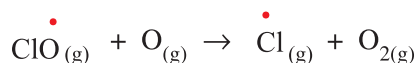
Thus, chlorine free radicals, produced continuously, deplete the ozone layer. Thus, chlorofluorocarbons are considered responsible for depletion of ozone layer.

(2) Reaction of NO_x with O_3 causes about 40 % reduction in concentration of ozone. NO_x enters into atmosphere through smoke of supersonic jet aircrafts. Amount of NO_x, resulting from atomic explosion experiments, cause reduction in concentration of ozone.

$$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$$

$$NO_{2(g)} + O_{3(g)} \rightarrow NO_{3(g)} + O_{2(g)}$$
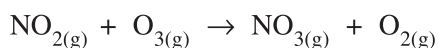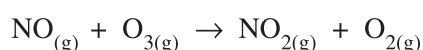
Effects of Depletion of Ozone Layer : Due to depletion of ozone layer, ultraviolet radiations of sunlight enter directly on the earth. These ultraviolet radiations cause skin cancer, harmful genetic changes in cell, reduction in soil moisture level and reduction in fish production.

Remedies to Protect Depletion of Ozone Layer : Depletion of ozone layer may be protected by spraying chemical compounds of alkane series in atmosphere, decreasing the production of CFC upto 50 %, forming more of polar stratospheric clouds and preventing the use of ODS.

7.4   Water Pollution

You might have read the slogans like - 'Water is life', 'Save Water, Water will save you' which tell us the importance of water. Such slogans indicate to save the amount of water. Not only the amount of water is important but its quality is also equally important. If the earth is divided into four parts then three parts will contain water, which indicates larger amount of water present. But not the whole amount of water is useful for us because its quality is not always good. 97 % of all available water on earth is sea water; we all know that the sea water is not usually utilized for drinking, agriculture or in other routine activities due to its salty nature. 2 % water of remaining 3 % is in the form of ice in polar regions. Thus, only 1 % water is left for utilization by human beings, which is available in the form of surface water-water in river, pond, spring and dam and the ground water-water in well. Surface and ground water become polluted due to negative effects of anthropogenic activities. Pollutants which pollute surface water, dissolved in universal solvent like water, percolate in ground and pollute ground water. These pollutants are shown in Table 7.1.

Table 7.1 Water Pollutants

No.	Pollutant	Sources
1.	Microorganisms	Domestic sewage, domestic waste water, dungheap
2.	Organic Wastes	Domestic sewage, excreta of animals, decaying of animals and plants, waste from food processing factories, detergents.
3.	Plant nutrients	Chemical fertilizers
4.	Heavy metals	Heavy metal producing chemical factories
5.	Sediments	Erosion of soil by agriculture and stripmining
6.	Pesticides	Chemicals used for killing insects, fungi and weeds
7.	Radioactive substances	Mining of uranium containing minerals
8.	Heat	Water used for cooling in industries

Pollutants listed in Table 7.1 cause mixing of soluble, insoluble, biological, physical and chemical impurities with water and pollute it. This discussion raises a question that what type of water is safe for drinking ? Types and amounts of which compounds or elements make it potable ? Attempts are being made at national and international levels to solve these questions. Institutions like **WHO (WHO : World Health Organization) at world level** and **BIS (BIS : Bureau of Indian Standards)** and **ICMR (ICMR : Indian Council of Medical Research)** at India level have prescribed standards for quality of drinking water. On the basis of this, we can decide whether the water is potable or not ? Standards prescribed by BIS, in 1991, for deciding the quality of drinking water are shown in Table 7.2 :

Table 7.2

Prescribed Standards by BIS for Quality of Drinking Water

Characteristics	Desirable limit
Physico-chemical characteristics	
pH	6.5 to 8.5
Total Dissolved Solids (TDS)	500 ppm
Total Hardness (as $CaCO_3$)	300 ppm
Nitrate	45 ppm
Chloride	250 ppm
Sulphate	200 ppm
Fluoride	1 ppm
Biological characteristics	
Escherichia Coli (E.Coli)	Not at all
Coliforms	Not to exceed 10 (In 100 ml water sample)

$1ppm = 1mgL^{-1}$

Standard analytical methods are available for estimation of physico-chemical and biological characteristics of water. We should take help of laboratory for estimation of these characteristics. Water, having higher values for physico chemical or biological characteristics than desirable limits, harms our health. So, such water cannot be considered safe for drinking.

pH : pH value of water that exceeds 8.5, reduces the effect of chlorination which is used to make the water germ free. If the water has pH values lower than 6.5 then corrosion of pipe for distribution of such water takes place. It results in mixing of harmful metals and releases Zn, Pb, Cd and Cu into drinking water.

Total Dissolved Solids (TDS) : Most of the salts are soluble in water. It includes cations like calcium, mangnesium, sodium, potassium, iron and anions like carbonate, biocarbonate, chloride, sulphate, phosphate, nitrate. Use of drinking water having total dissolved solids concentration higher than 500 ppm causes possibilities of irritation in stomach and intestine.

Total Hardness : Concentration of total hardness in water more than 300 ppm change the taste of drinking water. Regular intake of such water causes possibilities of heart disease. Such incidents are also reported.

Nitrate : Use of drinking water having the concentration of nitrate higher than 45 ppm causes possibilities of metheomoglobinemia (blue baby) diseases in children.

Chloride : Concentration of chloride in water higher than 250 ppm causes corrosion of pipes used for its distribution and results in higher amount of harmful metals in drinking water.

Sulphate : Diarrhoea and irritation is stomach are being caused by use of drinking water having concentration of sulphate more than 200 ppm.

Fluoride : Fluoride is essential for strength of bones and teeth, due to which use of tooth paste containing fluoride has increased. But higher concentration of fluoride causes harmful effect on our health. If the drinking water contains fluoride in concentration higher than 1 ppm, then it causes diseases of teeth and bones in human body. If the concentration of fluoride is higher than 2 ppm, then brown mottling of teeth occurs. If concentration of fluoride exceeds 10 ppm, it causes fluorosis diseases in which teeth and bones of a person become weak.

Escherichia Coli and Coliforms Bacteria : Escherichia Coli should be absent in drinking water. Use of water for drinking, having more than 10 coliforms in 100 ml water results swelling in stomach and intestine and causes urinary tract diseases.

Purification of Drinking Water : For purificaton, the drinking water is first analysed based on which the purification method is decided. Three methods are known for purification of drinking water.

(1) Chemical Method : To make the water safe for drinking, specific chemical is being added to it to remove specific impurity of constituent. Removal of obtained precipitate results in removal of impurities e.g. to remove fluoride from water, lime and calcium chloride are added to it. It results in precipitation of sparingly soluble calcium fluoride. Removal of this by precipitation results in easy removal of fluoride from water.

(2) Physical Method : Filtration, reverse osmosis and ion exchange methods are being used for removal or reduction of soluble salts and turbidity of water. Filters of different pore size, as per requirement are used in filtration. Filters having 0.0001μ pore size are available. In reverse osmosis, when water passes through semipermeable membrane, then only water can pass through it whereas salts are being accumulated. Biological impurities can also be removed by reverse osmosis, because the pore size of semipermeable membrane is 0.0001μ which easily removes the bigger size bacteria (minimum size 0.2-0.5μ) and viruses (minimum size 0.015μ). Ion exchange methods involve use of ion exchange resins. Resin removing cation and anion are known as cation and anion exchange resins,

respectively. Sequential use of cation and anion exchange resins easily remove cations like calcium, magnesium and anions like chloride, sulphate from hard water.

(3) Biological Method : We all are familiar with boiling of water to make it germ free. This method is easy, safe and reliable, due to which pediatricians recommend to use boiled drinking water for babies younger than 1 year. Except this, the water can be made germ free by chlorination (passing of chlorine gas or by use of bleaching power), by passing of ozone gas or by use of ultraviolet radiations. Water distributed by water supply unit in villages and cities is being chlorinated to make germfree. A person, if interested, can do chlorination of drinking water at residence, school or college or public institutions. For this, tablets of chlorine or bleaching powder having 33 to 35 % concentration available in market, can be used. Either one chlorine tablet should be added in about 20 litre water or 5 g bleaching powder should be added to 1000 litre water. Use of ozone gas makes the water germfree, effectively and rapidly. Passing of ultraviolet radiations from water makes it germfree. These two methods are being used intensively in industrial units for purification of drinking water. Water available in market in pouch or bottle are purified by these methods. Today general awareness of drinking water has increased with the use of water purification devices at residence, college or public places.

7.5   Soil Pollution

Soil is a thin layer of organic and inorganic materials covering the rocks of earth. The organic part of soil, which makes upper layer of soil, is formed by decomposition of animal and plant wastes. Inorganic part is formed by

constituents of rocks produced due to physical and chemical changes from thousands of years. The productive soil is needed to fulfil the requirement of food by the people. The main reasons for pollution of soil are indiscriminate uses of fertilizers and pesticides, dumping of solid waste in soil and deforestation.

Reasons for Soil Pollution :

(1) Indiscriminate use of artificial fertilizers : Soil nutrients are useful for growth and development of plants. Plant obtains carbon, hydrogen and oxygen from air or water. Whereas other essential nutrients like nitrogen, phosphorus, potassium, calcium, magnesium, sulphur are being absorbed from soil. To remove the deficiency of nutrients in soil, farmers add artificial fertilizers. The contaminants present in these fertilizers, harm the soil. These cotaminants in fertilizers come from the raw materials used for their production. e.g., mixed fertilizer contains ammonium nitrate, phosphorus (as P_2O_5) and potassium (as K_2O), which contains trace of elements like As, Pb and Cd from rock phosphate used for their production. Due to non-degradability, these elements get accumulated in soil. Increased use of phosphate fertilizers results in such a higher concentration in soil that it becomes harmful to plants. The over use of artificial fertilizers like NPK in soil, results in reduced production of crops and vegetables in that soil. Moreover, it reduces the protein content of wheat, maize and grams grown in that soil.

(2) Indiscriminate use of Pesticides : Insects, fungi, bacteria, viruses and other animals attack on plants for their nutrients, on which we depend for our food. For this, to protect the crop, farmers use pesticides. These pesticides are being absorbed in soil and reduce its fertility. These pesticides enter into plants from soil and respectively in human body and other living beings from plants that are harmful to their health. Pesticides include insecticides, fungicides and herbicides. Insecticide like DDT (Dichloro-diphenyltrichloroethane) is banned in India and in most of the other countries because of the evidences of its harmful effect on organs of the digestive system. Sodium chlorate and sodium arsenite used as herbicides are found toxic for mammals. Mercuric compounds used in fungicides are decomposed in soil and their products are harmful. Use of methyl mercury and its compounds caused many deaths in Iraq in 1972.

(3) Dumping of Solid Wastes in Soil : Generally, the wastes from garbage, commercial, industrial and agricultural units are in the form of solid wastes. They contain kitchen wastes, paper, cardboards, plastics, glass, old construction materials, toxic or hazardous substances in considerable amount. Among these, paper and kitchen wastes are biodegradable. Recycling of paper is possible. Although plasitc, glass and old construction materials are non-biodegradable, they can be recycled. Heavy metals, toxic and hazardous substances present in industrial effluents are non-biodegradable. When solid wastes are dumped in soil, then non biodegradable wastes remain in soil for a longer period. It disturbs the structure and fertility of soil.

(4) Deforestation : More deforestation occurs due to urbanization, industrialization and over population. To satisfy their needs human beings are destroying the forests. The soil gets exposed and it causes erosion of fertile layer of soil. Such soil cannot be utilized for agriculture.

Prevention of Soil Pollution :

(1) Use of natural fertilizers (e.g., farmyard manure, compost etc.) and biofertilizers (e.g., rhizobium, azotobacters, algae etc.) should be increased instead of chemical fertilizers to increase crop yield.

(2) Biological methods should be used instead of chemical compounds to control harmful pests. Extract of Neem, Aak and Dhatura leaves can act as insecticides. Furthermore, trichoderma fungi is well known as insecticide.

(3) Conversion of wastes of paper, plastic materials and glass should be done in such a way that they can be reused. This means recycling. It can reduce the amount of solid wastes and conservation of natural sources may occur. e.g. If 1 ton wastes of paper is being reproduced, then 17 trees can be saved.

(4) Industrial effluent should be treated first by physical, chemical and biological treatments to reduce its toxicity and then it should be removed.

(5) Adoption of a policy for less cutting and more growing of trees can reduce the erosion of soil and conserve soil fertility.

7.6 Pollution from Necessary Wastes of Industries

The negative side of industrial revolution is pollution from necessary wastes of industries. Wastes produced by different industries contain different amounts of various substances. Its removal into air, water or soil ultimately proves harmful to living beings. Here, we will discuss characteristics of wastes produced by different industries.

(1) Petroleum Industry : The waste produced by such industry contains various organic and inorganic compounds, free oil, phenolic compounds, suspended solids and H_2S.

(2) Paper and Pulp Industry : The waste produced by such industry contains organic materials like dimethyl sulphide, methyl mercaptan and inorganic materials like acid, alkali and salts of heavy metals.

(3) Leather Industry : The waste produced by such industry contains alkaline substances, suspended materials, ammonium salts, sodium sulphides, salts of chromium and arsenic, sulphuric acid, detergents, enzymes and animal protein and fat.

(4) Sugar Industry : Waste water produced by such industry becomes black in colour with time due to biological activities and it smells bad due to production of H_2S gas.

(5) Electroplating and Metal Refining Industry : The waste produced by such industry contains metal ions like nickel, chromium, zinc, lead, silver, mercury etc. and toxic materials like sulphide, cyanide, hydrogen sulphide, ammonia.

(6) Detergent Industry : The waste produced by such industry contains soluble organic compounds having long chains, soluble inorganic compounds, acids and solvents.

(7) Pesticide Industry : The waste produced by such industry contains considerable amount of aromatic organic compounds and acids.

(8) Fertilizer Industry : The waste produced by such industry contains compouds of nitrogen, phosphate, fluoride and arsenic.

(9) Thermal Power Industry : The waste produced by such industry contains fly ash, inorganic compounds and heavy metals.

(10) Dairy Industry : The waste produced by such industry contains suspended materials, nitrogen, phosphorus and organic compounds.

When the industrial waste is in liquid form, then to measure the amount of organic waste in it, two types of measures (methods) are used in environmental technology.

(i) Biochemical Oxygen Demand (BOD) : Generally, the organic compounds present in polluted water are also the food for bacteria. During their biochemical reactions these bacteria convert organic compounds into simple organic compounds through degradation. For it, the amount of dissolved oxygen utilized by these bacteria is called BOD. Thus, on the basis of required amount of dissolved oxygen the amount of organic materials which can be degraded by bacteria in liquid waste, can be measured. To measure BOD, the sample of liquid waste is kept at 293 K temperature for 5 days. On the basis of difference $(DO_1\text{-}DO_5)$ between amounts of dissolved oxygen on the fifth day (DO_5) and on the first day (DO_1), the amount of dissolved oxygen used up by bacteria for degradation of organic material of waste sample can be determined. This is known as BOD for liquid waste. The unit of BOD measurement is ppm or mgL^{-1}.

(ii) Chemical Oxygen Demand (COD) : The amount of dissolved oxygen required for oxidation of all the organic materials present in liquid waste is known as COD. Thus, on the basis of required amount of dissolved oxygen, the amount of all the organic materials present in liquid waste can be determined. Thus, generally, the COD value is higher than BOD for the same liquid waste. To measure the COD, mixture the strong oxidising agents like potassium dichromate and concentrated sulphuric

acid are used. This measurement requires only 2-3 hours. The unit of COD measurement is ppm or mgL^{-1}.

7.7 Remedies for Control of Environmental Pollution

Generally, we know that the main sources of environmental pollution are household wastes, like smoke from vehicles, industrial wastes and biomedical wastes. Thus, by controlling the pollution created by such sources, the control of environmental pollution becomes easy. Let us discuss the efforts to control them.

(1) Biodegradable and non-biodegradable materials of household waste should be kept separate. Municipality or Gram Panchayat should keep different containers to collect these wastes. Some developed countries follow this system. e.g. green coloured container for the collection of biodegradable materials and yellow or red coloured container for the collection of non-biodegradable materials. Compost can be prepared from biodegradable wastes whereas the non-biodegradable substances should be recycled.

(2) To control the air pollution created by exhaust smoke of vehicles, every person should check the amount of gases present in the smoke of their vehicles and regular service of the vehicles is also necessary. For this, it is essential to obtain PUC (Pollution Under Control) certificate for each vehicle.

(3) Air pollution control devices should be arranged to control the air pollutants like suspended particles, sulphur dioxide, ammonia, chlorine, hydrogen chloride, hydrogen sulphide etc. released in the air by industries. For protection against polluted air we should use gasmask.

(4) Specific treatment should be given to industrial effluent to make it non-harmful. For it, the industry should make effluent treatment plants either individually or collectively.

(5) To make germfree, biomedical wastes should be burnt or dumped in soil based on its characteristics for its removal.

Gujarat Pollution Control Board is established in Gandhinagar to control the environmental pollution in Gujarat.

7.8   Green Chemistry

Production of materials like fertilizers, pesticides, dyes, drugs, plastics and cosmetics used by human beings has become easy due to growth of chemical industries. But the effluents of these industries, which are harmful to living beings including human beings are thrown in air, water or soil. This pollutes environment. For this, presently, scientists are trying to develop methods to produce chemical compounds which are favourable to environment (eco friendly). The chemistry developed by such efforts is known as Green Chemistry. In short, green chemistry means science for environmentally favourable chemical synthesis.

In 2005, Nobel Prize for synthesis of new chemicals based on green chemistry was awarded to French scientist Professor Yves Chauvin and two other scientists of America, Robert H. Grubbs and Richard R. Schrok. Twelve principles as mentioned below are being formulated for green chemistry on the basis of works done by Paul T. Anastas for development of green chemistry. On the basis of these principles, synthesis of new chemicals are recommended in green chemistry.

Basic Principles of Green Chemistry :

During synthesis of chemical compounds,

(1) Formation of wastes or byproducts should be prevented.

(2) Reactants should be converted completely into products that means 100 % product should be obtained.

(3) Production of hazardous chemicals should be prevented.

(4) Production of safer chemicals should be aimed.

(5) Required energy for any synthesis should be minimum.

(6) Most appropriate solvent, should be selected.

(7) Appropriate starting materials for synthesis should be selected.

(8) Use of protecting group should be avoided whenever possible.

(9) Use of catalyst should be preferred wherever possible. Presently, phase catalysts are being used.

(10) Obtained product should be biodegradable.

(11) Design of manufacturing plant should be such that the possibility of accidents during operation can be eliminated.

(12) Analytical techniques should be strengthened to control hazardous compounds.

Green Chemistry in day-to-day life :

The use of principles of green chemistry in day-to-day life is being observed.

(1) In Drycleaning of Clothes : Tetrachloroethene ($Cl_2C=CCl_2$) was used earlier as solvent for dry cleaning of clothes. It pollutes ground water and is carcinogenic. For this, today, liquefied carbon dioxide with suitable detergent is used for drycleaning instead of tetrachloroethene. Today, the use of hydrogen peroxide as bleaching agent for washing of clothes has increased which produces good results using lesser amount of water.

(2) In Bleaching of Paper : We know that paper is made up of wood. For good quality of paper it is essential to remove its lignin completely. Most of the lignin is removed during production of paper. Chlorine gas is being used for removal of remaining lignin. But chlorine gas forms dioxins by reaction with aromatic rings of lignin, which is potential carcinogenic compound. For this, as alternative of chlorine gas for bleaching of paper, hydrogen peroxide in presence of suitable catalyst is being used today which is due to the development of green chemistry.

SUMMARY

Environmental chemistry means scientific study of chemical and biochemical processes occurring in environment. Through it we can know the reasons for changes and processes occurring in environment. Solid, liquid and gaseous pollutants, polluting environment can be generally classified as rapidly degradable, slowly degradable and non-biodegradable pollutants. Pollutants which degrade rapidly are known as rapidly degradable pollutants. e.g. discarded vegetables. Pollutants which degrade slowly are known as slowly degradable pollutants. e.g. agricultural waste. Some pollutants remain for decades in their original form without degradation. They are known as non-degradable pollutants. e.g. dichlorodiphenyltrichloroethane (DDT), plastic materials, heavy metals, radioactive wastes. Troposphere and stratosphere greatly affect the biosphere of earth due to which study of pollution in these two regions is most important for study of pollution in enviornment. Gaseous pollutants - SO_x, NO_x, CO, CO_2, H_2S, O_3, hydrocarbons and particulate pollutants - dust, mist, fumes, smoke, smog etc cause pollution in troposphere. The process of warming of the earth is known as 'Greenhouse effect' or 'Global warming' and the gases actively involved in it are called 'Greenhouse effect' . Carbon dioxide, methane, ozone, chlorofluorocarbon (CFC), nitrous oxide and water vapour present in atmosphere act as greenhouse gases. Heat retaining capacity of greenhouse gases are called Global Warming Potential (GWP). The GWP based sequence of green house gases is as $CFC > N_2O > CH_4 > CO_2$. When the pH of rain water becomes lower than 5.6 then it is called acid rain. Gaseous pollutants present in troposphere are responsible for it. The acid rain in water reservoirs like rivers, ponds adversely affect fishes, microorganisms and plants, in aquatic world. Ozone layer present in stratosphere protect the living being against harmful ultraviolet radiations from space. But ODS (Ozone Depletion Substances) used by human beings deplete ozone layer. To create awareness in the whole world about the depletion of ozone layer and the remedies to protect depletion, United Nations has decided to celebrate 16th September of every year as 'Ozone Layer Protection Day' at the international level. Today, a person hesitates to use natural water directly for drinking, because soluble, insoluble, biological, physical or chemical impurities from different sources mixing with surface water or ground water which pollute the water. Due to this, institutions like WHO (World Health Organization) at world level and BIS (Bureau of Indian Standards) and ICMR (Indian Council of Medical Research) at India level have prescribed standards for quality of drinking water. Chemical, physical and biological methods are known for purification of drinking water. For soil pollution, indiscriminate use of fertilizers and pesticides, dumping of solid wastes in soil and deforestation are observed as main causes. Removal of wastes, produced from different industries in air, water or soil are ultimately harmful for living beings. To determine the amount of organic waste in liquid effluents of industries, measurements of Biochemical Oxygen Demand (BOD) and Chemical

Oxygen Demand (COD) are important. By BOD measurement, the amount of organic materials present in liquid waste, which can be degraded by bacteria can be measured. By COD measurement, the amount of all the organic materials present in liquid waste can be determined. BOD measurement requires 5 days and COD measurement requires 2-3 hours. By controlling, managing or treating the waste from households, exhausts from vehicles, industrial wastes and biomedical wastes we can control the environmental pollution. Efforts to control environmental pollution resulted in delvelopment of science for synthesis of chemicals favourable to environment, which is called green chemistry. Gujarat State Government has established the Pollution Control Board for control of environmental pollution in Gujarat.

EXERCISE

1.   **Select the proper choice from the given multiple choices :**

(1)   Which one is not a green house gas ?

(A) H_2O (B) O_2 (C) CO_2 (D) O_3

(2)   Which sequence for green house gases is truly based on GWP ?

(A) CFC > N_2O > CO_2 > CH_4 (B) CFC > CO_2 > N_2O > CH_4

(C) CFC > N_2O > CH_4 > CO_2 (D) CFC > CH_4 > N_2O > CO_2

(3)   Which gas has greater contribution in global warming ?

(A) CO_2 (B) CFC   (C) NO_2 (D) CH_4

(4)   How many molecules of ozone gas are being depleted by one molecule of CFC ?

(A) 10^3 (B) 10^4 (C) 10^5 (D) 10^6

(5)   Which method is used for purification of water ?

(A) Reverse osmosis   (B) Biochemical Oxygen Demand

(C) Chemical Oxygen Demand   (D) Use of ODS

(6)   Which statement is true from the following ?

(A) Amount of whole organic materials present in liquid waste can be determined by measurement of BOD.

(B) Amount of microbially degradable organic materials in liquid waste can be determined by measurement of COD.

(C) COD is measured by use of mixture of potassium dichromate and concentrated sulphuric acid.

(D) Five days are required for COD measurement.

(7) Presence of higher amount of which ion than its desirable limit in drinking water may cause blue baby disease ?

(A) Fluoride   (B) Nitrate   (C) Chloride   (D) Sulphate

(8) Which of the following substances is non-biodegradable ?

(A) Paper   (B) Glass

(C) Kitchen waste   (D) Rotten vegetables

(9) Generally, which industry produces fly ash as a waste ?

(A) Dairy industry   (B) Detergent industry
(C) Thermal power industry   (D) Fertilizer industry

(10) Which of the following statements is not proper to basic principle of green chemistry ?

(A) Synthesized product should be biodegradable.

(B) Production of waste materials or byproducts should be prevented.

(C) Energy required for synthesis should be minimum.

(D) Use of catalyst should be avoided as far as possible.

2.   Answer the following questions in brief :

(1) Which compound is produced by combination of carbon monoxide with haemoglobin of blood ?

(2) When do we celebrate 'Ozone Layer Protection Day' at international level ?

(3) What should be the desirable amount of total dissolved solids in drinking water as per the BIS ?

(4) Write names of two physical methods used for purification of water.

(5) Which two chemicals are being used for dry cleaning of clothes as per the principles of green chemistry ?

(6) Write full forms : ODS, GWP, BOD, COD, WHO, BIS, ICMR, PUC

(7) Define :   (1) Environmental Chemistry

(2) Analytical Chemistry

(3) Green Chemistry

(4) Acid Rain

(5) Greenhouse Gas

3.   Write answers to the following questions :

(1)   What are rapidly biodegradable pollutants, slowly biodegradable pollutants and non-biodegradable pollutants ? Write one example of each.

(2)   List the pollutants of troposphere.

(3)   Mention names of viable and non-viable particulate pollutants.

(4)   Write names of four methods used in making the water germfree.

(5)   Write two differences : BOD and COD.

4.   Answer the following questions in detail :

(1)   Mention gaseous air pollutants. Discuss any two pollutants out of those in terms of their origin and effect.

(2)   What is smog ? Explain classical and photochemical smog.

(3)   Mention reasons, effects and remedies for global warming.

(4)   Mention reasons for the acid rain and discuss its effect.

(5)   Mention reasons, effects and remedies for depletion of ozone layer.

(6)   Describe water pollutants with their sources.

(7)   Mention standards prescribed by BIS for quality of drinking water.

(8)   Discuss methods for purification of drinking water.

(9)   Discuss main reasons for pollution of soil in detail.

(10)   Describe main remedies for prevention of soil pollution.

(11)   Mention characteristics of the wastes produced by petroleum and leather industries.

(12)   Which remedies should be used for the control of environmental pollution.

(13)   Mention the basic principles of green chemistry.

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