M.Sc. [Chemistry]
I - Semester
344 11

INORGANIC CHEMISTRY - I
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INTRODUCTION

Inorganic chemistry is the study of the structure, properties and reactions of all chemical elements and compounds except for organic compounds (hydrocarbons and their derivatives). It includes the study of the synthesis, reactions, structures and properties of compounds of the elements. Inorganic chemistry is fundamental to many practical technologies including catalysis and materials (structural, electronic, magnetic, etc.), energy conversion and storage, and electronics. Inorganic compounds are also found in biological systems where they are essential to life processes. Significant classes of inorganic compounds are the oxides, the carbonates, the sulfates, and the halides. Many inorganic compounds are characterized by high melting points. Inorganic salts typically are poor conductors in the solid state. Other important features include their high melting point and ease of crystallization.

Descriptive inorganic chemistry focuses on the classification of compounds based on their properties. Partly the classification focuses on the position in the periodic table of the heaviest element, the element with the highest atomic weight in the compound, partly by grouping compounds by their structural similarities. Fundamentally, the inorganic chemistry deals with the synthesis and behaviour of inorganic and organometallic compounds. It has applications in every aspect of the chemical industry, including catalysis, materials science, pigments, surfactants, coatings, medications, fuels, and agriculture.

This book, *Inorganic Chemistry-I*, is divided into four blocks that are further divided into fourteen units which will help to understand the basic concepts of inorganic chemistry, such as chemical periodicity, ionic radii, ionization potential, electron affinity, electro-negativity, hybridization, molecular orbitals, electronic configuration, VSEPR theory, structure and bonding in fluorine and oxygen compounds of xenon, bonding in simple triatomic molecules/ions, molecular orbital theory of covalent bonding (bond length, bond order, bond angle, bond energy and magnetism), symmetry and overlap of atomic and molecular orbitals, intermolecular forces and lattice energy, properties of ionic compounds (hardness and electrical conductivity), energetic of dissolution of ionic compounds in polar solvents, Bronsted concept of acids and bases, relative strength in aqueous medium, Lewis concept of acids and bases, relative order of acid strength of boron halides and basic strength of hydrides, HSBAB (Hard and Soft Acid and Bases) principle, pH and buffer solutions, polymers, isopoly and heteropoly acids, Anderson structure, Keggin structure, silicates, three dimensional silicates, silicate with frame work structures, crystal structure of solids, classification of ionic structures, defects in crystal, Schottky and Frenkel defects, electrical and magnetic properties of solids, conductor, semiconductors and insulators, structure of graphite and diamond.

The book follows the self-instruction mode or the SIM format wherein each unit begins with an ‘Introduction’ to the topic followed by an outline of the ‘Objectives’. The content is presented in a simple, organized and comprehensive form interspersed with ‘Check Your Progress’ questions and answers for better understanding of the topics covered. A list of ‘Key Words’ along with a ‘Summary’ and a set of ‘Self Assessment Questions and Exercises’ is provided at the end of the each unit for effective recapitulation.
BLOCK - 1
BASIC CONCEPTS IN INORGANIC CHEMISTRY

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1.1 Objectives
1.2 Historical Background of Element Classification
   1.2.1 Long Form of Periodic Table
1.3 Periodic Properties / Chemical Periodicity
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1.0 INTRODUCTION

The periodic classification of elements is one of the most important classification in science since it facilitate the study of the properties of various elements and compounds. After numerous attempts the scientists were ultimately successful in arranging the elements in such a way so that similar elements were grouped together and different elements were separated. The arrangement of elements in such a way that their similar elements fall within same vertical group and the dissimilar elements are separated is known as classification of elements. The classification of elements led to the formation of periodic table. Periodic table thus may be defined as, the table giving the arrangement of all the known elements according to their properties so that similar elements fall within the same vertical column and dissimilar elements are separated. In this unit, you will learn about the chemical properties of elements and concept of hybridization historical background of elements classification, periodic properties, chemical periodicity, etc., in detail.
1.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the classification of elements
- Explain the chemical properties of elements like atomic radii, ionic radii etc.
- Explain the concept of hybridization
- Understand and draw the shapes of polyatomic molecules

1.2 HISTORICAL BACKGROUND OF ELEMENT CLASSIFICATION

All the elements are systematically classified in the periodic table. The periodic table, or periodic table of elements, is a tabular arrangement of the chemical elements, arranged by atomic number, electron configuration, and recurring chemical properties, whose structure shows periodic trends. The seven rows of the table, called periods, generally have metals on the left and non-metals on the right. The columns, called groups, contain elements with similar chemical behaviour. Six groups have accepted names as well as assigned numbers. For example, group 17 elements are the halogens; and group 18 are the noble gases. Also displayed are four simple rectangular areas or blocks associated with the filling of different atomic orbitals.

The organization of the periodic table can be used to derive relationships between the various element properties, and also to predict chemical properties and behaviour of undiscovered or newly synthesized elements. Russian chemist Dmitri Mendeleev published the first recognizable periodic table in 1869, developed mainly to illustrate periodic trends of the then-known elements. He also predicted some properties of unidentified elements that were expected to fill gaps within the table. Most of his forecasts proved to be correct. Mendeleev’s idea has been slowly expanded and refined with the discovery or synthesis of further new elements and the development of new theoretical models to explain chemical behaviour. The modern periodic table now provides a useful framework for analysing chemical reactions, and continues to be widely used in chemistry, nuclear physics and other sciences.

Praet (1815) suggested that the atoms of elements are the simple multiples of hydrogen atom but the hypothesis soon was discarded. Dabereiner (1829) gave the law of triad but it could not accommodate all the elements. De Chancourtois (1863), plotted the values of the atomic weights in the increasing order of a vertical scale, along the spiral time and gave the idea of periodic arrangement of elements. Newland (1864), gave the Law of Octaves according to which the eight element startup from a given one is a kind of repetition of the first, like the eight note of an octave in music.
Lothar Meyer (1869) plotted a graph between atomic volumes of different elements against their atomic weights and found that similar elements occupied similar position on the curve.

Mendeleev (1869) drew up a comprehensive system on classification based on the atomic, weights of elements. They gave the periodic law, ‘the physical and chemical properties of elements are the periodic functions of their atomic weights’. He was able to arrange all the elements in the form of a table which is known as Mendeleev’s Periodic Table. In this periodic table the elements are arranged in nine vertical columns known as Groups and in seven horizontal lines known as Periods.

Moseley (1914) showed that the properties of elements are largely defined by their atomic numbers rather than the atomic weights. Hence atomic number is the fundamental property of an atom. This formulate the modern periodic law, viz., ‘The physical and chemical properties of elements are the periodic functions of their atomic numbers.’

It means that if elements are arranged in order of their inverse atomic numbers, the elements with similar properties recur after regular intervals. Many new forms of periodic table have been proposed in recent times with modern periodic law as the guiding principle, but the general plan at the table remained the same as proposed by Mendeleev. The most commonly known periodic table is the long form of periodic table.

1.2.1 Long Form of Periodic Table

The modern periodic law states that physical and chemical properties of the elements are the periodic function of the atomic numbers. The periodic table is a chart that shows how chemical elements are related to one another. The various elements with the similar properties repeat after certain regular intervals. This repetition occurs when the elements are arranged in order of their increasing atomic numbers.

The long form of the periodic table is based upon the electronic configuration of the elements. It is the present form or the modern periodic table of elements. The modern periodic table of elements consists of 18 vertical columns and 7 horizontal rows. We obtain these by arranging the elements in order of their increasing atomic numbers.

The scientists have made this arrangement in a very peculiar way. It keeps all the elements with similar electronic configuration under each other in the same vertical column. Groups are these vertical columns. On the other hand, periods are the horizontal rows.

Modern Periodic Table of Elements: D and F Block Elements

Groups in the Periodic Table

- The 18 vertical columns in the modern or long form of the periodic table are the groups.
Chemical Periodicity

- Each of the group consists of a number of elements having the same electronic configuration of the outermost shell.
- These groups are numbered as from 1 to 18.

NOTES

Periods in the Periodic Table

- The long form of periodic table consists of 7 periods.
- These are numbered as 1, 2, 3, 4, 5, 6 and 7 from top to bottom.
- The first period consists of only two elements – Hydrogen and Helium.
- The 2nd and 3rd period consists of 8 elements each. On the other hand, the 4th and 5th consists of 18 elements each while the sixth period consists of 32 elements.
- The 7th period is incomplete and like the 6th period would have a maximum of 32 electrons.
- In the long form of the periodic table, a separate panel at the bottom consists of 14 elements of the sixth period called the Lanthanoids and 14 elements of the seventh period called the Actinoids.

The Long or 32-Column Table

The modern periodic table is sometimes expanded into its long or 32-column form by reinstating the footnoted f-block elements into their natural position between the s- and d-blocks. Unlike the 18-column form this arrangement results in ‘no interruptions in the sequence of increasing atomic numbers’. The relationship of the f-block to the other blocks of the periodic table also becomes easier to understand. Following is the periodic table in 32-column format.

Blocks

On the basis of valence shell electronic configuration, periodic table is divided into four distinct blocks of elements.

1. s-block
2. p-block
3. d-block
4. f-block

s-Block Elements

All the elements in which last electron enters “ns” orbital are known as s-block elements. Elements of Group I-A and II-A belong to s-block. Their valence shell electronic is ns\(^1\) to ns\(^2\). All the elements of s-block are very reactive and electropositive in nature. s-block elements are good reducing agents. They form ionic compounds. They are all metals and solid. They are low density metals.
For example:

Li (z=3) 1s\(^2\), 2s\(^1\)
Na (z=11) 1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^1\)
Be (z=4) 1s\(^2\), 2s\(^2\)

**p-Block Elements**

The elements in which valence electrons enter p-orbital and this orbital is progressively filled are called p-block elements. Their valence shell electronic configuration is from ns\(^2\), np\(^1\) to ns\(^2\), np\(^5\). p-block consists of the elements of group III-A to VIII-A (zero-group). They include metals, nonmetals and metalloids. There are 30 elements in six sub-groups of p-block.

**d-Block Elements**

The elements in which last electron enters (n-1) d-orbital are called d-block elements or outer transition elements. Valence shell electronic configuration of these elements is ns\(^2\), (n-1)d\(^1\), (n-2) f\(^1\). d-block elements constitute 2 series of elements, Lanthanides and Actinides.

**Lanthanides:** Elements from Cerium (Ce; Z=58) to Lutetium (Lu; Z=71) in the periodic table are known as ‘Lanthanides’. It is a series of 14 elements occurring in the 6th period. They are all silvery and fairly reactive metals. Most of their compounds contain M\(^{3+}\) ions. Some other lanthanides are also form M\(^{4+}\) complex fluorides. They are also known as rare earth metals.

<table>
<thead>
<tr>
<th>Lanthanide Series</th>
<th>La 58</th>
<th>Ce 58</th>
<th>Pr 59</th>
<th>Nd 60</th>
<th>Pm 61</th>
<th>Sm 62</th>
<th>Eu 63</th>
<th>Gd 64</th>
<th>Tb 65</th>
<th>Dy 66</th>
<th>Ho 67</th>
<th>Er 68</th>
<th>Tm 69</th>
<th>Yb 70</th>
<th>Lu 71</th>
</tr>
</thead>
</table>

**Actinides:** Elements from Thorium (Th; Z=90) to Lawrencium (Lw; Z=103) in the periodic table are known as ‘Actinides’. It is a series of 14 elements occurring in the 7th period. All actinides are radioactive elements. Most of them have very short half-life. They are fairly reactive metals. Most of their compounds contain M\(^{3+}\) ions. Among the heavier elements M\(^{2+}\) state becomes stable. They are also known as artificial elements as they do not occur naturally. They were discovered as products formed during nuclear reactions.

| Actinide Series | Th 90 | Pa 91 | U 92 | Np 93 | Pu 94 | Am 95 | Cm 96 | Bk 97 | Cf 98 | Es 99 | Fm 100 | Md 101 | No 102 | Lr 103 |
1.3 PERIODIC PROPERTIES/ CHEMICAL PERIODICITY

NOTES

The word ‘periodic’ means that when elements are arranged in the order of their atomic numbers, there appears a periodicity, i.e., repetition not only in their chemical properties but also in the physical properties.

Cause of Periodicity: From atomic structure we know that atom has a small positively charged nucleus with electrons distended around it. The atomic nucleus does not undergo any change during the ordinary chemical reactions. Thus, it may be assumed that the physical and chemical properties of the elements must be related to the arrangement of electrons in their atoms. Since the electrons present in the inner shells do not take part in chemical contribution, so the electrons of outer most shells are responsible for the properties of atoms. Thus, if the outer most arrangement of electrons in atoms in same, their properties will also be similar.

Thus it can be concluded that the periodic repetitions of properties is due to the reoccurrence of similar valence shell configurations after certain regular intervals.

The use of long form of periodic table is more reasonable for the study of periodic properties of the elements. This can be illustrated by studying the following properties.

1.3.1 Atomic Radii

The term atomic radius for an atom is the distance from the centre of the nucleus to the outer shell of the atomic particle. It is impossible to isolate an individual atom and determine its radius because its size or radius is affected by the association with other particles.

According to L.A. Campbell, the size of atoms (atomic radii) in a compound depend upon the following factors.

(i) Multiplicity of the bond, i.e., whether the bond is single, double or triple;
(ii) The extent of covalent bonding;
(iii) The oxidation numbers of the atoms which indicate the number of electrons involved in the bonding;
(iv) The number of neighbours with which the particle under consideration is associated;
(v) The repulsive forces between atoms not directly bonded to each other.

It is obvious that any of the combinations of above factors may produce significant size variations. The atomic size (or radius) of particular element may differ from one substance to another.

Types of Atomic Radii

Following are the different types of atomic radii.
1. Metallic Radii: The metallic radius may be defined as one-half of the distance between atoms of a metal in the metallic close packed crystal lattice in which the metal exhibits a co-ordination number of twelve.

It is generally observed that metallic radii are about 10 to 15% higher than the single covalent bound radii. For example the inter nuclear distance between two adjacent sodium atoms in a metallic crystal of sodium metal is 3.72 Å, so that the metallic or atomic radius of sodium is 3.72/2 or 1.86 Å.

Assuming the atoms to be spheres, knowing the density of the metal, the nature of unit cell, i.e. the arrangement of other atoms around the central atom, the radius of an atom in a metallic crystal can be calculated.

Metallic radii of s-and p-block elements have been given in Table 1.1. These values have been found to be true for the coordination number of 12.

<table>
<thead>
<tr>
<th>s-Block Elements</th>
<th>p-Block Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>IA</td>
<td>IIA</td>
</tr>
<tr>
<td>H</td>
<td>1.55</td>
</tr>
<tr>
<td>Na</td>
<td>1.90</td>
</tr>
<tr>
<td>K</td>
<td>2.35</td>
</tr>
<tr>
<td>Rb</td>
<td>2.48</td>
</tr>
<tr>
<td>Cs</td>
<td>2.67</td>
</tr>
</tbody>
</table>

As the metallic bond which controls the proximity of the metal atoms to one another in the metallic crystal is not a localized bond between the bonded atoms, as is covalent bond, the bonded metal atoms in the metallic crystal lattice would not be drawn close to each other as they are in a covalent bond.

The metallic radii have been smaller than the van der Waal’s radii, because the bonding forces in the metallic crystal lattice have been much stronger than the van der Waal’s force.

2. Van der Waal’s Radii or Collision Radii: It is essentially the distance between two non-bonded atoms of two adjacent molecules. For example, the van der Waal’s radius of hydrogen is 1.2 Å nuclei of two hydrogen atoms cannot approach nearer than 2 × 1.2 or 2.4 Å from each other without overlapping of their electron charge clouds to form a bond. For example, in solid chlorine, each atom is found to have one close neighbor at a distance of 1.98 Å and another at distance of 3.60 Å.

Thus, the covalent radius of chlorine atom is 0.99 Å whereas the van der Waal’s radius is 1.80 Å. Some special features of the van der Waal’s radius are:
(i) Generally, covalent radius is smaller than van der Waal’s radius because in the formation of a chemical bond, the atoms have to come close to each other. This can be realized from the following table.

(ii) The values of van der Waal’s radii are obtained from X-ray studies of various elements in the solid state.

<table>
<thead>
<tr>
<th>Element</th>
<th>H</th>
<th>N</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals radius Å</td>
<td>1.2</td>
<td>1.5</td>
<td>1.80</td>
<td>1.90</td>
<td>2.15</td>
</tr>
<tr>
<td>Covalent radius Å</td>
<td>0.3</td>
<td>0.70</td>
<td>0.99</td>
<td>1.14</td>
<td>1.33</td>
</tr>
</tbody>
</table>

3. Covalent Radii. The covalent radius of an atom is equal to half the internuclear distance between two identical atoms that are joined by a covalent bond. The covalent bond should essentially be a single covalent bond. If it is double or triple bond, the value of covalent radius changes. For example, the single bond distance between carbon to carbon (interatomic distance) is 1.54 Å. Thus, the covalent radius of carbon is 0.77 (one half of the C–C bond distance). Similarly, the single bond distance between atoms in pure silicon is 2.34 Å and the radius of silicon is therefore 1.17 Å.

In order to calculate the covalent radius of an atom in a heteronuclear diatomic molecule, the substitution method is used if the internuclear distance between two similar atoms is known, i.e.,

\[ A - B = r_a + r_b \]  

...(1.1)

where \( A - B \) is the internuclear distance, and \( r_a \) and \( r_b \) are the covalent radii of two atoms \( A \) and \( B \) respectively. For Example,

\[
\begin{align*}
I - Cl & = A - B = 2.32 \text{ Å} \\
\text{Cl} & = B = 0.99 \text{ Å} \\
\text{r}_I & = A = ?
\end{align*}
\]

Making these substitutions in equation (1.1), we get

\[ 2.32 = r_I + 0.99 \text{ Å} \quad \text{or} \quad r_I = 2.32 - 0.99 = 1.33 \text{ Å} \]

This value is in good agreement with the experimental value of 1.35 Å for I–Cl.

Very often there is considerable deviation for the expected values due to difference in electronegativities of two dissimilar atoms. Schomaker and Stevson have proposed the following relation to compensate this factor.

\[ A - B = r_a + r_b - 0.09 (X_a - X_b) \]  

...(1.2)

where \( r_a \) and \( r_b \) are the covalent radii of the atom \( A \) and \( B \), and \( X_a \) and \( X_b \) their respective electronegativities.

The correction given by Equation (1.2) gives better agreement between the observed and calculated values.

In case of some bonds (for example, N – C bond, Si – C bond), the discrepancy between experimental and covalent radius has been greatly reduced.
by the application of Equation (1, 2). However, in case of some bonds (C – Cl bond) the discrepancy increases. In order to calculate the covalent radii of such atoms, Pauling used the following equation:

\[ A - B = r_A + r_B - C(x_A - x_B) \]

where C is called the Schomaker and Stevenson coefficient and has different values in Å for atoms A and B as shown below:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Atoms</th>
<th>Value of C in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>All bonds involving one atom or two atoms of second period (B, C, N, O and F)</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>Bonds between Si, P or S and a more electronegative atom, but not of the first period element</td>
<td>0.06</td>
</tr>
<tr>
<td>3</td>
<td>Bonds between Ge, As or Se and a more electronegative element, but of the first period element</td>
<td>0.04</td>
</tr>
<tr>
<td>4</td>
<td>Bonds of Sn, Pb and Te with a more electronegative atom but not with one of the first two period elements</td>
<td>0.025</td>
</tr>
</tbody>
</table>

**Types of Covalent Radii:** Along with single covalent radii (as discussed above), there are double and triple covalent radii which involve double and triple bonds respectively. The covalent radii involving double or triple bonds are known as **multiple covalent bond radii.**

The multiple bond radius of an atom is equal to half the internuclear distance between the identical atoms that are joined by a double or triple bond. The multiple bond radii of some non-metallic elements are given in the following table:

<table>
<thead>
<tr>
<th>Multiple Bond Radius</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double Bond Radius</td>
<td>0.76</td>
<td>0.67</td>
<td>0.60</td>
<td>0.57</td>
<td>0.64</td>
</tr>
<tr>
<td>Triple Bond Radius</td>
<td>0.68</td>
<td>0.60</td>
<td>0.65</td>
<td>0.56(O²⁻)</td>
<td>–</td>
</tr>
</tbody>
</table>

**Method of Determining Covalent Radii:** Interatomic distances in free elements and in covalent molecules can be determined by the methods of X-ray, electrons and neutron diffraction and spectroscopy. For calculating the covalent radii from these interatomic distances, it is assumed that an atom behaves as an effective sphere which is in contact with other atoms in the solid state. Thus, interatomic distances between such atoms in the sum of the atomic radii of the two touching atoms.

**Variation of Atomic Radii in the Periodic Table:** The size of radius of an atom is an important physical property of the elements which is a periodic function of the atomic number. In the long form of the periodic table, the elements show periodic regularities in relation with atomic size.

(i) **Along the Period:** As we move from left to right in a period, the atomic radii or sizes of elements decrease. Thus, in any period alkalali metal is largest and the halogen is smallest atom. This is because as the atomic number
increases across a period, the nuclear charge increases and the electrons are attracted more and more strongly towards the nucleus, i.e., electrons lie closer and closer to the nucleus and hence the atomic size or radii decreases as we move from left to right across a period. This can be seen from the following table.

(ii) Down the Group: The size of the atoms increases on descending a group in the periodic table. In group IA atomic size or radius increases steadily from lithium to cesium. As we move down the group, the number of valence electrons in the outermost shell remains the same but the number of shells increases with atomic number. This causes in increase in size or radii as the atomic number increases down a group.

As we go down in a group the nuclear charge also increases. Because of this electrons are attracted more and more towards the nucleus and the shells become smaller and smaller. The effect however, is much smaller as compared to the effect on the size of the atom because of addition of new shells which cause increase in the atomic radii or sizes. The atomic radii or sizes, therefore, gradually increase as we move down a group.

In order to understand the change in atomic radii of the atoms in the same group, i.e. alkali metals. The following table may be considered.

<table>
<thead>
<tr>
<th>Alkali Metal</th>
<th>Atomic Number</th>
<th>Atomic Radius, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>3</td>
<td>1.23</td>
</tr>
<tr>
<td>Na</td>
<td>11</td>
<td>1.54</td>
</tr>
<tr>
<td>K</td>
<td>19</td>
<td>2.03</td>
</tr>
<tr>
<td>Rb</td>
<td>37</td>
<td>2.16</td>
</tr>
<tr>
<td>Cs</td>
<td>55</td>
<td>2.35</td>
</tr>
</tbody>
</table>

1.3.2 Ionic Radii

Ions are formed when the natural atoms lose as gain electrons. A positive ion or cation is formed by the loss of one or more electrons by the natural atom whereas a negative ion or anion is formed by the gain of one or more electrons by the atom. The term ionic radii refers to the size of the ions in the ionic crystals. Ionic radius thus may be defined as “the effective distance from the nucleus of the ion to the point upto which it has an influence in the ionic bond.” The values of ionic radii are very small and are generally expressed in Angstrom units.

Determination of Ionic Radii: The problem of determining ionic radii is very much different from that of obtaining covalent radii. Since like atoms do not form ionic bonds with each other, the measured distances between nuclei held by ionic
bonds cannot be halved to give the desired ionic radii. The actual internuclear distance does not give a value for an ionic radius until the ionic radius is obtained from some other method. Different methods have been used in order to fix the absolute value of the ionic radius of an ion. Pauling’s method is the most widely accepted method.

(a) Lande’s Method: Lande (1920) determined the interionic distance \( \text{Li}^+ - \text{Br}^- \) in the lithium bromide. The lithium ion is so small ion is so small that he was able to assume that is this compound the bromide ions are close-packed and the lithium ions are accommodate in the octahedral holes without disturbing the close–packing (Figure 1.1). The internuclear distance \( d \) in the diagram was determined by X-ray analysis. It can be seen from the diagram that \( B_j \). The radius of bromide ion is equal to i.e.

\[
\frac{1}{2} B_j = \frac{1}{\sqrt{2}} d \quad \text{(1.3)}
\]

(b) Bragg’s Method: Bragg used an arrangement similar to that of Lande, but he applied it to certain distances in which \( \text{O}^2^- \) ions are close packed and small silicon ions are in the tetrahedral holes. He used X ray analysis to ascertain the Si – O distance.

The radius of the \( \text{O}^2^- \) ion is equal to \( \frac{1}{2} \sqrt{2} d \).

(c) Pauling’s Method: The Pauling’s method has been utilized for calculating ionic radii or such ionic crystals which have isoelectronic ions. This method is based on the following assumptions.

Internuclear distance = Ionic radius of cation + Ionic radius of anion

\[
d = r_c^+ + r_a^- \quad \text{(1.4)}
\]

Or

where \( r_c^+ \) and \( r_a^- \) are the ionic radii of cation \( \text{c}^+ \) and anion \( a^- \), respectively.

(ii) For a noble gas configuration, the radius of an ion is inversely proportional to the effective nuclear charge, \( Z_{eff} \), i.e.,
Chemical Periodicity

\[ r_{\text{ion}} \propto \frac{1}{Z_{\text{eff}}} \] ... (1.5)

**NOTES**

The effective nuclear charge \( Z_{\text{eff}} \) is equal to the actual nuclear charge \( Z_{\text{a}} \) minus the screening constant \( S \) of the other electrons present in the ion. Therefore, Equation (1.5) becomes as

\[ r_{\text{ion}} \propto \frac{1}{Z_{\text{a}} - S} \]

\[ r_{\text{ion}} = C \frac{1}{Z_{\text{a}} - S} \] ... (1.6)

Or, where \( C \) is the proportionally constant depending only upon the principal quantum number of the outermost electrons. Hence, once the values of proportionally constant and screening constant are known, it is possible to evaluate the radius for any isoelectronic ion.

Applying Equation (1.6) to cation and anion, we get

\[ r_{+} = \frac{C}{Z_{+}^{\text{eff}} - S_{+}^{\text{eff}}} = \frac{C}{\left( Z_{\text{eff}} \right)_{+}} \] ... (1.7)

\[ r_{-} = \frac{C}{Z_{-}^{\text{eff}} - S_{-}^{\text{eff}}} = \frac{C}{\left( Z_{\text{eff}} \right)_{-}} \] ... (1.8)

Dividing Equations (1.7) by (1.8), we get

\[ \frac{r_{+}}{r_{-}} = \frac{Z_{\text{+}}^{\text{eff}} - S_{\text{+}}^{\text{eff}}}{Z_{\text{-}}^{\text{eff}} - S_{\text{-}}^{\text{eff}}} = \left( \frac{Z_{\text{eff}}}{Z_{\text{eff}}} \right) \] ... (1.9)

From the Equation (1.9) it follows that the ionic radii of the isoelectronic ions \( + \) and \( - \) are inversely proportional to the effective nuclear charge \( Z_{\text{eff}} \) acting on the ion.

**Illustration:** Let us illustrate the Pauling’s method by calculating the radii for \( \text{Na}^{+} \) and \( \text{F}^{-} \) ions. We know that the internuclear distance is sodium fluoride is 2.31 Å, i.e.,

\[ r_{\text{Na}^{+}} + r_{\text{F}^{-}} = 2.31 \text{ Å} \] ... (1.10)

Also sodium and fluoride ions both have a neon configuration. \( 1s^{2}2s^{2}2p^{6} \) for which the Screening constant is found to be \([2 \times 0.85 + 8 \times 0.35] \) or 4.5 (Using Slater’s rules). From this value the effective nuclear charge for \( \text{Na}^{+} \) ion will be 11
− 4.5 or 6.5, while that of F− ion will be 9 − 4.5 = 4.5. Substituting these values in Equations (1.7) and (1.8), we get

\[ r_{Na}^+ = \frac{C}{6.5} \]  

\[ r_{F}^- = \frac{C}{4.5} \]  

...(1.11)

By adding Equations (1.11) and (1.12), we get

\[ r_{Na}^+ + r_{F}^- = \frac{C}{6.5} + \frac{C}{4.5} \]

or \(2.31 = \frac{C}{6.5} + \frac{C}{4.5}\) [Using Equation (1.10)]  

...(1.13)

Substituting Equation (1.13) in Equation (1.11), we get

\[ r_{Na}^+ + r_{F}^- = r_{Na}^+ = \frac{6.41}{6.5} = 0.95\,\text{Å} \]  

...(1.14)

Similarly, substituting Equation (1.14) in Equation (1.12), we get

\[ r_{Na}^+ = \frac{6.41}{4.5} = 1.36\,\text{Å} \]

After obtaining the ionic radius of Na+ and F−, the other values were then readily obtained from measured internuclear distances. These values have been summarized in Table 1.2.

**Calculation of Screening Constant:** Screening constant \(S\) is known as the difference between the true nuclear charge and the charge actually experienced.

\[ S = Z − Z^* \]

where \(Z^*\) is the effective nuclear charge and \(Z\) is the actual nuclear charge and \(S\) is the screening constant.

### Table 1.2 Internuclear Distance

<table>
<thead>
<tr>
<th>II Row</th>
<th>III Row</th>
<th>IV Row</th>
<th>VII Group</th>
<th>VT Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Be</td>
<td>Na+</td>
<td>Ca2+</td>
<td>Mg2+</td>
</tr>
<tr>
<td>0.60</td>
<td>0.31</td>
<td>0.95</td>
<td>0.99</td>
<td>0.65</td>
</tr>
<tr>
<td>K+</td>
<td>Ca2+</td>
<td>F−</td>
<td>Cl−</td>
<td>Br−</td>
</tr>
<tr>
<td>1.53</td>
<td>1.36</td>
<td>1.06</td>
<td>1.31</td>
<td>1.05</td>
</tr>
</tbody>
</table>

---

**Chemical Periodicity**

**NOTES**

---

**Self-Instructional Material**

13
Chemical Periodicity

Screening constant is a measure of the extent to which the other electrons in an atom are able to screen the nucleus from the chosen electron. The expression for energy of an electron becomes as

\[ E = -\frac{2\pi^2 me^4}{n^2 \hbar^2} \]

J.C. Slater proposed a set of approximate orbitals, called Slater’s orbitals in 1930 using the concept of screening constant. In Slater’s orbitals, the angular distributions are identical to the exact hydrogen orbitals, but the radial distribution is changed. The pattern of the orbitals is the same:

1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, and so on. The radial part of each orbital has the following form which is very similar to, but a little simpler than the hydrogen orbitals; the part of the wave function is equal to,

\[ \rho = (4\pi^2 mZe^2/h^2)^{1/2}(Z-S\rho)^{n^*}\]

Here \( n^* \) is the effective principal quantum number.

According to Slater, the screening constant is estimated by summing the following contributions;

(a) Any orbital group outside the one considered will have no contribution towards \( S \).
(b) \( n^* \) is assigned a value according to real quantum number \( n \) for the orbital being considered.

\[
\begin{align*}
  n & = 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \\
n^* & = 1 \quad 2 \quad 3.7 \quad 4.0 \quad 4.2
\end{align*}
\]

(c) In order to determine \( S \), the electrons are divided into the following groups from the inside of the atom to the outside

1s : 2s - 2p : 3s, 3p ; 3d ; 4s - 4p; 4d - 4f; 5s - 5p; 5d - 5f; 6s - 6d

(d) The screening constant for an s or p electron is made up of the following contributions.

(i) 0.35 for each additional electron in the same group (except 0.30 in the 2s group in He).
(ii) 0.85 for each electron in the \( (n - 1) \) group.
(iii) 1.00 for each electron still closer, i.e. in \( (n - 2) \) group or one still nearer to the nucleus.

(e) The screening constant for a d – or f – electrons is made up of the following contributions:
(i) 0.356 for each electron in the shell considered.
(ii) 1.0 for each other electron including those in the next inner shell.

**Factors Influencing the Magnitude of Ionic Radii**

The important factors influencing the magnitude of ionic radii are:

(i) **Coordination Number** - With the increase of coordination number, the inter–ionic distance and hence the ionic radius also increases, for example the radius of Cl ion in CsCl crystal (8:8 coordination) is somewhat higher than that of Cl in NaCl crystal (6:6 co-ordination). The reason is that CsCl crystal each ion is surrounded by a greater number of ions as compared with NaCl crystal and this results in less attraction between different ions of CsCl crystal and consequently greater is the radius of Cl ion.

In case of three common structures of AB type ionic crystals (e.g. ZnS, NaCl and CsCl), Nacl coordination number) and ZnS (4:4 coordination number) are expressed with respect to those in NaCl. Thus, if the radii of NaCl are taken equal to 1, relative radii of ZnS are found to be 0.95 (i.e. 5% lower than that in NaCl) and those in CsCl are 1.03 (8.3% higher). This is shown below:

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>ZnS</th>
<th>NaCl</th>
<th>CsCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordination Numbers</td>
<td>4:4</td>
<td>6:6</td>
<td>8:8</td>
</tr>
<tr>
<td>Relative Radii</td>
<td>0.95</td>
<td>1.00</td>
<td>0.03</td>
</tr>
</tbody>
</table>

(ii) **Radius Ratio** \( (R) \). The radius ratio \( R \), which is given by:

\[
R = \frac{r^+}{r^-}
\]

also influences the magnitude of ionic radii. As the value of \( R \), decreases towards limited value for an ion-anion constant. The repulsion between anions will progressively increase and thus tend to distend the structure to increase the apparent radii of the component ions.

(iii) **Covalent Character in the Ionic Bond** – Covalent character in the ionic bond existing between the cation and anion forming the ionic crystal decreases the measured inter–ionic distance and hence the ionic radius is decreased.

**Periodic Variations of Atomic and Ionic Radii**: Atomic or ionic radius has been regarded as a periodic function of the atomic number i.e., it changes with the atomic number in the periodic table as shown below:

(a) **In a Period** – Atomic and ionic radii both decrease from left to right across a period in the periodic table when we consider only normal elements, for example in the element in 2nd period the covalent radii decrease as we move from Li to F as shown below:
**Chemical Periodicity**

**Elements of 2nd Period:**  Li  Be  B  C  N  O  F  
**Covalent Radii (Å):**  1.23  0.90  0.82  0.77  0.75  0.73  0.72  
**Values Decreasing →**

**NOTES**

Thus in any period the alkali metals (that are present at the extreme left of the periodic table) have the largest size while the halogens (that are present at the extreme right, excluding the zero group elements) have the smallest size.

**Explanation:** It is known that as we proceed from left to right in a period, the electrons are added to the orbitals of the same main energy level. Addition of differentiating electrons to the same main energy level puts the electrons, on the average, no farther from the nucleus and hence cannot add to the size. But with the addition of each electron, the nuclear charge (i.e. atomic number) increases by one. The increased nuclear charge attracts the electrons more strongly close to the nucleus and thus decrease the size of the atoms.

(b) **In a Group:** On moving down a group of regular elements both atomic and ionic radii increase with increasing atomic number, for example in the elements of IIA group both covalent and ionic radii of $M^{2+}$ ions increase when we pass from Be to Ba.

**Elements of IIA Group:**  Be  Mg  Ca  Sr  Ba  
**Covalent Radii (Å):**  0.90  1.36  1.74  191  1.98  
**Ionic Radii of $M^{2+}$ Cations (Å):**  0.31  0.65  0.99  1.13  1.35  
**Values Decreasing →**

**Explanation:** When we proceed from top to bottom in a group, the following two opposite forces act simultaneously. On proceeding downwards in a group the electrons are added to higher main energy levels which are, on the average farther from the nucleus. This effect depresses the electrostatic attraction between the nucleus and the valence – shell electrons and this decreased electrons.

### 1.3.3 Ionization Potential or Ionization Energy

The electrons in an atom are attached by the positively charged nucleus. In order to remove the electron from an atom, energy has to be supplied to it to overcome the attractive force.

The voltage required to remove most loosely bound electron, from the isolated neutral atom to produce an ion is called ionization potential and is expressed in electron volts (eV). The energy required for this purpose is known as ionization energy and is represented in kilojoules per gram atom (kJ mol$^{-1}$). This may be represented as:

$$A(g) + \text{Energy} \rightarrow A^+(g) + e^-$$
The values of ionization potential of s- and p- block elements are given in Table 1.3.

Table 1.3 Ionization Potentials (in eV) of s- and p- Block Elements

<table>
<thead>
<tr>
<th>IA</th>
<th>IIA</th>
<th>IIIA</th>
<th>IVA</th>
<th>VA</th>
<th>VIA</th>
<th>VIIA</th>
<th>Zero</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>13.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>He</td>
</tr>
<tr>
<td>Li</td>
<td>5.4</td>
<td>Be</td>
<td>Be</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.3</td>
<td>11.2</td>
<td>14.5</td>
<td>13.6</td>
<td>17.4</td>
</tr>
<tr>
<td>Na</td>
<td>5.1</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>7.6</td>
<td>8.1</td>
<td>11.0</td>
<td>10.4</td>
<td>13.0</td>
</tr>
<tr>
<td>K</td>
<td>4.3</td>
<td>Ca</td>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.1</td>
<td>7.8</td>
<td>9.8</td>
<td>9.8</td>
<td>11.8</td>
</tr>
<tr>
<td>Rb</td>
<td>4.2</td>
<td>Sr</td>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.7</td>
<td>7.3</td>
<td>8.6</td>
<td>9.0</td>
<td>10.4</td>
</tr>
<tr>
<td>Cs</td>
<td>3.9</td>
<td>Ba</td>
<td>Ti</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
<td>At</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.1</td>
<td>7.4</td>
<td>7.2</td>
<td>8.4</td>
<td>Ra</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Successive Ionization Potentials or Energies

The energy required to remove an electron gram an isolated gaseous atom is called the first ionization potential or energy. For example,

\[ \text{Na} \rightarrow \text{Na}^+ + 1e^- \]

The removal of a second electron is called the second ionization potential and is higher than the first ionization potential since the electron must be removed against the greater net positive charge on the ion.

\[ \text{Na} \rightarrow \text{Na}^{2+} + 1e^- \]

The process may be repeated until all the electrons of the atom have been removed.

\[ \text{Na}^{2+} \rightarrow \text{Na}^{3+} + 1e^- \]

\[ \text{Na}^{3+} \rightarrow \text{Na}^{4+} + 1e^- \]

Each successive ionization potential or energy is greater than the previous one since the electron must be removed against the net positive charge on the ion as shown in Table 1.4.
Table 1.4 Values of $I_1, I_2, \ldots, I_n$ of Some Elements (in eV)

<table>
<thead>
<tr>
<th>Elements with Atomic Numbers</th>
<th>Electronic Configuration</th>
<th>Successive Ionization Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1s</td>
<td>21.6</td>
</tr>
<tr>
<td>Ne</td>
<td>2s, 2p</td>
<td>13.0</td>
</tr>
<tr>
<td>Ar</td>
<td>3s, 3p</td>
<td>8.8</td>
</tr>
<tr>
<td>Kr</td>
<td>4s, 4p</td>
<td>7.6</td>
</tr>
<tr>
<td>Xe</td>
<td>5s, 5p</td>
<td>6.8</td>
</tr>
<tr>
<td>Rn</td>
<td>6s, 6p</td>
<td>6.3</td>
</tr>
<tr>
<td>Cs</td>
<td>7s, 7p</td>
<td>6.1</td>
</tr>
<tr>
<td>Ba</td>
<td>8s, 8p</td>
<td>5.9</td>
</tr>
<tr>
<td>In</td>
<td>9s, 9p</td>
<td>5.7</td>
</tr>
</tbody>
</table>

From Table 1.4, we find that second ionization energy is greater than the first, third ionization energy is greater than second and so on. Further it will be seen that as each sub-shell is depleted and the first electron is drawn from the next lower sub shell, there is a large increase in ionization energy, when whole of the electron shell, is depleted there is a very large increase in ionization energy since the main quantum number decreases by one unit. For example, in lithium $I_1$ is about fifteen times $I_2$ and $I_3$ is not even two times that of $I_1$, $I_2$ represents the removal of 2s electron, while $I_3$ represents the removal of one the 1s electrons.

**Measurement of Ionization Potential**: This is done by bombarding the atoms with high energy electrons which are generated by a hot filament and accelerated by an electric field (Figure 1.2). When ionization occurs, a current flows though the circuit. The energy necessary is determined by the conversion of the accelerating voltage to energy units. The experiment can be extended to determine successive ionization energy.

**Factors Controlling the Values of Ionization Potential**: Ionization energy depends upon the following factors:

![Fig. 1.2 Diagrammatic Representation of Ionization by Electron Bombardment](image)
(a) **Size of Atom or Ion**. The ionization potential decreases with increasing size of atom. The larger the size of atom, lesser is the ionization potential. This is due to the fact that electrons are tightly held in smaller atoms whereas in large atoms, electrons are held quite loose, i.e., lesser energy is required for removal of electrons from larger atom than the smaller one. Hence, ionization energy is lower for larger atoms and higher for smaller atoms. For example, ionization energy in case of sodium (large) is less as compared to lithium (small atom).

(b) **Nuclear Charge**: The higher the nuclear charge (protons in nucleus), the higher is ionization potential. Because of the higher nuclear charge, the electrons are bound with more force and hence higher shall be the energy required for its removal. Magnesium has higher nuclear charge (12 protons) as compared to sodium (11 proton). Hence ionization energy in case of magnesium is higher as compared to sodium.

(c) **Effect of Shape of Orbital**. The shape of the orbitals also influences the ionization potential. An s electron penetrates nearer to the nucleus than a p-, d- or f-electrons and is more tightly held. The other being the same, the ionization potentials decreases in the order given below:

\[ s > p > d > f \]

In general, the ionization potential increases on crossing a period (i.e. Li through Ne) and decreases on descending in a group (He through Rn), although since s electrons are more difficult to remove than p- or d-, the change across a period may not be quite regular. Also, since the removal of successive electrons becomes more difficult and hence, First Ionization Potential < Second Ionization Potential < Third Ionization Potential < ……….

Table 1.4 gives the ionization potentials of a few elements as derived from the analysis of atomic spectra.

(d) **The Shielding (Screening) Effect of the Inner Electrons on the Outer Electrons**. The attractive force exerted by the nucleus on the most loosely held electrons is at least partially counter – balanced by the repulsive forces exerted by the inner electrons. The electron to be removed is thus shielded from the nucleus by these inner shells and decrease in ionization potential results (Figure 1.3).

![Fig. 1.3 Shielding Effects of Inner Electrons on the Outer Electrons](image-url)
The shielding effect of inner electrons is affected by (i) the number of inner electrons and (ii) the type of the orbitals in which the inner electrons reside.

**Generalisation of Some Facts:** Several useful generalizations can be drawn from our study of ionization potentials that will help us to understand the behavior or electrons in atoms and molecules.

(i) It is apparent that as electrons are added to orbitals of the same principal quantum number in successive elements, the ionization potential increases due to the increase in nuclear charge. This explains the general trend in ionization potential along any row of the periodic table.

(ii) Electrons of the highest principal quantum number are shielded from the nucleus by the inner electrons. This is one of the reasons that the ionization potentials of the alkali metals are so low.

(iii) When several p- or d- orbitals are available, one electron enters each orbital until all are half-filled. It is found that all the electrons in these half-filled orbitals have the same spin.

This half-filled set of orbitals with all spins the same, seems to be particularly, stable, as addition of another electron often results in a decrease in the ionization potential.

**Variation of ionization energy in a group.** As we move down a group, the size of atom increases with the increase in atomic number, it means that on moving down a group, the distance between the electron and nucleus increases. As a result there occurs a decrease in the force of attraction and therefore lesser energy is required to remove the electron. It means that the value of ionization energy decreases as we move down a group.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic No.</th>
<th>Ionization Energy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>3</td>
<td>520</td>
</tr>
<tr>
<td>Na</td>
<td>11</td>
<td>495</td>
</tr>
<tr>
<td>K</td>
<td>19</td>
<td>418</td>
</tr>
<tr>
<td>Rb</td>
<td>37</td>
<td>403</td>
</tr>
<tr>
<td>Cs</td>
<td>55</td>
<td>374</td>
</tr>
</tbody>
</table>

Another factor is that as we move down a group, the number of shells increases. This cause an increase in the shielding and screening effect of the electrons lying between the nucleus and outermost shell. Thus, the attraction between the nucleus and electron becomes still less. Hence the ionization energy decreases as we move down a group. The trend in ionization energy with in a group is shown in Table 1.5.

Ionization energies of the elements are plotted against their atomic number as shown in Figure 1.4. The figure shows that ionization energy is lowest in the alkali metals and highest in the noble gases.
**The Variation of Ionization Energy along a Period:** As we move along a period from left to right, the positive charge on the nucleus increases and therefore the size of atom decreases. As a result of that there occurs an increase in the forces of attraction between the electron and the nucleus. Thus, it becomes more difficult to remove an electron. This explains why there is an increase in ionization energy as we move along a period. This is shown in Table 1.6.

**Table 1.6 Variation of Ionization Energy**

<table>
<thead>
<tr>
<th>Element</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Number</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Ionization Energy (kJ mol(^{-1}))</td>
<td>520</td>
<td>900</td>
<td>800</td>
<td>1086</td>
<td>1403</td>
<td>1314</td>
<td>1081</td>
<td>2085</td>
</tr>
</tbody>
</table>

When a half-filled sub-shells is reached, ionization potential increase is somewhat more. For example, nitrogen (1s\(^2\)2s\(^2\)2p\(^3\)) has a higher value of ionization energy than oxygen (1s\(^2\)2s\(^2\)2p\(^4\)). This is shown in the above Table 1.6.

**Special Periodic Trends**

(i) When a half filled sub – shell is reached, ionization potential increase is somewhat more. For example, nitrogen (1s\(^2\)2s\(^2\)2p\(^3\)) has a higher value than oxygen (1s\(^2\)2s\(^2\)2p\(^4\)) has.

(ii) It is extra hard to remove an electron from a completed octet. For this reason, ionization potentials of inert gases are very much more than those of their neighbours.
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(iii) Ionisation of a p sub – shell electron is easier than that of a s – sub- shell electron in the same main shell. Thus, aluminium has a lower ionization potential than magnesium which is in the same period.

Application of Ionization Potential

(i) To Determine the Number or Valence Electrons in an Atom: The ionization potentials provide excellent experimental evidence about the number of valence electrons in an atom. In the case of lithium, the first ionization potential is low (5.4 eV) but the second is much higher (75.6 eV) indicating that one electron is much more readily removed than the rest. Therefore, the experimental evidence confirms the presence of one valence electron in lithium. Similarly, the number or valence electrons in the other elements can be calculated.

(ii) Relative Reactivity of Elements: Elements having high values of ionization energy are less reactive (for example, inert gases), while those having low values are extremely reactive (for example, alkali and alkaline earth metals).

(iii) Relative Energy States of the Different Electrons in an Atom: From the successive values of ionization potentials of an atom it is possible to predict relative energy states of different electrons in any atom. Figure 1.5 shows the case of potassium.

(iv) Nature of Bond: The relative values of ionization potential and electrons affinity of two elements decide the nature of the bond when they combine together. If the difference between both the values is small (as ionization energy is always greater), the bond is ionic. Greater differences of energy which cannot be compensated by lattice energy will induce partial covalent character in the molecule.

Fig. 1.5 Successive Ionisation Energies for K Atom
(v) **Reducing Power of an Element:** Lower the ionization potential of an element, the greater would be its reducing power because the easily removed electron would be accepted by species which would lower oxidation state.

(vi) **Basic Character of Elements:** Lower the value of ionization potential of an elements, the greater would be its basic character.

### 1.3.4 Electron Affinity

The energy released when an extra electron is added to a neutral gaseous atom is called the electron affinity.

\[ \text{Atom} (g) + \text{Electron} (g) \rightarrow \text{Negative ion} (g) + \text{Energy} \]

The greater the energy released in the taking up the extra electron, the greater will be the electron affinity.

**Successive Electron Affinities (EA):** As more than one electron can be introduced in an atom, it is called first electron affinity for the addition of one electron, called second electron affinity for the addition of two electrons and so on. The first EA of active non-metal is positive (exoothermic) while second EA even for the formation of oxide or sulphide ion is negative (endoothermic). For example, the overall EA for the formation of oxide or sulphide ions has been found to be endothermic to the extent of 640 and 390 kJ mol⁻¹ 390 kJ mol⁻¹ respectively.

\[ \text{X} (g) + e^- + \text{Energy} \rightarrow \text{X}^-(g) \]

It is interesting to note that the electron affinity of elements having a d⁰s² configuration has been found to be negative. This is because of the accommodating of the electron in the higher p – orbital (Zn = -87, Cd = -56 KJ mol⁻¹)

Elements of group VIIa possess high electron affinity. The reason for this is that by picking up an electron halogens attain the stable noble gas electronic configuration.

The electron affinity is expressed in KJ mol⁻¹. It is interesting to note that electron affinity data are available for a limited number of elements and are given in Table 1.7.

#### Table 1.7 Electron Affinities of Elements (kJ mol⁻¹)

|     | H → H⁻ | Li → Li⁺ | Be → Be²⁺ | B → B⁻ | C → C⁻ | N → N⁻ | O → O⁻ | F → F⁻ | Na → Na⁺ | Mg → Mg²⁺ | Al → Al⁻ | Si → Si⁺ | P → P⁻ | S → S⁻ | Cl → Cl⁻ |
|-----|--------|---------|-----------|--------|--------|--------|--------|--------|----------|----------|---------|--------|--------|--------|--------|---------|
|     | 72     | 57      | 46        | 15     | 122    | -31    | 120    | 320    | 21       | 26       | 26      | 155    | 60     | 200    | 348.7   |
| Also for two electrons | O → O²⁻ | Br → Br⁻ | S → S²⁻ | I → I⁻ |
|                  | -640   | 324     | -390     | 295    |
**Chemical Periodicity**

**Change of Electron Affinity along a Group:** On moving down a group, the size of atom decreases significantly and therefore, the effective nuclear attraction for the electron decreases. Consequently the atom will possess less tendency to attract additional electrons towards itself. It means that electron affinity would decrease as we move down a group. In case of halogens the decrease in electron affinity from chlorine to iodine is due to steady increase in ionic radii from Cl to I.

On moving down a group the electron affinity decreases. Thus, the electron affinity of Cl should be less than F. But actually the electron affinity of F (320 kJ mol⁻¹) is less than Cl (348 kJ mol⁻¹). The reason for this is probably due to small size of fluorine atom. The addition of an extra electron produces high electron density which increases strong electron–electron repulsion. The repulsive forces between electrons result in low electron affinity.

Electron affinities of noble gases are zero. As these atoms possess s⁰p⁰ configuration in their valence shells, these are stabllest atoms and there are no chances for the addition of an extra electron. Thus, the electron affinities of noble gases are zero.

Electron affinities of beryllium and nitrogen are almost zero. This may be due to the extra stability of the full completed 2s orbital in beryllium and of the exactly half 0 filled p – orbital in nitrogen. As these are stable electronic configurations, they do not have tendency to accept electrons and therefore, the electron affinities for beryllium and nitrogen are zero.

**Change of Electron Affinity along a Period:** On moving across a period, the size of atoms decreases and nuclear charge increase. Both these factors favour in increase in force of attraction exerted by the nucleus on the electrons. Consequently, the atom will possess a greater tendency to attract the additional electron, i.e., its electronic affinity would increase as we move from left to right. Due to this reason electron affinities of non-metals are high whereas those of metals are low.

Of all the metals, the EA of gold is comparatively high (222.7 kJ mol⁻¹). This value may be attributed to the higher effective nuclear, charge and poor shielding of the nucleus by d electrons.

The EA values of the second period elements have been found to be lower than the of the third row elements. This trend is probably due the increases the inter-electron transition repulsions which are more for the smaller elements due to higher electron densities.
Relation with Ionisation Potential (IE): When E/A and IE values for the same atom are plotted against the charge q on the species, a smooth curve is obtained (Figure 1.7) which may be represented by the following quadratic equation.

\[ E = \alpha q + \beta q^2 \]

where \( \alpha \) and \( \beta \) are constant.

**Factors on Which Electron Affinity Depends**

1. **Size of the Atom** – It is known that smaller the size of the atom, stronger would be the attraction of its nucleus for electron to be added. Thus, smaller the size of an atom, greater would the electron affinity.

2. **Magnitude of the Nuclear Charge** – Higher the magnitude of nuclear charge of elements (along a period), stronger would be the attraction of its nucleus for the electron to be added. Thus, greater the nuclear charge, greater would be the electron affinity.

3. **Electronic Configuration** - An atom having stable configuration is having no tendency to gain an electron. Such atoms are having zero or almost zero electron affinity. An atom is said to have stable configuration when it has.
   (i) Fully filled orbitals.
   (ii) Half-filled orbitals belonging to the same sub shell
   (iii) Inert gas configuration, i.e. having 8 electrons in the outermost orbit.

1.3.5 **Electronegativity**

Electronegativity is the tendency of an atom in a molecule to attract electron towards itself the showed pair of electrons. Unlike ionization potential and electron affinity, electronegativity is not a measurable quantity.

Consider two atoms which are not identical, for example H and Cl, farming the covalent compound H\(_2\)Cl. The polarity of the molecule arises done to differences between the electronegativity of hydrogen and that of chlorine. Since the electronegativity of Cl is greater than that of hydrogen, the former has the large share in the electron pair than latter and can be shown as \( \text{H}^+\text{Cl}^- \), the chlorine end of the molecule is the negative end of the dipole. Electro negativities of elements of group I to group VII are given in the Table 1.7.
Chemical Periodicity

Table 1.7 Electro Negativities of s- and p- Block Elements

<table>
<thead>
<tr>
<th>Group I</th>
<th>Group II</th>
<th>Group III</th>
<th>Group IV</th>
<th>Group V</th>
<th>Group VI</th>
<th>Group VII</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
<td>H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
</tr>
<tr>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>3.0</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
</tr>
<tr>
<td>0.9</td>
<td>1.2</td>
<td>1.5</td>
<td>1.8</td>
<td>2.1</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>K</td>
<td>Ca</td>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
</tr>
<tr>
<td>0.8</td>
<td>1.0</td>
<td>1.6</td>
<td>1.8</td>
<td>2.0</td>
<td>2.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Rb</td>
<td>Sr</td>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
</tr>
<tr>
<td>0.8</td>
<td>1.0</td>
<td>1.7</td>
<td>1.8</td>
<td>1.9</td>
<td>2.1</td>
<td>2.5</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
<td>Ti</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
<td>At</td>
</tr>
<tr>
<td>0.7</td>
<td>0.9</td>
<td>1.8</td>
<td>1.8</td>
<td>1.9</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Fr</td>
<td>Ra</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From the table it is seen that:

(i) Small atoms possess higher values of electro negatives as compared to larger atoms.

(ii) Atoms having nearly filled shell of electrons (halogens) possess higher electronegativity as compared to those having thinly populated shells.

(iii) Electronegativity is a periodic function of atomic number.

Periodic Trends

Along the Group: In moving down a group as the nuclear charge increasers, the electronegativity of a lower element should be more than that of upper element. But actually it is not the case because the disadvantages of increase in atomic radii and electron shielding effects are more than the advantages gained though increase in the nuclear charge. Consequently a lower element of group is less electronegative than the upper end of the same group. In general, therefore small atoms attract electrons more than bigger ones and are more electronegative.

Along the Period: As we move from left to right across a period, the values of electronegativity increases gradually. This is due to the reason that the atomic size gradually decreases and, therefore the additional electron can be held more tightly.

Electronegativity Scales

As mentioned earlier, electronegativity is not a measurable quantity, however in order to compare the electronegativity values of different elements, various electronegativity scales have been proposed. Electronegativity scale is an arbitrary scale and import arrives are discussed here.

(a) Pauling’s Electronegativity Scale. The bond between the two atoms A and B will be generally intermediate between pure covalent A-B and pure...
ionic A⁺B⁻. Because of the partial ionic character, the bond is strengthened or in other words bond energy is increased. The bond is fact is stabilized by resonance. In deriving the Pauling’s scale, the following measurements are made:

Actual bond energy measured experimentally = H
Bond energy if the bond was truly covalent = Q
Resonance energy caused by ionic character of bond = H – Q
or Δ = H – Q
where Δ is the resonance energy.

As Δ is a measure of partial ionic character of a covalent bond and the difference in electronegativity between the bonded atoms is also related to the ionic character of the bond, so Δ is also related to the difference in the electronegativity of the bonded atoms. IF Xₐ are the electronegativity of atoms A and B and Xₐ > Xₐ then,

\[ X_A - X_B = k \sqrt{\Delta} \]  
...(1.15)

where k is a proportionality constant.

Pauling has found that, \( k = 0.208 \)

Thus 

\[ X_A X_B = 0.208 \sqrt{\Delta} \]  
...(1.16)

The factor 0.208 comes from the conversion of experimental value, measured in kcal/mole into eV energy. Pauling fixed arbitrarily 4.0 as electronegativity value of fluorine and 2.1 of hydrogen. From these other electronegativities were calculated by using the equation 1.16.

Calculation of Δ. From Equation (1.15), we know

\[ \Delta = H - Q \]

Values of H can be measured experimentally and the value of Q can only be obtained indirectly. If we consider the energy \( E_{A-B} \) of a purely covalent bond between two atoms A – B, we might expect that it would be exactly equal to the arithmetic mean of the bond energies between A – A and B – B. Thus we would expect,

\[ \Delta = H = Q = E_{A-A} = \frac{1}{2} (E_{A-A} + E_{B-B}) \]  
...(1.17)

Combining Equations (1.16) and (1.17), we get

\[ X_A - X_B = 0.280 \left[ E_{A-A} - \frac{1}{2} (E_{A-A} + E_{B-B}) \right]^{1/2} \]  
...(1.18)

Pauling showed that the postulate of the additivity of normal covalent bonds is valid for a large number of single bonds and he used Δ values calculated from...
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Equation (1.17) to formulate an extensive scale of electronegativities of elements. However the failure of the additive postulate in certain cases, notably the alkali metal hydrides, led Pauling to postulate the geometric mean in place of the arithmetic mean. Thus, Equation (1.17) modified to,

\[ \Delta = H - Q = E_{A-A} - (E_{A-B} + E_{B-B})^{1/2} \quad \ldots (1.19) \]

and then Equation (1.18) becomes,

\[ X_A - X_B = 0.208 [E_{A-A} - (E_{A-B} + E_{B-B})^{1/2}]^{1/2} \quad \ldots (1.20) \]

Again, the value calculated by using Equation (1.20) are not very much successful in all cases. Pauling in 1960 produced new scale based on a new equation which is represented as,

\[ X_A - X_B = 0.18 [E_{A-A} - (E_{A-B} + E_{B-B})^{1/2}]^{1/2} \quad \ldots (1.21) \]

The method employed by Pauling is not universally applicable because the energy terms used such as bond dissociation energy cannot be determined easily and correctly.

(b) Mulliken’s Method. Mulliken defined the electronegativity of atom as the arithmetic mean of its ionization energy and electron affinity.

\[ X_A = \frac{1}{2} (IP + EA) \]

Mulliken gave another formula for calculating the electronegativity as,

\[ X_A = \frac{\text{Ionisation potential - Electron affinity}}{5.6} \quad \ldots (1.22) \]

where \( X_A \) is the electronegativity value of atom A on Mulliken’s scale and 5.6 is the adjustment factor with the help of which the electronegativity of atom A on Mulliken’s scale approximates that on Pauling’s scale.

In equation (1.22), the factor 1/5.6 is used when ionization potential and electron affinity are expressed in electron volts. If the ionization potential and electron affinity are expressed in kcal/mole, equation (1.22) becomes as follows:

\[ X_A = \frac{\text{Ionisation potential - Electron affinity}}{2 \times 62.5} \quad \ldots (1.23) \]

On the basis of Mulliken’s scale, the conditions for the formation of purely covalent A - B bond and ionic A - B or A’ - B bond may be written as follows:

(i) When there is the formation of purely covalent A–B bond.

\[ \frac{(IP)_A - (EA)_A}{5.6} = \frac{(IP)_B - (EA)_B}{5.6} \]

and hence \( X_A = X_B \).
(ii) When there is the formation of A' - B' bond, then
\[
\frac{(IP)_{A'} - (E_{A'})}{5.6} > \frac{(IP)_{B'} - (E_{A'})}{5.6}
\]
hence \(X_A > X_B\)

(iii) When there is the formation of A' - B bond, then
\[
\frac{(IP)_{A'} - (E_{A'})}{5.6} > \frac{(IP)_{B} - (E_{A'})}{5.6}
\]
hence \(X_A > X_B\)

The Mulliken’s scale has the advantage that it can account for the different hybridizations of the element in chemical compounds.

The values of electronegativity obtained by Mulliken’s method are in consistent with those obtained by other methods but the method has limitations due to the following reasons:

(i) The accurate values of electron affinities are only available for a limited number of elements.

(ii) During the formation of bond the transference of electron between two atomic orbitals occurs whose exact constitution may not be known.

(c) Sanderson’s Method. Sanderson suggested that electronegativity of an atom is stability ratio (S.R) which may be defined as the ratio of the average electron density of an atom to that of a hypothetical inert atom, i.e.,

\[
S.R. = \frac{D}{D_i}
\]

...(1.24)

where \(D\) is the average electron density and is a measure of the comparative compactness of the atom, and \(D_i\) is the density of a hypothetical inert atom. The value of \(D\) is calculated by the following relation:

\[
D = \frac{\text{Atomic Number}}{\text{Atomic Volume}}
\]

\[
= \frac{Z}{4\pi r^3/3} = \frac{3Z}{4\pi r^3} = \frac{Z}{4.19r^3}
\]

...(1.25)

In the above equation \(r\) is the non-polar covalent radius. In order to calculate \(D_i\), the electron densities of inert gas atoms are plotted against atomic numbers and the value for a particular atomic number is found by interpolation.

The Sanderson (SR) and Pauling values (X) are related by the expression.

\[
\sqrt{X} = 0.21 \text{ S. r.} + 2.77
\]

The two scales agree quite closely except for germanium, arsenic and antimony, where the Sanderson values are appreciably higher than the

---

**NOTES**

---

*Chemical Periodicity*

---

*Self-Instructional Material*
corresponding Pauling electro negatives. A high value for germanium is also obtained on an electronegativity scale given by Allred and Rochow. Sanderson, Allred and Rochow claim that here is a great deal of evidence in favour of the high value for germanium.

(d) Conclusion: There are many other scales to describe the electronegativity. In all there scales a few useful points that are common to all include:
  (i) The halogens are high in scale.
  (ii) The alkali metals are low in scale.
  (iii) The other elements follow each other up the scale in the same order as the live in the periods of periodic table.
  (iv) The transition elements are given the values which are uncertain.

Applications of Electronegativity Concept

(i) Percent Ionic Character of Bond: The electronegativity scale provides a ready method of expressing the percent ionic character. This was first done by Pauling in an empirical manner by establishing a relation between the amount of ionic character of a single bond between two atoms, A and B and their electronegativity difference, $X_A - X_B$.

According to Pauling: The bond between two atoms is 50% ionic if the difference in electronegativity values is more or less than 1.7, the bond is correspondingly more or less ionic.

![Graph of Percent Ionic Character in a Bond A – B Against the Electronegativity Difference $X_A - X_B$](image)

A curve is obtained for halogen halides by plotting electronegativity difference against percent ionic character (Figure 1.7). The percent ionic character for this purpose has been obtained from the work of Hanny and Smyth, who developed the following relationship.
Percent ionic character  = 100[0.16 (X_A – X_B) + 0.035 (X_A – X_B)²]
= (16X_A – X_B) + 3.5(X_A – X_B)²

(ii) Stability of Bond: The electro negativity scale has been utilized by Pauling to indicate roughly the stability or strength of a bond. According to him. 
(a) The greater the difference in electro negativities of two elements A and B, the greater the strength of the bond A – B.

HF > HCl > HBr > HI

Thus, the strength of bond is hydric acids of halogen decreases because the difference in electro negativities between H and halogen decreases.

(b) When the electronegativity of the two elements undergoing combination is approximately the same, the strength of the bond is small, i.e., the compound tends to be unstable.

NCl₃, AsH₃, SbH₃ and BiH₃ are well known examples of this class.

(c) Stability of compounds in which electronegativity differences is very large: Such compounds will be those which are formed by the combination of metals (whose electro negativity is very low) and non-metals (whose electronegativity is very high). Such compounds are very stable.

3. Metallic and Non-Metallic Character of Elements: The element having higher value of electronegativity will be a non-metal while that with a lower value will possess a metallic character.

4. Acid Base Character of the Normal Oxides of the Elements of the Same Period: On moving from left to right in a period, the acidic character of the normal oxides of the elements goes on increasing. The change from strongly basic to strongly acidic character is due to the increase in the electronegativity value of the element, (Xₚₐₓ) and the resulting decrease (Xᵤₐₗ – Xₚₐₓ) value where Xₚₐₓ and Xᵤₐₗ are the electronegativity values of M and oxygen. M is that element whose normal oxide is under consideration.

5. Organic Chemical Reactions and Theories: The electronegativity scale offers a method to have a definite comparison of atoms from different groups and periods in the periodic table. This formation is helpful in the development of organic chemical theories dealing with the tendencies of various atoms or groups to retain or repel the bonding pair of electrons in a chemical reaction.

6. Colour of Salts: It is interesting to mention that there exists a close relationship between the degree of ionic character and the colour of the salt. As a rule, bonds that give rise to coloured substance possess less than 205 ionic character.

If the ionic character is more than 20%, the compound is colourless.

Another rule is that when the value of ionic character becomes lesser than 20%, the substance takes on a colour passing through yellow and orange to red and black, i.e., the colour is deepening.
Chemical Periodicity:

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Percent Ionic Character</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>80%</td>
<td>White</td>
</tr>
<tr>
<td>AgI5r</td>
<td>24%</td>
<td>Pale Yellow</td>
</tr>
<tr>
<td>AgI</td>
<td>15%</td>
<td>Yellow</td>
</tr>
<tr>
<td>AgI5</td>
<td>4%</td>
<td>Black</td>
</tr>
</tbody>
</table>

Limitations: It is important to mention that electronegativity of an atom is not a fixed quantity as the actual electron attracting power of an atom depends on its environment. In general the electronegativity value given to an element is a mean value for the element in its most common oxidation state. The higher the charge number of an atom in a compound, the greater the electronegativity shown by the element.

Check Your Progress
1. What is periodic table?
2. What is atomic radii?
3. Define the term ionic radii.
4. What is ionization potential?

1.4 HYBRIDIZATION

From valence bond theory, it is learnt that covalency of an element is equal to the number of half-filled orbitals present is the valence shell of its atoms. On applying this concept to carbon, we find that the valency of carbon should be equal to 2 because it has only two half-filled orbitals in the valence shell. Contrary to this, carbon atom always exhibit a valency of four. This can be explained by the concept of hybridization.

Atomic number of carbon is 6 and its electronic configuration is 1s², 2s², 2pₓ, 2pᵧ, 2pz.

\[
\begin{array}{ccc}
1s & 2s & 2p \\
\uparrow & \uparrow & \uparrow \\
\end{array}
\]

Carbon (ground state)

\[
\begin{array}{ccc}
\uparrow & \uparrow & \uparrow \\
\end{array}
\]

Carbon (excited state)

In the ground state, carbon has two unpaired electrons and therefore it is bivalent. But in almost all its compounds. It shows a tetravalency. In order to explain the tetravalency of carbon it is assumed that one of the 2s electrons become unpaired and gets excited to the vacant 2pₓ orbital resulting in the configuration. Now carbon contains four unpaired electrons and, therefore, it is capable of forming four bonds. If these four electrons now form four bonds, three bonds (involving the electrons 2pₓ, 2pᵧ, and 2pz) would be of one type and at right angle to each
other and fourth bond (involving the electron of 2s orbital) would be different with new directional properties. But it is known with certainty that four bonds formed by the carbon atom are equivalent.

In order to get four equivalent bonds, it is assumed that one of 2s electrons becomes unpaired, gets excited to the 2p orbital and then four orbitals (2s, 2p, 2p) get mixed up and finally redistribution of energy takes place between them, resulting in the formation of four equivalent hybrids (Refer Figure 1.8). This phenomenon of mixing of the atomic orbitals and the formation of new orbitals of equal energy is known as hybridization and the new orbitals formed are known as hybrid orbitals. The bonds formed by such orbitals are called hybrid bonds. The compounds which are formed from these bonds are known as hybrids.

![Formation of Four sp³ Hybrid Orbitals by Overlapping of One s and Three p Orbitals](image)

**Fig. 1.8** Formation of Four sp³ Hybrid Orbitals by Overlapping of One s and Three p Orbitals

### 1.4.1 Rules of Hybridization

Hybridization is a theoretical concept which has been introduced to explain some structural properties such as shapes of molecules or equivalency of bonds, etc. which cannot be explained by simple theories of valency.

**Concept of Hybridization is Based on Following Rules:**

1. Only orbitals of similar energies belonging to the same atom or ion can undergo hybridization.
2. Number of hybrid orbitals produced is equal to the number of orbitals mixed. Hybrid bonds are stronger than the single non-hybridized bonds of comparable energy.
3. Most of the hybrid orbitals are similar but they are not necessarily identical in shape. They differ from one another in orientation in space.
4. For equivalent hybrids, the orientation in space is determined by:
   - (i) The number of orbitals mixed and consequently the number of hybrids obtained, and
   - (ii) Which of x, y and z directions are preferred by the orbitals when pure.
5. Once an orbital has been used to build a hybrid it is then no longer available to hold electron in its pure form.
6. The type of hybridization indicates the geometry of molecules. From the type of hybridization one can tell about the bond angles and structure (see in table given below).

### Notes

<table>
<thead>
<tr>
<th>Shape of Molecule</th>
<th>Hybrid Type</th>
<th>Bond Angle</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>sp</td>
<td>180°</td>
<td>BeCl₂, H₂Cl₂</td>
</tr>
<tr>
<td>Planar</td>
<td>sp²</td>
<td>120°</td>
<td>BF₃, BCl₃, CO₂⁺, NO⁺</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>sp³</td>
<td>109° 18'</td>
<td>CH₄, NH₃⁺, BH₄⁻</td>
</tr>
<tr>
<td>Square Planar</td>
<td>dsp³</td>
<td>90°</td>
<td>[Ni(CN)₄]²⁻, (PCl₄)²⁻</td>
</tr>
<tr>
<td>Trigonal Bipyramidal</td>
<td>dsp²</td>
<td>90° 120°</td>
<td>PF₅⁻, SF₅⁻</td>
</tr>
<tr>
<td>Octahedral</td>
<td>spd²</td>
<td>90°</td>
<td>(SiF₆)³⁻, SF₆, [Cu(NH₃)₄]²⁺</td>
</tr>
</tbody>
</table>

### 1.4.2 Types of Hybridization

There are different types of hybridization depending upon the type of orbitals involved in mixing such as sp, sp², sp³, sp³d, sp³d² etc. Let us discuss various types of hybridization with examples.

1. **sp Hybridization**: A linear combination of one s- and one p- orbital yields two sp hybrid orbitals. This mixing of orbitals is known as sp hybridization. This is shown in Figure 1.9.

![Fig. 1.9 Formation of Two sp Hybrid Orbitals](image)

### Properties of sp-Hybrid Orbitals

(i) Two sp hybrid orbitals [sp and sp₁] are completely equivalent in energy.

(ii) Each sp hybrid s- and pure p-orbital form which it is formed after hybridization. Its predicted relative overlapping power is 1.93.

(iii) In sp-hybrid orbital, there is one large lobe and one small lobe. The larger lobe, which is much bigger than the p-orbital, brings about a higher degree of overlapping with the orbital or a reacting atom. Thus, the resulting bond is comparatively stronger.

(iv) The normalized wave function \(Ψ(sp₂)\) and for sp and sp₁ hybrid orbitals are as follows:

\[
Ψ(sp₂) = \frac{1}{\sqrt{(2)}}[Ψ(s)+Ψ(p)]
\]
\[ \Psi(sp_3) = \frac{1}{\sqrt{2}} \left[ \Psi(s) - \Psi(p) \right] \]

From the above equations, it follows that the ratio of \( p \)-character of \( s \)-character is \( 1:1 \) in each of the two hybrid orbital wave functions and that both the hybrid orbital wave functions are orthogonal to each other.

**Example of sp-Hybridisation:** An interesting example involving sp-hybridisation is beryllium fluoride, BeF\(_2\).

**Beryllium Fluoride:** The atomic number of beryllium is 4. Its electronic configuration is \( 1s^2 \), \( 2s^2 \). As no unpaired electrons are available, the formation of BeF\(_2\) is not expected to be formed. But BeF\(_2\) is known. In order to explain its formation, it is assumed that one of the 2s electrons becomes unpaired and gets excited to 2p-orbital (Figure 1.10). Now two unpaired electrons are available in the excited state of beryllium and, therefore, it can form BeF\(_2\) by sharing its two electrons from two fluorine atoms. But formation of BeF\(_2\) involves one \( s \) and one \( p \)-orbital. Therefore, the two bonds should be of different strength. But actually these are of equal strength and the molecule BeF\(_2\) is linear with the bond angle \( \text{F-Be-F} \) equal to \( 180^\circ \). However, it is explained by hybridisation.

- Be (Ground State) = \( 1s^2, 2s^2 \) (Figure 1.10 (A))
- Be (Excited State) = \( 1s^2 2s^2 2p^1 \) (Figure 1.10 (B))
- \( F = 1s^2 2s^2 2p_y \)

\[
\begin{align*}
\text{Be} & \quad \begin{array}{c}
\text{Be} \\
\text{F}
\end{array} \\
\begin{array}{c}
1s \\
2s \\
2p_y
\end{array}
\end{align*}
\]

\( \text{sp-hybridisation in boron (A) = ground state of boron, (B) = excited state of boron and (C) = hybridised state of boron atom} \)

**Fig. 1.10 sp-Hybridisation**

The energy of one \( s \)- and one \( p \)-orbitals is combined and two \( s \)-hybrid orbitals of the same shape and energy are obtained. These two sp-hybrid orbitals overlap with \( p \)-orbitals of two fluorine atoms to form BeF\(_2\).

If BeF\(_2\), the two hybrid orbitals must lie as far apart from each other as possible in order to minimize the force of repulsion and thus to have a stable structure. Hence, the two hybrid orbitals point in opposite directions as shown in Figure 1.11. The molecule will therefore be linear and the bond angle F-Be-F will be equal to \( 180^\circ \).
Thus, hybridization in BeF$_3$ explains that:
(i) Two bonds are of equal strength, and
(ii) The shape of the molecule is linear.

2. sp$^2$ Hybridization. The combination of one s and two p-orbitals to form three orbitals of equal energy is known as sp$^2$ hybridization. There three bonds are coplanar and directed at angle of 120° to each other (Figure 1.12).

![Figure 1.12](image)

**Properties of sp$^2$ Hybrid Orbitals**

(i) All the three sp$^2$ hybrid orbitals are completely equivalent in energy and shape.

(ii) The relative overlapping power of each hybrid orbital is 1.99.

(iii) All the three sp$^2$ hybrids lie in the plane of p-orbital and are oriented at 120° with respect to each other.

(iv) The three sp$^2$ hybrids have their maximum overlapping along one of the three axes. The three hybrids are denoted by $\psi_1$, $\psi_2$, and $\psi_3$. The normalized wave function for these hybrids are as follows:

\[
\psi_1 = \frac{1}{\sqrt{3}} \psi(s) + \frac{2}{\sqrt{3}} \psi(p)
\]

\[
\psi_2 = \frac{1}{\sqrt{3}} \psi(s) + \frac{1}{\sqrt{6}} \psi(p) + \frac{1}{\sqrt{2}} \psi(p')
\]

\[
\psi_3 = \frac{1}{\sqrt{3}} \psi(s) - \frac{1}{\sqrt{6}} \psi(p) + \frac{1}{\sqrt{2}} \psi(p)
\]

From the above equations it follows that the ratio of p-character to s-character is 2 : 1 in each of the hybrid wave functions.
Examples: (i) An interesting example of explain sp\(^3\) hybridization is the formation of boron trifluoride (BF\(_3\)).

The boron atom is the central atom is BF\(_3\) and its electronic configuration is 1s\(^2\) 2s\(^2\) 2p\(^3\). The atom in its ground state has one unpaired electron so that it can form one covalent bond but in the excited state (shown in Figure 1.13), there are three unpaired electrons and hence three bonds of unequal strength can be formed with three fluorine atoms. But all bonds are of equal strength. In order to explain this, it is assumed that one s and two p-orbitals of excited boron atom undergo hybridization to produce the three sp\(^3\) hybrid orbitals or equivalent energy. In the formation of BF\(_3\) molecule, the half-filled p-orbital of each fluorine atom overlaps with each of the half-filled sp\(^3\) hybrid orbitals of the boron atom (Figure 1.14).

In BF\(_3\), three bonds are equivalent and are 120\(^\circ\) apart. Therefore, the shape of BF\(_3\) is triangular and planar.

\[
\begin{array}{c}
2p & 2s & 1s \\
\hline
\bullet & \bullet & \bullet \\
\bullet & \bullet & \bullet \\
\end{array}
\]

Hybridisation in (A) = ground state of beryllium atom
(B) = excited state of beryllium atom
(C) = hybridised state of beryllium atom

Fig. 1.13

(ii) NO\(^3\) Ion. X-rays studies have shown this ion to be planar trigonal shape. This reveals that the central nitrogen atom has sp\(^3\) hybridization. But this ion is having a unit negative charge. Therefore, one of the three oxygen atoms would be assumed to be having an extra electron. Suppose three oxygen atoms are represented as O\(_x\) O\(_y\) and O\(_z\). The valence shell configurations of N, O\(_x\), O\(_y\) and O\(_z\) are as follows:

Fig. 1.14 Formation of BF\(_3\)
Chemical Periodicity:

N → 2s\(^2\), 2p\(^x\), 2p\(^y\), 2p\(^z\) \( (\psi = 1) \)

O\(_x\) → 2s\(^2\), 2p\(^x\), 2p\(^y\), 2p\(^z\) \( (\psi' = 2) \)

O\(_y\) → 2s\(^2\), 2p\(^x\), 2p\(^y\), 2p\(^z\) \( (\psi' = 2) \)

O\(_z\) → 2s\(^2\), 2p\(^x\), 2p\(^y\), 2p\(^z\) \( (\psi' = 3) \)

(NOTES)

(Having an Extra Electron)

The 2s, 2p, and 2p\(_x\) atomic orbitals of nitrogen undergo hybridization to form three sp\(^3\) hybrid orbitals. The half-filled 2p orbital does not take part in hybridization. Thus, the electronic configuration of nitrogen atom becomes as follows:

\[
\text{N} \rightarrow 2s^2 \left| 2p_x^1 \right| 2p_y^1 \left| 2p_z^1 \right| (\psi = 1)
\]

Hybrid orbital having an electron pair forms a coordinate bond with O\(_x\)-atom gives a covalent bond. Also the overlapping of the remaining half-filled 2p-orbital of O\(_x\)-atom gives another covalent bond. Half-filled 2p-orbital or N atom, which is not participating in sp\(^3\) hybridization, undergoes overlapping laterally with half-filled 2p orbital to form a p\(^x\)-p\(^y\) bond. Hence the structure of ion may be represented as follows:

\[
\text{O} - \text{N} \rightarrow \text{O}_x \quad \text{or} \quad \text{O} - \text{N} \rightarrow \text{O}
\]

Double bond is made up of one \(\sigma\) and one \(\pi\) bond. This double bond does not alter planar trigonal and symmetrical shape of ion in which O – N – O angle is 120° (Figure 1.15). In this all the three \(\sigma\) bonds are sp\(^3\) – p \(\sigma\) bonds.

![Fig. 1.15 Planar Trigonal Shape of NO\(_3\) Ion Resulting from sp\(^3\) Hybridization](image)

3. sp\(^3\) Hybridization. The mixing of three p-and one s-orbitals to form four orbitals of equal energy is known as sp\(^3\) hybridization. (Refer Figure 1.16)

Each sp\(^3\) hybrid orbital has 25% s-character and 75% p-character.
Properties of $sp^1$- Hybrid Orbitals

(i) The four $sp^3$ hybrids are directed towards the four corners of a regular tetrahedron whose centre is occupied by an atom that has undergone hybridization.

(ii) The predicted relative overlapping power of each of the $sp^3$ hybrid is 2.00 whereas it is 1.93 and 1.99 for $sp$ and $sp^3$ hybrid, respectively. This shows that $sp^3$ hybrids are the strongest as compared to $sp$ and $sp^3$.

(iii) The angle between hybrid orbitals should be 190° 28'.

![Diagram of $sp^3$ hybridization](image)

**Fig. 1.16 Formation of Four $sp^3$ Hybrid Orbitals by Overlapping One $s$ and Three $p$ Orbitals**

Typical example of $sp^1$-hybridization are:

(i) **Formation of $CH_4$ Molecule**: Carbon, the central atom is $CH_4$ has only two unpaired electrons in the ground state. In excited state, four unpaired electrons are available for bonding. The four bonds so formed should not be of equal strength but actually they are the equal strength. In methane, one $s$- and three $p$- orbitals of carbon atom undergo hybridization and form four equivalent $sp^3$-hybrid orbitals (Refer Figure 1.17).

![Diagram of CH4 molecule](image)

**Fig. 1.17 Hybridisation of a Carbon Atom**

There four hybrid orbitals conform four covalent bonds with hydrogen atoms to give a molecule of methane (Refer Figure 1.18).
NOTES

According to Sidwick–Powell theory, the repulsion between four orbitals is smallest if they point to the corner of a regular tetrahedron, and make a bond angles of 109°28'. The carbon atom is at the centre of the tetrahedron and four hydrogen atoms are at its corners.

(ii) Formation of Ethane Molecule: In ethane both the carbon atoms assume sp³ hybrid state. One of the sp³ orbitals of one carbon atom overlaps with one of sp³ orbitals of the other to establish a C-C σ bond. The other sp³ orbitals of each carbon atom overlap with s-orbitals of hydrogen from C-H σ bonds (Refer Figure 1.19).

(iii) Shape of NH₃: In a molecule of ammonia, nitrogen is the central atom and has three unpaired electrons in its ground state sufficient to form three bonds.

\[
\begin{array}{ccc}
1s & 2s & 2p \\
\uparrow\downarrow & \uparrow\downarrow & \uparrow\uparrow\uparrow \\
\uparrow\downarrow & \uparrow\downarrow & \uparrow\uparrow\uparrow
\end{array}
\]

Electronic structure of nitrogen atom (ground state)

Electronic structure of nitrogen having gained three electrons from three H atoms.

Three unpaired electrons in the 2p orbitals are sufficient to form three bonds with three hydrogen atoms resulting ammonia molecule without involving any excitation of the atom. Thus, the molecule having three orbitals would have been triangular in structure and also symmetrical and non-polar. But
actually ammonia molecule is asymmetrical with a high dipole moment and is pyramidal in structure. In order to explain it is postulated that the s-orbitals (containing a lone pair of electrons) hybridizes with three orbitals (each containing a bond pair of electrons) to give rise to four \( sp^3 \) hybrid orbitals of equivalent energy as shown in Figure 1.20.

According to the Sidgwick-Powell theory, the distribution of these four orbitals should be tetrahedral so that the force of repulsion between them is minimum.

The force of repulsion between a lone pair and a bond pair is greater than the force of repulsion between two bond pairs of electrons. Therefore, the molecule gets a little distortion and the bond angle \( H – N – H \) decreases from 109.5° to 107°. Thus, the shape of ammonia molecule is pyramidal having nitrogen atom at the centre, three hydrogen atoms at the base of the pyramid and the lone pair of electron at the apex of the pyramid, as shown in Figure 1.20.

![Fig. 1.20 Lone Pair of Electrons](image)

(iii) **Formation of Water Molecule:** In a molecule of water, oxygen, atom (central atom) has two unpaired electrons which are sufficient to form two bonds with hydrogen atoms, without involving any excitation of the oxygen atom. Like \( \text{BeF}_2 \), \( \text{H}_2\text{O} \) molecule involving only two orbitals should be linear and non-polar. According to some experimental evidences, water molecule has a bent structure and is highly polar. This latter structure of \( \text{H}_2\text{O} \) molecule can be explained on the basis of hybridization. Two lone pairs of electrons, and the other two containing bond pairs undergo hybridization to give four \( sp^3 \) hybrid orbitals of equivalent energy. According to Sidgwick-Powell theory, these hybrid orbitals should result in a tetrahedral structure having two corners occupied by hydrogen atoms and two occupied by one pairs of electrons as depicted in Figure 1.21.
NOTES

Chemical Periodicity

<table>
<thead>
<tr>
<th>1s</th>
<th>2s</th>
<th>2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
</tbody>
</table>

Oxygen atom (around state)

Oxygen atom, having gained two electrons from hydrogen atoms in H2O

Here the two lone pairs distort the bond angle more than at was distorted by the one lone pair of electrons in ammonia; the bond angle HOH in water is 104°27', (Refer Figure 1.21).

**Fig. 1.21 Shape of Water Molecule**

4. **sp^3d-Hybridization**: This type of hybridization in values mixing of one s-, three p- and one d- orbitals to form five sp^3d-hybrid orbitals which adopt trigonal bipyramidal geometry as shown in Figure 1.22.

**Fig. 1.22 Fine sp^3 - Hybrid Orbitals**

All these fine orbitals are not of the same type but they can be divided into two non-equivalent sets:

(i) The first set consists of three equivalent hybrid orbitals which are oriented in a plane towards the corners of a triangle. This set is known as equatorial set of orbitals in which the hybrid orbitals are inclined at 120 to each other. This set is supposed to be formed by the hybridization of one s and 2p_π orbitals forming three sp^3 hybrid orbitals.

(ii) The second set is known as axial set which consists of two equivalent hybrids, obtained by mixing one p_z and one orbitals. The hybrids of this set make an angle of 180 to each other but with the hybrids situated in the triangular plane they make an angle of 90.
**Example:** An interesting example involving sp’d hybridization is provided by PCl₅.

<table>
<thead>
<tr>
<th>Electronic structure of phosphorus atom</th>
<th>3s</th>
<th>3p</th>
<th>3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ground state)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphorus atom (excited state)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphorus having gained five electrons from chlorine atoms in PCl₅</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*sp’d hybridization*

The electronic configuration of phosphorus is 1s², 2s², 2p³, 3s², 3p⁴ and may be shown above. The phosphorus in its ground state has only three unpaired electrons. In order to explain the formation of PCl₅, five unpaired electrons are required. This can be achieved by the unpairing of electrons in the 3s orbital by the excitation of the atom. These five electrons (one s, three p and one d) undergo hybridization to five hybrid orbitals. These five hybrid orbitals combine with five chlorine atoms to give PCl₅. Thus, the phosphorus pentachloride has a trigonal bipyramidal structure as shown in Figure 1.23.

![Figure 1.23 Shape of PCl₅](image)

The structure is not symmetrical one and hence unstable. Thus PCl₅ is highly reactive and split into and ions in this solid state which have tetrahedral and octahedral structure respectively.

5. **Hybridisation of sp’d Type:** The mixing of one s, three p and two d orbitals to form 6 orbitals of equal energy is known as sp’d hybridization. All the six hybrid orbitals in energy.

**Example:** An interesting example is SF₆. The atomic number of sulphur atom is 16. Its electronic configuration is 1s², 2s², 2p⁶, 3s², 3p⁴. As sulphur atom has two unpaired electrons in 3p orbital, it means that it should combine with two fluorine atoms to form SF₆. But it forms SF₆. In order to explain its formation it is assumed that two paired electrons from 3s and 3p become unpaired and get excited to the vacant 3d orbitals by absorbing energy. Now six unpaired electrons are available which undergo sp’d hybridisation forming six hybrid orbitals which overlap with six unpaired 2p orbitals of six fluorine atoms forming SF₆.
In sulphur hexafluoride, the six hybrid orbitals are directed towards the six corners of a regular octahedron (Figure 1.24)

**Fig. 1.24 Octahedral Shape of SF₆**

**6. sp³d³ Hybridisation:** The mixing of one s, three p and three d orbitals to form seven orbitals of equal energy is known as sp³d³ hybridisation.

The sp³d³ hybrid orbitals are directed towards the corners of a pentagonal-bipyramid. These are not equivalent because five of them are directed towards the vertices of a regular pentagon whereas the remaining two are oriented perpendicular (90°) to the plane having the first set of five hybrid orbitals.

Iodine heptafluoride is perhaps the only example of seven orbitals and sp³d³ hybridisation. The shape expected is pentagonal bipyramid.

Axial I-F distances have not been found to be same as equatorial I-F distances. This confirms the non-equivalent nature of sp³d³ hybrid orbitals.

**Fig. 1.25 Pentagonal bipyramidal IФ molecule resulted from sp³d³ hybridisation**
7. **dsp²- Hybridisation**: Combination of one d-, one s-, and two p- orbitals gives four dsp² equivalent hybrid orbitals. There are directed towards the corners of a square in the xy-plane. In other words, it means that three hybrid orbitals point away from the origin in ±x and ±y directions of x- and y-axes (Figure 1.26).

![Figure 1.26 Four Square Planar dsp² Hybrid Orbitals](image)

8. **dsp³- Hybridisation**: It involves the combination of one d-, one s-, and three p- orbitals giving five non-equivalent dsp³ hybrid orbitals. There are directed towards the apices of a square pyramid. Out of the five hybrid orbitals, four are forming the based set of equivalent orbitals whereas the remaining fifth is farming the axial orbital as shown in Figure 1.27.

![Figure 1.27 Five Square Pyramidal dsp³ Hybrid Orbitals](image)

The number of outer orbitals and commonly occurring shapes and types of hybridisation are summarized.

<table>
<thead>
<tr>
<th>Number of Outer Orbitals</th>
<th>Shape</th>
<th>Hybridisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>Sp</td>
</tr>
<tr>
<td>3</td>
<td>Plane Triangular</td>
<td>sp²</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>sp³</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal Bipyramidal</td>
<td>sp³/s'</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>sp³/d²</td>
</tr>
<tr>
<td>7</td>
<td>Pentagonal Bipyramidal</td>
<td>sp³/d³</td>
</tr>
</tbody>
</table>
1.5 MOLECULES HAVING BOND PAIRS AND LONE PAIRS OF ELECTRONS - SHAPES OF POLYATOMIC MOLECULES

In some molecules, due to the present of lone pairs of electrons in the valence shell, there occurs some distortion in the shape of the molecule. Thus, the geometry of the molecule will not be the same as expected from typical cases of hybridization. Geometries of some such compounds are discussed below:

(i) SnCl₂ Molecule: It stannous chloride, tin has electronic structure of outermost shell as 5s², 5p⁰, 5p¹, 5p². In SnCl₂, two electrons are used for bond formation with two atoms of chlorine, while one electron pair is left unused as lone pair. Thus, there are three electron pairs – two bond pairs and one lone pair. The hybridization is sp² and SnCl₂ is expected to be trigonal planar but actually it is bent or V-shaped because of the greater repulsion due to lone pair (Figure 1.28)

![Figure 1.28 SnCl₂ Molecule](image)

(ii) Structure of XeF₂ Molecule:

Electronic configuration of Xe = 5s²5p⁰

and the electronic configuration for Xe²⁻ = 5s⁰5p⁰

Thus, in xenon two unpaired electrons are available which form covalent bonds with 2 fluorine atoms to give rise to the formation for XeF₂⁻.
Orbital representation of XeF$_4$

\[ \text{Sp\textsuperscript{d} hybridization trigonal bipyramidal with the three equatorial positions occupied by lone pairs.} \]

As XeF$_4$ involves sp\textsuperscript{d} hybridization, it means that the structure of XeF$_4$ may be trigonal bipyramid with three equatorial positions occupied by the lone electron pairs (Figure 1.29)

The structure of XeF$_4$ has been investigated by crystal structure study, Raman and infra-red spectra. All the study favours the trigonal bipyramidal structure in both the vapour and crystalline state.

![Fig. 1.29 Structure of XeF$_4$ Molecule](image)

(iii) Structure of XeF$_4$ Molecule

Electronic configuration of Xe in the ground state = \ldots 5s$^2$5p$^6$

Electronic configuration of Xe in the compound XeF$_4$

\[ \text{= \ldots 5s}^25p^65d^1 \text{structure of} \]

d$^4$sp$^3$ hybridization octahedral with two positions occupied by lone pairs.

Thus the formations of XeF$_4$, sp$^3$d$^2$ hybridisation is involved which gives rise to an octahedral shape with lone pairs projecting along the axis and fluorine atoms occupying the corners of a square plane having xenon at the centre (Figure 1.30)
(iv) **Structure of ClF₃:** In this compound chlorine is the central atom and three fluorine atoms are arranged around it.

The electronic configuration of fluorine atoms is

\[ \text{F} = 1s^2 \ 2s^2 \ 2p^5 \ 2p^3 \ 2p^1 \]

The electronic configuration of chlorine atom is

\[ \text{Cl} = 1s^2 \ 2s^2 \ 2p^6 \ 2p^3 \ 3p^5 \]

The electronic configuration of chlorine atom is

\[ \text{Cl} \text{ (excited)} = 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^4 \ 3d^1 \]

Electron configuration of chlorine atom

\[ \text{sp}^3 \text{d hybridization Trigonal bipyramidal with two positions occupied by lone pairs} \]

In the excited state of chlorine atom, three unpaired electrons are available which form three bonds with three fluorine atoms involving sp³d hybridization. Therefore ClF₃ may have trigonal bipyramidal structure like I, II and III with two positions occupied by lone pairs (Refer Figure 1.31) possible to predict which of the three possible arrangements I, II and III will be formed. From micro-wave data, the structure of ClF₃ is planar and T-shaped with bond angles almost 90°. This indicates structure (III). The slight distortion is due to the lone electron pair (IV).

**Fig. 1.30 XeF₂ Molecule**

**Fig. 1.31 Structure of Chlorine Trifluoride**
(V) Structure of IF₅: In this molecule, iodine is the central atom. The electronic configuration of fluorine atom is

\[ F = 1s^2 \ 2s^2 \ 2p^2 \ 2p^2 \ 2p^2 \]

The electronic configuration of iodine atom is given as

\[ I = 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^{10} \ 4s^2 \ 4p^6 \ 5s^2 \ 5p^6 \]

and that of excited state is put as:

\[ ^{3}I = 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^{10} \ 4s^2 \ 4p^6 \ 4d^0 \ 5s^2 \ 5p^5 \ 5d^6 \]

In the excited iodine atom, five unpaired electrons are available, resulting in \( sp^3d^5 \) hybridization.

Electronic configuration of Iodine atom

<table>
<thead>
<tr>
<th>5s</th>
<th>5p</th>
<th>5d</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑</td>
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<td>↑</td>
</tr>
</tbody>
</table>

(excited state)

Formation of IF₅

\[ \text{Formation of IF}_5 \]

\[ \text{sp}^3d^5 \text{ hybridisation} \]

Thus, IF₅ is formed by \( sp^3d^5 \) hybridization and has, therefore, an octahedral shape with one position occupied by lone electron pair (Figure 1.32(a))

![Figure 1.32](image)

Fig. 1.32 Structure of IF₅

Alternatively, IF₅ may be described as having square-based pyramid (Figure 1.32 (b)). The above structure of IF₅ has been confirmed by infra-red spectrum, Raman spectrum, the nuclear magnetic resonance and vibrational spectra.
Chemical Periodicity

5. What is electron affinity?
6. What is hybridization?
7. What are the different types of hybridisation?

1.6 ANSWERS TO CHECK YOUR PROGRESS

1. The periodic table is a chart that shows how chemical elements are related to one another. The various elements with the similar properties repeat after certain regular intervals. This repetition occurs when the elements are arranged in order of their increasing atomic numbers.

2. The term atomic radius for an atom is the distance from the centre of the nucleus to the outer shell of the atomic particle.

3. The term ionic radii refers to the size of the ions in the ionic crystals. Ionic radius thus may be defined as "the effective distance from the nucleus of the ion to the point upto which it has an influence in the ionic bond."

4. The voltage required to remove most loosely bound electron, from the isolated neutral atom to produce an ion is called ionization potential and is expressed in electron volts (eV).

5. The energy released when an extra electron is added to a neutral gaseous atom is called the electron affinity.

6. The phenomenon of mixing of the atomic orbitals and the formation of new orbitals of equal energy is known as hybridisation and the new orbitals formed are known as hybrid orbitals.

7. There are different types of hybridisation depending upon the type of orbitals involved in mixing, such as sp, sp², sp³, sp³d, sp³d², etc.

1.7 SUMMARY

- Periodic table thus may be defined as, the table giving the arrangement of all the known elements according to their properties so that similar elements fall within the same vertical column and dissimilar elements are separated.
- The word ‘periodic’ means that when elements are arranged in the order of their atomic numbers, there appears a periodicity, i.e., repetition not only in their chemical properties but also in the physical properties.
- The periodic table is a chart that shows how chemical elements are related to one another. The various elements with the similar properties repeat after certain regular intervals.
• The modern periodic table of elements consists of 18 vertical columns and 7 horizontal rows.
• On the basis of valence shell electronic configuration, periodic table is divided into four (i.e. s, p, d and f) distinct blocks of elements.
• The term atomic radius for an atom is the distance from the centre of the nucleus to the outer shell of the atomic particle.
• The metallic radius may be defined as one-half of the distance between atoms of a metal in the metalic close packed crystal lattice in which the metal exhibits a co-ordination number of twelve.
• Van der Waal’s radii or collision radii is the distance between two non-bonded atoms of two adjacent molecules.
• The covalent radius of an atom is equal to half the internuclear distance between two identical atoms that are joined by a covalent bond.
• Ionic radius thus may be defined as “the effective distance from the nucleus of the ion to the point upto which it has an influence in the ionic bond.”
• The voltage required to remove most loosely bound electron, from the isolated neutral atom to produce an ion is called ionization potential and is expressed in electron volts (eV).
• The energy released when an extra electron is added to a neutral gaseous atom is called the electron affinity.
• Electronegativity is the tendency of an atom in a molecule to attract electron towards itself the showed pair of electrons.
• The phenomenon of mixing of the atomic orbitals and the formation of new orbitals of equal energy is known as hybridisation and the new orbitals formed are known as hybrid orbitals. The bonds formed by such orbitals are called hybrid bonds. The compounds which are formed from these bonds are known as hybrids.
• There are different types of hybridisation depending upon the type of orbitals involved in mixing, such as sp, sp², sp³, sp³d, sp³d² etc.

1.8 KEY WORDS

• Ionic radius: It refers to radius of the atom’s ions in the ionic crystals.
• Ionization potential: It is the minimum amount of energy required to remove the most loosely bound electron of an isolated neutral gaseous atom or molecule.
• Electron affinity: It is the energy released when an extra electron is added to a neutral gaseous atom.
1.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

NOTES

Short Answer Questions
1. Define the following terms.
   (i) Atomic radii
   (ii) Ionic radii
   (iii) Ionization energy
   (iv) Electron affinity
2. What are artificial elements?
3. What are the different types of atomic radii?
4. What are the factors influencing the magnitude of Ionic Radii?
5. What are the factors controlling the values of ionization potential?
6. Discuss the factors on which electron affinity depends.

Long Answer Questions
1. What is historical background of element classification?
2. Explain the block wise classification of periodic table.
3. What are the different methods to determine the ionic radii? Explain.
4. Explain the various applications of electro negativity.
5. What are the different types of hybridisation? Explain each with an example.
6. Draw the shapes of any two polyatomic molecules. Also, give necessary explanation.

1.10 FURTHER READINGS


UNIT 2 VSEPR THEORY

Structure
2.0 Introduction
2.1 Objectives
2.2 Valence Shell Electron Pair Repulsion (VSEPR) Theory
2.3 Shape of Molecules/Ions (Only σ-bps Around Central Atom and no lps)
2.4 Shape of Molecules/Ions (With σ-bps as well as lps Around the Central Atom)
2.5 Oxyfluorides of Xenon
2.6 Answers to Check Your Progress Questions
2.7 Summary
2.8 Key Words
2.9 Self Assessment Questions and Exercises
2.10 Further Readings

2.0 INTRODUCTION

Covalent bonds are directional in nature, so the atoms constituting the molecules occupy definite positions with respect to one another. This definite arrangement of the bonded atoms in a molecule is known as geometry of the molecule. The space model which is obtained by joining the points representing various bonded atoms describes the shape of the molecule. VSEPR theory provides the simple method to predict the shape or geometry of simple covalent molecules and ions of non-transition elements. This theory was firstly proposed by Sidgwick and Powell in 1940 and was further improved by Gillespie and Nyholm in 1957. This theory is primarily based upon the fact that in a polyatomic molecule, the direction of bonds around the central atom depends upon the total number of electron pairs (bonding as well as non-bonding) in its valence shell. These electron pairs place themselves as far apart as possible in space so as to have minimum repulsive interactions between them. The minimum repulsions corresponded to the state of minimum, energy and maximum stability of the molecule.

In this unit, you will study about valence shell electron pair repulsion theory, shape of molecules/ions, oxyfluorides of xenon in detail.

2.1 OBJECTIVES

After going through this unit, you will be able to:

- Discuss the postulates of VSEPR theory
- Draw the shapes of molecules/ions having only σ-bps around central atom and no lps
- Shape of molecules/ions with σ-bps as well as lps around the central atom
2.2 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

The main postulates of this theory are:

1. According to Lewis structure of a given molecule or ion only the valence shell electrons of the central atom participate in bonding forming various bonds. Based on the nature of central atom’s valence shell surrounding the central atom, the various species can be grouped into following categories:
   (a) Species whose central atom is surrounded by σ-bonding electrons pairs (σ-bps) only. Examples of such species are BeF₂, CH₄, PF₃, SF₆, IF₆ etc.
   (b) Species whose central atom is surrounded by σ-bps as well as by lone pairs of electrons (lps). Examples of such species are SnCl₂, NH₃, H₂O, SF₆, SIF₆, XeF₆, IF₆, XeF₆ etc.
   (c) Species whose central atom is surrounded by σ-bps as well as by π-bps. Lps are absent. Examples of such species are CO₂ (O = C = O), HCN (H-C≡N), H₂C₂ (H-C≡C-H), etc.
   (d) Species whose central atom is surrounded by σ-bps, lps and π-bps.

   Examples are SO₂ (O = S → O) ClO₃⁻
   \[ \text{O} \leftarrow \text{Cl} \rightarrow \text{O} \]
   \[ \downarrow \]
   \[ \text{O}^- \]

The type of spatial arrangement (for example, linear, trigonal planar, tetrahedral, etc.) the electron pairs surrounding the central atom depends on the sum of σ-bps and lps surrounding the central atom. The presence of π-bps does not influence the spatial arrangement of the electron pairs. The spatial arrangement takes place in such a way that the electron pairs occupy their positions in space as far away from each other as possible because in this case the electrostatic repulsion between the electron pairs is reduced to minimum. The system with minimum repulsive forces is the most stable.

It has been observed that when (σ-bps + lps) is equal to 2, 3, 4, 5, 6 and 7, the spatial orientation of these electron pairs round the central atom is linear (angle – 180°), trigonal planar (angle = 120°), tetrahedral (angle = 109.5°), trigonal bipyramidal (angle = 120°, 90°), octahedral (angle = 90°) and pentagonal bipyramidal (angle = 72°, 90°). The orientation of π-bps for the molecules whose central atom is surrounded only by σ-bps and no lps is shown in Figure 2.1 in which A is the central atom and B are the surrounding atoms with which A (central atom) is linked by σ-bps only.
Fig. 2.1 Spatial Arrangement of 2, 3, 4, 5, 6 and 7 σ-bonding Electron Pairs (σ-bps) Round the Central Atom (A). The Central Atom is not Surrounded by Any Lone Pair of Electrons (Lps). B are the Atoms with which Central Atom (A) is Linked by σ-bps.

2. While determining geometry of a given molecule or ion on the basis of VSEPR theory, the presence of π-bps surrounding the central atom of the species should not be considered, since these electron pairs do not influence the geometry of the molecule or ion. It is only σ-bps and Lps surrounding the central atom which decide the shape of the species and hence only these electron pairs (i.e., σ-bps and Lps) should be considered.

3. If the central atom is surrounded purely by σ-bps, then the shape (geometry) of the molecule or ion is the same as the spatial arrangement of the σ-bps round the central atom. However, if the central atom is surrounded by σ-bps as well as by Lps, then the geometry of the molecule or ion gets distorted from its expected geometry and becomes different from the spatial arrangement of (σ-bps + Lps) (Refer Table 2.1). Due to the presence of Lps, bond angle also becomes different from the expected bond angle between the σ-bps. For example since C-atom (central atom) in CH₄ molecule is surrounded only by four σ-bps, it has the expected tetrahedral shape with the expected H-C-H bond angle of 109.5° (expected angle). On the other hand, since N-atom (central atom) in NH₃ molecule is surrounded by three σ-bps and one lp, it does not have the tetrahedral shape; rather it has pyramidal shape with H-N-H bond angle = 107.5°.
Table 2.1 Effect of Lone Pairs of Electrons (lps) on the Geometry of a Given Species

<table>
<thead>
<tr>
<th>No. of (σ-bps + lps) surrounding the central atom and examples of molecules/ions having these electron pairs</th>
<th>No. of σ-bps and lps. Type of molecule/ion is given in bracket</th>
<th>Spatial arrangement of σ-bps + lps. Bond angle are given in parentheses</th>
<th>Actual shape (Geometry of the molecule/ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. BeF₂, BeCl₂</td>
<td>σ-bps = 2  λ = 0 (AB₁)</td>
<td>Linear (180°)</td>
<td>Linear</td>
</tr>
<tr>
<td>2. BF₃, BCl₃, GaCl₃, BH₃, SnCl₃, PbCl₂</td>
<td>σ-bps = 3  λ = 0 (AB₁)  λ = 1 (AB₂)</td>
<td>Trigonal planar (120°)</td>
<td>Trigonal planar V-shape or Angular</td>
</tr>
<tr>
<td>3. CH₄, CCl₄, SiCl₄*, BH₄, NH₃, PH₃, PX₃, H₂O₂, H₂S₂</td>
<td>σ-bps = 4  λ = 0 (AB₁)  λ = 1 (AB₂)  λ = 2 (AB₃)</td>
<td>Tetrahedral (109.5°)</td>
<td>Tetrahedral Trigonal pyramidal V-shape or Angular</td>
</tr>
<tr>
<td>4. PCl₅, (g), PF₅, SBCl₅, SF₅, TeCl₆, CCl₄*, BF₅, BF₃, IC₃, IF₃, XeF₂, IC₃⁻</td>
<td>σ-bps = 5  λ = 0 (AB₁)  λ = 4 (AB₄)  λ = 2 (AB₂)  λ = 3 (AB₃)</td>
<td>Trigonal bipyramidal (120°, 90°)</td>
<td>Trigonal bipyramidal Trigonal bipyramidal Trigonal bipyramidal</td>
</tr>
<tr>
<td>5. SF₆, TeF₆, (SF₆)²⁺, BrF₅⁺, BrF₃, BrCl₆, SF₅⁻, XeF₂, IC₃⁻</td>
<td>σ-bps = 6  λ = 0 (AB₁)  λ = 5 (AB₅)  λ = 4 (AB₄)  λ = 2 (AB₄)  λ = 3 (AB₃)</td>
<td>Octahedral (90°, 90°)</td>
<td>Octahedral Octahedral Square planar</td>
</tr>
<tr>
<td>6. IF₇</td>
<td>σ-bps = 7  λ = 0 (AB₁)  λ = 6 (AB₆)</td>
<td>Pentagonal bipyramidal (72°, 90°)</td>
<td>Pentagonal bipyramidal Distorted octahedral</td>
</tr>
</tbody>
</table>

NOTES

4. σ-bps are considered to be localized between the two atoms linked together by covalent bond while a lp is held by only one atom, i.e., bonding electron pair is under the influence of two atoms and a lp is under the influence of

Self-Instructional Material
one atom only, viz., central atom. Thus we expect that the orbital containing an lp is more spread out in space in comparison to that (i.e., orbital) which contains a bonding electron pair. Consequently an lp will exert more repulsion on the bonding electron pair as compared to the repulsion exerted by a bonding electron pair on the other bonding electron pair as,

$$(lp - bp) > (bp - bp) \quad ...(2.1)$$

On similar lines of argument it can be shown that:

$$(lp - lp) > (lp - bp) \quad ...(2.2)$$

On combining the above two relations we get:

$$(lp - lp) > (lp - bp) > (bp - bp) \quad ...(2.3)$$

Relation (2.3) gives us the order of the magnitude or repulsion between electron pairs.

The repulsions between the electron pairs at 90° are stronger than that between the electron pairs at 120°. These repulsions are the weakest (lowest) when the electron pairs are at 180°.

### 2.3 SHAPE OF MOLECULES/IONS (ONLY σ-BPS AROUND CENTRAL ATOM AND NO LPS)

1. **AB₂ Types (Linear Species)**

Consider the BeCl₂ molecule in vapour phase. The Lewis structure of this molecule is Cl-Be-Cl in which the central atom (Be-atom) is surrounded by two σ-bps and no lp. These two σ-bps will occupy their positions as far apart as possible so that the electrostatic repulsion between them is reduced to minimum. This is possible only when these bonding electron pairs are at 180° about the central atom, i.e. the bonding electron pairs occupy positions on the opposite sides of Be-atom forming Cl-Be-Cl angle equal to 180°.

Thus BeCl₂ molecule in the vapour phase has linear geometry.

Other examples of linear molecules are CO₂, MCN, HC≡CH.

2. **AB₃ type (Trigonal Planar species)**

Consider the following examples.

(a) **BCl₃ Molecule**: Lewis structure of the molecule is $\begin{bmatrix} Cl & B - Cl \\
Cl & Cl \end{bmatrix}$ which shows that B-atom (central atom) is surrounded by three σ-bps and no lp. This molecule can have any of the two shapes shows in Figure
2.2. T-shaped geometry has two bp-bp repulsions at 90° and one bp-bp repulsion at 180°, while trigonal geometry has three bp-bp repulsions at 120°. Consequently in hence this structure is the most probable structure of BCl$_3$ molecule. BBr$_3$, GaCl$_3$ and BH$_3$ molecules also have trigonal planar geometry.

Fig. 2.2 Two Possible Shapes of BCl$_3$ Molecule

(b) SO$_3$ Molecule: Lewis structure of this molecule as given alongside (fig. 12.3) suggests that S-atom (central atom) is linked with one O-atom by a double bond and with two O-atoms by coordinate (covalent) bonds. Now since S-atom is surrounded by three π-bps and no lp (π-bonds have not been considered), SO$_3$ molecule, like BCl$_3$ molecule, has trigonal geometry as shown in Figure 2.3.

Fig 2.3 Lewis Structure and Trigonal Planar Shape of SO$_3$ Molecule

3. AB$_3$ Type (Tetrahedral Species): Common examples of this type include:

\[
\text{H} \\
\text{H} \\
\text{C} \\
\text{H}
\]

(a) CH$_4$ molecule: Lewis structure of this molecule is \( H - C - H \) which shows that C-atom (central atom) is surrounded by four σ-bps and no lp. This molecule can have any of the two structures shown in Figure 2.4.
Fig. 2.4 Two Possible Structures of CH₄ Molecule

Clearly, since the repulsive interactions in tetrahedral shape are minimum, this shape is the most probable shape of CH₄ molecule. A tetrahedron is a solid figure which contains four faces each of which is an equilateral triangle. Each of the four H-C-H bond angles is equal to 190.5°.

CCl₄ and SiCl₄ molecules also have tetrahedral geometry.

(b) NH₄⁺ and SO₄²⁻ ions: Lewis structure of these ions can be written as:

\[
\begin{array}{c|c}
H^+ & O^- \\
\uparrow & | \downarrow \\\nH-N-H & O-S-O \\
\mid & \mid \mid \\
H & H
\end{array}
\]

Since N-atom in NH₄⁺ ions and S-atom is SO₄²⁻ ions are surrounded by four electron pairs, both these ions have tetrahedral shape as shown in Figure 2.5 H-N-H and O-S-O bond angles are equal to 109.5°.

See hard copy

Fig. 2.5 Tetrahedral Shape of NH₄⁺ and SO₄²⁻ Ions.

4. AB₅ Type (Trigonal Bipyramidal Species): In this type, we will discuss the shape of PF₅ molecule. Lewis structure of the molecule is
VSEPR Theory

which shows that the central atom P is surrounded by five σ-bonds and no π-bonds. Theoretically PF₅ molecule can have any of the geometries shown in Figure 2.6. Of these three geometries, in trigonal bipyramidal shape the bp-bp repulsion are minimum and hence, this is the most probable geometry. PCI₃ (g), SbCl₅ etc., have similar geometries.

![Figure 2.6 Three Possible Geometries of PF₅ Molecule](image)

5. **AB₅ Type (Octahedral Species):** Common examples of this type are SF₆ and TeF₆. We will discuss the geometry of SF₆. The Lewis structure of this molecule is 

![Lewis Structure of SF₆](image)

The S-atom is surrounded six σ-bonds and no π-bonds.

This molecule may have various structures as shown in Figure 2.7. Of these structures, octahedral structure is most stable, each F-S-F bond angle is equal to 90°.

![Figure 2.7 Three Possible Geometries of SF₆ Molecule](image)

- **Planar pentagonal structure:** (bond angle = 72°, bp-bp repulsions at 72° = 5)
- **Square pyramidal geometry:** (bond angle = 90°, bp-bp repulsions at 90° = 8)
- **Trigonal bipyramidal geometry:** (bp-bp repulsions at 90° = 6)

**Planar hexagonal geometry:** (bp-bp repulsions at 60° = 6). These repulsions are strong.
6. **AB, Type (Pentagonal Bipyramidal Species):** Commonest example of this type is IF₇. Lewis structure of the molecule is which shows that the central atom I is surrounded by seven σ-bps only and no lp. So, according to VSEPR theory, this molecule has pentagonal bipyramidal geometry as shown in Figure 2.8.

![Pentagonal Bipyramidal Structure of IF₇ Molecule](image)

**Fig. 2.8** Pentagonal Bipyramidal Structure of IF₇ Molecule

### 2.4 SHAPE OF MOLECULES/IONS (WITH σ-BPS AS WELL AS LPS AROUND THE CENTRAL ATOM)

When lone pairs are also present in addition to bond pairs around the central atom, the repulsive interactive between the electron pairs around the central atom become unequal. This causes distortion in geometrical arrangement of electron pairs. Such a molecule is said to have an irregular or distorted geometry. Let us consider the structure of the species of the following types:

1. **ABₓ (Ip) Type:** There species contain two σ-bps and one Ip. Common examples are SOₓ, SCNₓ, PbClₓ etc. Consider the structure of SOₓ molecule. Lewis structure of the molecule is O=S→O.

   The S-atom (central atom) is surrounded by two σ-bps and on op (σ-bps = 2 and Ip = 1). The spatial arrangement of these three electron pairs round the central atom is trigonal planar (according to VSEPR theory). Due to the presence of one Ip which occupies one of the three vertices of the triangular plane, the shape of SOₓ molecule is not trigonal planar but it is angular with O-S-O bond angle equal to 120°.
**NOTES**

**Fig. 2.9** Angular Shape of SO$_2$ Molecule

2. **AB$_{1}$(lp) Type:** These species contain three $\sigma$-bonds and one lp. The common examples of this type are NH$_3$, PCl$_3$, PH$_3$, RNH$_3$ etc. Here we will consider the example of NH$_3$, Lewis structure of this molecule is which shows that since N-atom (central atom) is surrounded by 4 electron pairs ($\sigma$-bonds = 3 and lp = 1), the spatial arrangement of these four electron pairs round N-atom (central atom) is tetrahedral (according to one of the postulates of VSEPR theory). Due to the presence of one lp at one of the four vertices of the tetrahedron, the shape of NH$_3$ molecule is not tetrahedral but it gets distorted and becomes trigonal pyramidal as shown in Figure 2.10

**Fig. 2.10** (a) Trigonal Pyramidal Shape of NH$_3$ Molecule. lp Indicates a Lone Pair of Electrons. (b) To Explain by H-N-H Bond Angle is NH$_3$ is Less than the Tetrahedral Bond Angle (~ 109.5°). lp Indicates a Lone Pair of Electrons on N-Atom

Although the orientation of 4 electron pairs ($\sigma$-bonds = 3, lp = 1) round N-atom is tetrahedral, H-N-H bond angle is not equal to the expected tetrahedral angle (109.5°); rather this angle is 107.5° which is less than 109.5°. Why H-N-H bond angle is less than 109.5° has been explained as follows:

We know that, according to VSEPR theory, repulsion in comparison to that of (lp - lp) repulsion that the two N-H bonding electron pairs are pushed closer to each other and the result is that H-N-H bond angle decreases from the expected tetrahedral bond angle (~109.5°) and becomes 107.5°. (Refer Figure 2.10)
3. **AB₂(lp) Type**: These species contain two σ-bps and two lps. Common examples of this type are H₂O, SeCl₂, SCl₂, ICl₂ etc. Consider the example of H₂O molecule. Lewis structure of this molecule is

Here the central atom O is surrounding by two σ-bps and two lps. According to VSEPR theory, the orientation of these 4 electron pairs should be tetrahedral. Due to the presence of two lps located at two tetrahedral positions, the shape of H₂O molecule get distorted from tetrahedral shape to bent an V-shaped as shown in Figure 2.11.

![Figure 2.11 Angular (V-Shaped or Bent) Structure of H₂O](image)

The H-O-H bond angle is H₂O is not equal to the expected tetrahedral angle (109.5°) rather this angle is equal to 105.5°.

We know that, according to VSEPR theory the magnitude of the repulsion between electron pairs is in the order:

(\( lp - lp \)) > (\( lp - bp \)) > (\( bp - bp \))

The above order shows that (\( lp - lp \)) repulsion is the maximum, (\( lp - bp \)) repulsion is medium while (\( bp - bp \)) repulsion is minimum. The two lps on O-atom not only repel each other, but also repel the two bps. The repulsion between two lps pushes the two O – H bonding electron pairs closer to each other and this results in that H–O–H bond angle decreases from the expected tetrahedral bond angle (109.5°) and becomes 105.5°. (Refer Figure 2.12)

![Figure 2.12 The Explain Why H-O-H Bond Angle is H₂O Molecule is Less than the Tetrahedral Bond Angle](image)

4. **AB₃(lp) Type**: In these species there are four σ-bps and one σ-bps. Common examples include SF₆, TeCl₆, SeCl₆ etc. Lewis structure of this
molecule is \( \text{SF}_6 \) which shows that since S-atom (central atom) is surrounded by five electron pairs (\( \sigma\)-b.ps = 4 and \( \text{lp} = 1 \)), the spatial arrangement of these electron pairs round S-atom is trigonal bipyramidal. Due to the presence of one lp of electrons, \( \text{SF}_6 \) molecule has irregular or distorted tetrahedral (also called see-saw) geometry in which the lp can occupy either one of the two axial positions or one of the three equatorial (also called basal) positions. Thus theoretically \( \text{SF}_6 \) molecule can have any of the two distorted tetrahedral geometries shown in Figure 2.13.

![Figure 2.13 Two Possible Geometries of \( \text{SF}_6 \) Molecule](image)

5. \( \text{AB}_n (\text{lp}) \), Type: These species have three \( \sigma\)-b.ps and two lps species of this type include inter halogen compounds like \( \text{ClF}_2 \), \( \text{BrF}_3 \), etc. Consider the case of \( \text{ClF}_3 \) molecule. Lewis structure of this molecule is \( \text{Cl}-\text{F}\cdots\text{F} \) which indicates that since Cl-atom (central atom) is surrounded by five electron pairs 9 \( \sigma\)-b.ps = 3 and \( \text{lp} = 2 \), the spatial orientation of these 5 electron pairs round Cl-atom is trigonal bipyramidal. Due to the presence of two lps, \( \text{ClF}_3 \) molecule has slightly bent T-shaped structure.

Theoretically, depending on the position occupied by the two lps. \( \text{ClF}_3 \) molecule can have any of the three geometries namely (a), (b) and (c) shown in Figure 2.14.

![Figure 2.14 Three Possible Geometries of \( \text{ClF}_3 \) Molecule](image)
If we do not consider the electron pair electron pair repulsions where the angle between them is greater than 100°, we find that geometry (c) in which both the lps occupy the equatorial positions of the trigonal bipyramid involves minimum repulsion. Thus geometry (c) which is called bent T-shaped geometry is the most stable geometry for CIF₃ molecule i.e., CIF₃ molecule or any other molecule or ion of AB₅ (lp) type has bent T-shaped geometry.

Each of the F–Cl–F (F–Cl–F) bond angles is equal to 87.5°. The basal Cl–F(Cl–F) bond length is equal to 1.60 Å.

6. **AB₅ (lp) Type:** These species have two σ-bps and three lps. Common example of this type is XeF₃. Lewis structure of this molecule is F – X =e – F which shows that since Xe=atom (central atom) is surrounded by five electron pairs (σ-bps = 2 and lps = 3), the spatial arrangement of 5 electron pairs round the central atom (Xe=atom) is trigonal bipyramidal. Due to the presence of three lps, XeF₃ molecule assumes linear shape with F–Xe–F bond angle equal to 180°.

Depending on the positions occupied by the three lps, XeF₃ molecule can have any of the three structures shown in Figure 2.15. The number of electron pair-electron pair repulsions shown in each geometry indicates that this repulsion in geometry (c) is minimum and hence this geometry is the most stable. In other words we can say that all the three lps occupy the equatorial positions of the trigonal bipyramid and hence XeF₃ or any other species of AB₅ (lp) type has linear shape in which the length of each of Xe–F bonds is equal to 2.0 Å.

![Fig 2.15 Three Possible Geometries of XeF₃ Molecule](image)

7. **AB₅ (lp) Type:** These species have five σ-bps and one lp. Common examples include IF₅, BrF₅, CIF₅ etc. Consider the case of IF₅ molecule.

Lewis structure of this molecule is . This structure shows that I-
atom (central atom) is surrounded by six electron pairs (σ-bps = 5 and lp = 1) and hence the spatial arrangement of the six electron pairs round I-atom is octahedral. The lone pair of electrons may occupy either one of the four equatorial positions of the octahedron or any of the two axial position of the octahedron. Thus, depending on the position occupied by the lp, IF₅ molecule may have any of the two geometries viz., (a) and (b) shown in Figure 2.16.

It has been shown that the (lp – bp) repulsion in geometry (b) is minimum and hence IF₅ molecule assumes square pyramidal shape shown at (b) of Figure 2.16. In this geometry the lp occupies the axial position.

![Diagram](image)

**Fig. 2.16 Two Possible Geometries of IF₅ Molecule**

8. **AB₅ (lp)₂ Type:** These species contain four σ-bps and two lps XeF₅ is the commonest example. Lewis structure of this molecule is \( \text{Xe} \sim \text{F} \sim \text{F} \sim \text{F} \sim \text{F} \). This structure clearly shows that since Xe-atom (central atom) is surrounded by six electron pairs (σ-bps = 4 and lps = 2), spatial arrangement of these six electron pairs round Xe-atom is octahedral.

Depending on the positions occupied by the two lps, XeF₅ molecule can have any of the three geometries (a), (b) and (c) depicted in Figure 2.17. It has been observed that electron pair-electron pair repulsions in geometry (c) in which the two lps occupy the axial positions of the octahedron are minimum and XeF₅ has square planar geometry in which each of the two \( \text{F}_2\text{XeF}_3 \) bond angles is equal to 90° and each of the four \( \text{Ex} \sim \text{F} \) bond angles is equal to 90° and each of the four \( \text{Xe} \sim \text{F}_5 \) bond lengths is equal to 1.95 Å.
2.5 OXYFLUORIDES OF XENON

Xenon is a noble gas. The term noble gas is used to describe the elements in Group 18 (VIIIA) of the periodic table. ‘Noble gas’ suggests a group of elements that is “too far above other elements” to react with them. The noble gases are also called the inert gases and only react with other elements under very unusual conditions.

Xenon is very rare in the atmosphere. Its abundance is estimated to be about 0.1 parts per million and hence it does not have many practical applications. Mostly, it is used to fill specialized lamps.

Symbol - Xe
Atomic Number - 54
Atomic Mass - 131.29
Family - Group 18 (VIIIA), Noble Gas

Xenon has different oxides, fluorides and oxyfluorides. A number of xenon oxyfluorides are known, including XeOF, XeOF₂, XeO₂F₂, and XeO₃F₂. XeOF is formed by reacting OF₂ with xenon gas at low temperatures. It may also be obtained by partial hydrolysis of XeF₄. It disproportionates at ~20°C.
into \( \text{XeF}_2 \) and \( \text{XeO}_2 \text{F}_2 \). \( \text{XeOF}_2 \) is formed by the partial hydrolysis of \( \text{XeF}_6 \), or the reaction of \( \text{XeF}_6 \) with sodium perxenate, \( \text{Na}_2\text{XeO}_4 \). The latter reaction also produces a small amount of \( \text{XeO}_2 \text{F}_2 \). \( \text{XeOF}_2 \) reacts with CsF to form the \( \text{XeOF}_4^- \) anion, while \( \text{XeOF}_2 \) reacts with the alkali metal fluorides \( \text{KF}, \text{RbF} \) and \( \text{CsF} \) to form the \( \text{XeOF}_4^- \) anion.

### Methods of Preparation of Xenon Oxyfluorides

Xenon tetrafluoride and Xenon hexafluoride undergoes partial hydrolysis to give oxyfluorides, such as Xenon Oxydifluoride (\( \text{XeOF}_2 \)), Xenon Oxytetrafluoride (\( \text{XeOF}_4 \)) and Xenon Dioxydifluoride (\( \text{XeOF}_2 \)) as shown below.

\[
\begin{align*}
\text{XeF}_4 + \text{H}_2\text{O} & \rightarrow \text{XeOF}_2 + 2\text{HF} \\
\text{XeF}_6 + \text{H}_2\text{O} & \rightarrow \text{XeOF}_2 + 2\text{HF} \\
\text{XeF}_8 + 2\text{H}_2\text{O} & \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}
\end{align*}
\]

### Xenon Oxydifluoride (\( \text{XeOF}_2 \))

It is formed by partial hydrolysis of \( \text{XeF}_2 \) at 193 K, as shown in the given reaction.

\[
\text{XeF}_2 + \text{H}_2\text{O} \xrightarrow{193\text{K}} \text{XeOF}_2 + 2\text{HF}
\]

The structure of \( \text{XeOF}_2 \) has trigonal bipyramid geometry due to sp\(^3\) d-hybridization of Xe. Two equatorial positions are occupied by lone pairs of electrons giving a T-shape to the molecule. There is one Xe–O double bond containing p\(\Delta\)–d\(\Delta\) overlapping.

![Structure of Xenon Oxydifluoride](image)

The sp\(^3\) d-hybridization remains valid, 3 bonds, 2 lone pairs for xenon. The two equatorial lone pairs create a T-Shaped molecule as shown below.

**Fig. 2.18 Structure of \( \text{XeOF}_2 \)**

The structure of compound \( \text{XeOF}_2 \), shows that the central Xe atom is sp\(^3\) d-hybridized, and contains 2\(\Delta\)p and 3\(\Delta\)p. Therefore according to the Bent rule, the
molecule has trigonal bipyramidal structure in which two lone pairs and one Xe = O bond occupies the three equatorial position.

**Xenon Dioxydifluoride (F₂O₂Xe)**

It has a chemical structure of a molecule includes the arrangement of atoms and the chemical bonds that hold the atoms together. The Xenon dioxydifluoride molecule contains a total of 4 bonds. There are 4 non-H bond(s), 2 multiple bond(s) and 2 double bond(s). Following is the figure of the chemical structure of Xenon dioxydifluoride.

![2D Chemical Structure Image of Xenon Dioxydifluoride (F₂O₂Xe)](image)

The 2D chemical structure image of Xenon dioxydifluoride is also called skeletal formula, which is the standard notation for organic molecules. The central atom in xenon dioxydifluoride undergoes sp³d hybridisation. Xenon dioxydifluoride has seven electron pairs. Of these, six are bond pairs and one is a lone pair. The structure of Xenon dioxydifluoride is considered as see-saw owing to the presence of a lone pair of electrons on the central Xenon atom.

**Xenon Oxytetrafluoride (XeOF₄)**

It is an inorganic chemical compound. As are most xenon oxides, it is extremely reactive and unstable, and hydrolyses in water to give dangerously hazardous and corrosive products, including hydrogen fluoride:

$$2\text{XeOF}_4 + 4\text{H}_2\text{O} \rightarrow 2\text{Xe} + 8\text{HF} + 3\text{O}_2$$

In addition, some ozone and fluorine are also formed. This reaction is extremely dangerous, and xenon oxytetrafluoride should therefore be kept away from any trace of water or water vapour under all conditions. Xenon oxytetrafluoride is a colourless liquid.

The reaction of XeF₄ with small amounts of water produces XeOF₄ which will appear as an impurity in most XeF₄ samples unless it is handled in completely dry equipment. Further reaction with water produces the explosive XeO₄. However, if the hydrolysis is carried out slowly at low temperature with large excess of H₂O, the XeF₄ may be quantitatively converted to an aqueous solution of XeO₄.

The central atom Xe is sp³d³ hybridized containing 1lp 5sp, therefore the structure is square pyramidal as shown below.
Fig. 2.20 2-Dimensional (2D) Chemical Structure Image of Xenon
Oxytetrafluoride (XeOF₄)

The central atom in Xenon oxytetrafluoride undergoes sp³d² hybridisation. Xenon oxytetrafluoride contains seven electron pairs, of these, six are bond pairs and one is a lone pair. The structure of xenon oxytetrafluoride is square pyramidal owing to the presence of a lone pair of electrons on the central Xenon atom.

Reactions

\[ \text{XeOF}_4 + \text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 2\text{HF} \]
\[ \text{XeO}_2\text{F}_2 + \text{H}_2\text{O} \rightarrow \text{XeO}_4 + 2\text{HF} \]

XeO₄ is a dangerous explosive, decomposing explosively to Xe and O₂:

\[ 2\text{XeO}_4 \rightarrow 2\text{Xe} + 3\text{O}_2 \]

Table 2.2 Hybridization and Shapes of Some Oxyfluorides

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Hybridization</th>
<th>Geometry</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeOF₂</td>
<td>sp³d</td>
<td>Trigonal</td>
<td>I-Shaped</td>
</tr>
<tr>
<td>XeOF₂⁺</td>
<td>sp³d²</td>
<td>Square Pyramidal</td>
<td>Square Pyramidal</td>
</tr>
<tr>
<td>XeO₂F₂</td>
<td>sp³d</td>
<td>Trigonal</td>
<td>Distorted</td>
</tr>
<tr>
<td>XeO₂F₂⁺</td>
<td>sp³d²</td>
<td>Trigonal</td>
<td>Trigonal</td>
</tr>
<tr>
<td>XeO₂F₄</td>
<td>sp³d²</td>
<td>Octahedral</td>
<td>Octahedral</td>
</tr>
</tbody>
</table>

Fig. 2.21 Geometry of Oxyfluorides
Check Your Progress

1. What do you understand by geometry of a molecule?
2. Give the examples of trigonal planar species.
3. What are the common examples of $AB_2$ (lp) Type?
4. What are different types of oxyfluorides?

2.6 ANSWERS TO CHECK YOUR PROGRESS

1. The atoms constituting the molecules occupy definite positions with respect to one another. This definite arrangement of the bonded atoms in a molecule is known as geometry of the molecule.
2. $\text{BCl}_3$ and $\text{SO}_2$ are the examples of trigonal planar species.
3. Common examples of $AB_2$ (lp) Type are $\text{IF}_4$, $\text{BrF}_4$, and $\text{ClF}_4$.
4. A number of xenon oxyfluorides are known, including $\text{XeOF}_2$, $\text{XeOF}_4$, $\text{XeOF}_5$, and $\text{XeO}_2\text{F}_2$. $\text{XeOF}_2$ is formed by reacting $\text{OF}_2$ with xenon gas at low temperatures.

2.7 SUMMARY

- The space model which is obtained by joining the points representing various bonded atoms describes the shape of the molecule.
- According to Lewis structure of a given molecule or ion only the valence shell electrons of the central atom participate in bonding forming various bonds.
- While determining geometry of a given molecule or ion on the basis of VSEPR theory, the presence of $\pi$-bonds surrounding the central atom of the species should not be considered.
- If the central atom is surrounded purely a $\sigma$-bonds, then the shape (geometry) of the molecule or ion is the same as the spatial arrangement of the $\sigma$-bonds round the central atom.
- If the central atom is surrounded by $\sigma$-bonds as well as by $\pi$-bonds, then the geometry of the molecule or ion gets distorted from its expected geometry and becomes different from the spatial arrangement of ($\sigma$-bonds + $\pi$-bonds).
- $\sigma$-bonds are considered to be localized between the two atoms linked together by covalent bond while a $\pi$ is held by only one atom, i.e., bonding electron pair is under the influence of two atoms and a $\pi$ is under the influence of one atom only, viz., central atom.
VSEPR Theory

NOTES

2.8 KEY WORDS

- **Lewis structure**: These are diagrams that show the bonding between atoms of a molecule and the lone pairs of electrons that may exist in the molecule.
- **Spatial arrangement**: It is the three-dimensional arrangement of the atoms that constitute a molecule.

2.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions

1. What are the different categories of species based on the nature of central atom’s valence shell surrounding the central atom?
2. What are the factors that determine the geometry of a given molecule or ion?
3. What are the different types of spatial arrangements?

Long Answer Questions

1. What are the postulates of VSEPR theory?
2. Explain the effect of lone pair of electrons on the geometry of molecule.
3. Draw the geometry of CO₂ in vapour phase.
4. Explain the formation of different types of oxyfluorides.

2.10 FURTHER READINGS


UNIT 3  MOLECULAR ORBITAL THEORY OF COVALENT BONDING

Structure
3.0 Introduction
3.1 Objectives
3.2 Postulates of Molecular Orbital Theory
  3.2.1 Formation of Molecular Orbitals in H₂ Molecule by LCAO Method/
        Formation of Bonding and Anti Bonding Molecular Orbitals by LCAO
        Method
3.3 Shapes of Molecular Orbitals
  3.3.1 Energy Level Diagram for Molecular Orbitals
  3.3.2 Electronic Configuration of Molecules and their Related Properties
3.4 Molecular Orbital Diagram of Homonuclear and Hetronuclear Molecules
  3.4.1 Homonuclear Species
  3.4.2 Hetronuclear Molecules
3.5 Answers to Check Your Progress Questions
3.6 Summary
3.7 Key Words
3.8 Self Assessment Questions and Exercises
3.9 Further Readings

3.0 INTRODUCTION

Molecular orbital theory was developed mainly by Hund and Mullikan in 1932 and later on developed by Lennard Jones and Coulson. This theory is based upon the effects of the various electron field upon each other and employs molecular orbitals rather than atomic orbitals. Each such orbitals characterizing the molecule as a whole is described by a definite combination of quantum numbers and possesses a relative energy value. According to this theory the atomic orbitals combine and form a resultant orbital known as the molecular orbital in which the identity of both the atomic orbitals is lost. All the elections pertaining to both the atoms are considered to be moving along the entire molecule under the influence of all the nuclei. The combination of atomic orbitals occur by LCAO method.

In this unit, you will study about the postulates of molecular orbital theory, shapes of molecular orbitals, molecular orbital diagram of homonuclear and hetronuclear molecules in detail.
### 3.1 OBJECTIVES

After going through this unit, you will be able to:

- Explain the postulates of molecular orbital theory
- Understand the formation of molecular orbitals by LCAO method
- Draw the energy level diagram and electronic configuration of molecules
- Draw the molecular orbital diagram of homonuclear and heteronuclear molecules

### 3.2 POSTULATES OF MOLECULAR ORBITAL THEORY

1. When nuclei of two atoms come close to each other, there electron cloud interact and result in the formation of molecular orbitals.
2. Each molecular orbital can be described by a wave function \( \psi \), known as molecular orbital wave function \( \psi \) represent the probability density or electron density.
3. Each \( \psi \) is associated with a definite set of quantum number which describes the shape and energy of the molecular orbital.
4. Each \( \psi \) is associated with a discrete value of energy.
5. The total energy of the molecule is the sum of the energies of the occupied molecular orbitals.
6. Elections tend to fill in molecular orbitals in similar way as they do in atomic orbitals by obeying Aufbau’s principle, Pauli’s exclusion principle and Hund’s rule.
7. Each election in a molecular orbital belong to all the nuclei present in the molecule.
8. Each election in as molecular orbital is either having clockwise \( \frac{1}{2} \) or anticlock wise \( -\frac{1}{2} \) spin.

#### 3.2.1 Formation of Molecular orbitals in \( \text{H}_2 \) molecule by LCAO method/Formation of bonding and anti bonding molecular orbitals by LCAO method

According to linear combination of atomic orbitals (LCAO) method, there are two ways of linear combination of atomic orbitals or their wave functions forming bonding and anti-bonding molecular orbitals. Suppose that the wave functions of
two atomic orbitals on two atoms A and B of AB type molecule (hetero-diatomic molecule) are represented as \( \psi_A \) and \( \psi_B \) respectively. There are two different ways in which \( \psi_A \) and \( \psi_B \) can combine linearly with each other. These two different ways are discussed below:

(a) **Additive overlap (also called positive overlap of + + overlap) and formation of bonding molecular orbital:** In this type of linear combination, the positive lobe (i.e., the lobe having + sign) of \( \psi_A \) overlaps with the positive lobe of \( \psi_B \) and a molecular orbital is formed. This molecular orbital has lower energy than each of the two isolated atomic orbital wave functions viz. \( \psi_A \) and \( \psi_B \) (decrease in energy) and hence the formation of this molecular orbital produces attraction between the two nuclei of A and B atoms. This attraction results in the establishment of a stable chemical bond between A and B. Since this molecular orbital leads to the formation of a stable bond, it is called bonding molecular orbital which is represented as \( \psi^+ \).

(b) **Subtractive overlap (also called negative or + - overlap) and formation of anti-bonding molecular orbital:** In this type of linear combination the positive lobe of \( \psi_A \) overlaps with the negative lobe (i.e., the lobe having - sign) of \( \psi_B \) and a molecular orbital is formed. This molecular orbital has higher energy than each of the two atomic orbital wave functions \( \psi_A \) and \( \psi_B \) (increase in energy) and hence the formation of this molecular orbital produces repulsion between the two nuclei of A and B. This repulsion opposes the formation of any bond between the nuclei. Since this molecular orbital opposes the formation of any bond between the nuclei, it is called anti-bonding molecular orbital which is represented as \( \psi^- \).

Here, it should be understood clearly than + and – signs of the lobes are only geometric signs of the atomic orbital wave function and should not be confused with positive (+) and negative (-) charges.

Above discussion shows that the formation of bonding molecular orbital wave function \( \psi^+ \) and anti-bonding molecular orbital wave function \( \psi^- \) by the linear combination of two atomic orbital wave functions viz., \( \psi_A \) and \( \psi_B \), can be represented by the following equations:

\[
\psi^+ = \psi_A + \psi_B \quad \text{( + + overlap)} \quad ..., (3.1)
\]

\[
\psi^- = \psi_A - \psi_B \quad \text{( + - overlap)} \quad ..., (3.2)
\]

When we show the contributions made by \( \psi_A \) and \( \psi_B \) in \( \psi^+ \) and \( \psi^- \) molecular orbitals, equations (3.1) and (3.2) are written as:

\[
\psi^+ = \frac{1}{\sqrt{2}} (\psi_A + \psi_B) \quad ..., (3.3)
\]

\[
\psi^- = \frac{1}{\sqrt{2}} (\psi_A - \psi_B)
\]

---

**Molecular Orbital Theory of Covalent Bonding**

**NOTES**

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\[ \psi = \frac{1}{\sqrt{2}} (\psi_a - \psi_b) \]  
\[ \text{\ldots (3.4)} \]

Obviously the sum of the squares of the coefficients of atomic orbital wave functions \( \psi_a \) and \( \psi_b \) appearing in the bonding molecular orbital wave function is equal to unity:
\[ \left( \frac{1}{\sqrt{2}} \right)^2 + \left( \frac{1}{\sqrt{2}} \right)^2. \]

Similarly this sum for anti-bonding molecular orbital is also equal to unity.

The relative order of the energy of \( \psi_a, \psi_b, \psi^* \) and \( \psi' \) can be shown pictorially in Figure 3.1.

\[ \text{Fig. 3.1 Relative Order of the Energy of} \ \psi_a, \ \psi_b, \ \psi^* \ \text{and} \ \psi'. \]

**Probability Density Variation with Internuclear Distance in \( \text{H}_2 \) Molecule**

Consider two H-atoms \( \text{H}_a \) and \( \text{H}_b \) combine to form \( \text{H}_2 \) molecule let the wave function of these atoms may be represented by \( \psi_a \) and \( \psi_b \). The positive overlap of \( \psi_a \) and \( \psi_b \) will give bonding molecular orbital \( \psi_{b^*} \), and the negative overlap of \( \psi_a \) and \( \psi_b \) will produce anti-bonding molecular orbital, \( \psi_{b^*} \) thus

\[ \psi_a = \psi_{b^*} + \psi_b \]  
\[ \text{\ldots (3.5)} \]

\[ \psi_b = \psi_{b^*} - \psi_a \]  
\[ \text{\ldots (3.6)} \]

On squaring equation (3.5), we get:

\[ \psi_a^* \psi_a = \psi_{b^*}^* \psi_{b^*} + 2 \psi_{b^*} \psi_a \psi_b \]  
\[ \text{\ldots (3.7)} \]

In equation (3.7) \( \psi_{b^*} \) denotes electron probability density or electron charge density in the bonding molecular orbital \( \psi_{b^*} \) while \( \psi_a \) and \( \psi_b \) indicate the electron charge density in the isolated (i.e., uncombined) atomic orbitals viz. \( \psi_a \) and \( \psi_b \). From equation (3.7), it is clear that \( \psi_{b^*} \) is greater than \( \psi_a \) and \( \psi_b \). This means that the electron charge
density in the bonding molecular orbital \( \psi_{\text{b,1}} \) is greater by \( 2\psi_{n_a} \psi_{n_b} \) than the sum of the electron charge densities of the isolated atomic orbitals, \( \psi_{n_a} \) and \( \psi_{n_b} \). The excess or increase in electron charge density \( 2\psi_{n_a} \psi_{n_b} \) occurs in the region lying in between the two positively charged nuclei. The increase in electron charge density between the two positive nuclei shields (i.e., screens) the two nuclei from mutual repulsion, i.e., due to the increase in electron charge density, the two nuclei are attracted towards each other. Thus the formation of bonding molecular orbital produces attraction between the two nuclei and hence leads to the establishment of a stable chemical bond. The attraction between the nuclei (i.e., the formation of a stable bond) leads to a decrease in the energy of the bonding molecular orbital in the event of its being occupied by electrons. In other words, the bonding molecular orbital has lower energy than each of the isolated atomic orbitals from which this molecular orbital is derived.

![Fig. 3.2 Inter Nuclear Distance and Electron Density Graph in H₂ Molecule](image)

At this stage it should be easy to understand since \( \psi_{\text{b,1}} \) leads to the formation of a state bond, it is called bonding molecular orbital.

On squaring equation (3.6), we get:

\[
\left( \psi_{\text{b,1}} \right)^2 = \psi_{n_a}^2 + \psi_{n_b}^2 - 2\psi_{n_a} \psi_{n_b}
\]

\[(3.8)\]

In this equation \( \left( \psi_{\text{b,1}} \right)^2 \) represents the electron charge density in the anti-bonding molecular orbital \( \psi_{\text{a}} \). As is evident from equation (3.8), \( \left( \psi_{\text{b,1}} \right)^2 \) is smaller than \( \psi_{n_a}^2 + \psi_{n_b}^2 \) by an amount equal to \( 2\psi_{n_a} \psi_{n_b} \). This means that electron charge density \( \psi_{\text{a}} \) the anti-bonding molecular orbital \( \psi_{\text{a}} \) is smaller by \( 2\psi_{n_a} \psi_{n_b} \) than the sum of the electron charge densities of the uncombined atomic orbitals, \( \psi_{n_a} \) and \( \psi_{n_b} \). The decrease in the electron charge density \( 2\psi_{n_a} \psi_{n_b} \) occurs in the region lying in between the two positively charged nuclei. The decrease in electron charge density between the nuclei means that there is no shielding of the nuclei, i.e., due to the decrease in electron charge density between the nuclei, these are repelled from each other. Thus the formation of anti-bonding molecular
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orbital produces repulsion between the two nuclei and hence opposes the formation of any bond between the nuclei. The repulsion between the nuclei leads to an increase in the energy of the anti-bonding molecular orbital in the event of its being occupied by electrons. In other words, the anti-bonding molecular orbital has higher energy than each of isolated atomic orbitals from which this molecular orbital is derived (Refer Figure 3.2). Since \( \psi_{\alpha} \), molecular orbital opposes the formation of any bond, it is called anti-bonding molecular orbital.

3.3 Shapes of Molecular Orbitals

1. Sigma (\( \sigma \)) Molecular Orbitals

The molecular orbitals which have cylindrical symmetry around the internuclear axis (bond axis) are termed as \( \sigma \) molecular orbitals. These are formed by additive of subtractive combination of s-orbitals or p-orbitals. A covalent bond resulting from the formation of a molecular orbital by the end-to-end overlap of atomic orbitals, denoted by the symbol s. The following illustration shows that how this end-to-end overlapping occurs.

(a) Combination of s-orbitals: Combination of 1s orbital with 1s orbital or combination of 2s orbital with 2s orbital results in the formation of \( \sigma \) molecular orbital (\( \sigma \) bond). The additive overlap of orbitals gives \( \sigma \) bond (\( \sigma_{\alpha} \)) having lower energy and thus gets stabilized. The subtractive overlap gives anti-bonding molecular orbitals (\( \sigma^* \) bond) possessing higher energy. Figure 3.3 shows the combination of 1s orbitals.
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2. **π (π) molecular orbitals**

A covalent bond resulting from the formation of a molecular orbital by side-to-side overlap of atomic orbitals along a plane perpendicular to a line connecting the nuclei of the atoms, denoted by the symbol π. The following illustration shows that how the side-to-side overlapping occurs.

Molecular orbitals formed by the lateral or sidewise overlap of either two 2p, orbitals or two 2p, orbitals are designated as π-molecular orbitals. The lateral overlap of p-orbitals is poor and thus the π bond so produced is a weak bond as compared to σ-bond.

*Fig. 3.3 Formation of Bonding and Antibonding σ Molecular Orbitals*

(b) **End-on overlapping of p-orbitals**: When p, orbitals of two atoms combine linearly with each other with assumption that the internuclear axis is x-axis, it results in the formation of σ bond, shown in figure 3.4

*Fig. 3.4 Formation of σ Bond by Overlap of p Orbitals*
Fig. 3.5 Overlap of 2p, Atomic Orbitals

The +ve sign in orbitals represents that the probability of electron is maximum in that lobe while the −ve sign corresponds to minimum probability of electron in that lobe. Bonding molecular orbital is formed when both lobes rich of electrons, overlap each other, while anti-bonding molecular orbital is the outcome when one lobe rich of electron overlaps the lobe deficient of electron.

Table 3.1 Comparison of σ and π Molecular Orbitals

<table>
<thead>
<tr>
<th>σ Molecular orbital</th>
<th>π Molecular orbital</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. These involve in head-on overlapping or linear overlapping.</td>
<td>1. These involve in sidewise or lateral overlapping.</td>
</tr>
<tr>
<td>2. The overlap region is quite large.</td>
<td>2. The overlap region compared to σ M.O. is less.</td>
</tr>
<tr>
<td>3. σ M.O. results in strong bond i.e. higher stabilization energy.</td>
<td>3. π M.O. gives weak bond of lower stabilization energy.</td>
</tr>
</tbody>
</table>

3. Delta (δ) Bond

In chemistry, delta bonds (δ bonds) are covalent chemical bonds, where four lobes of one involved atomic orbital overlap four lobes of the other involved atomic orbital. This overlap leads to the formation of a bonding molecular orbital with two nodal planes which contain the inter-nuclear axis and go through both atoms.

The Greek letter δ in their name refers to δ orbitals, since the orbital symmetry of the δ bond is the same as that of the usual (4-lobe) type of δ orbitals when seen down the bond axis. This type of bonding is observed in atoms that have occupied d orbitals with low enough energy to participate in covalent bonding, for example, in organometallic species of transition metals. Some rhenum, molybdenum and chromium compounds contain a quadruple bond, consisting of one σ bond, two π bonds and one δ bond.

The orbital symmetry of the δ bonding orbital is different from that of a π anti-bonding orbital, which has one nodal plane containing the inter-nuclear axis and a second nodal plane perpendicular to this axis between the atoms.
### 3.3.1 Energy Level Diagram for Molecular Orbits

On the basis of Aufbau’s rule, the increasing order of energies of various molecular orbitals is as given below:

\[ \sigma_{1s} < \sigma_{2s}^* < \sigma_{2s} < \sigma_{2p_x} < \sigma_{2p_y} = \pi_{2p_z}^* = \pi_{2p_z}^* < \sigma_{2s}^* \]

The pictorial representation of energy diagram for simple homonuclear diatomic molecules specially like \( \text{O}_2 \), \( \text{F}_2 \) or \( \text{Ne}_2 \) is given in Figure 3.6.

Energy level diagram for \( \text{B}_2 \), \( \text{C}_2 \) and \( \text{N}_2 \) molecules is somewhat different as shown in Figure 3.6. The energy level of \( \pi_{2p} \) is lower than \( \sigma_{2s} \) in these molecules. The reason for the exceptional behavior of \( \text{B}_2 \), \( \text{C}_2 \) and \( \text{N}_2 \) molecules is that the energy of \( 2s \) and \( 2p \) atomic orbitals lie fairly close. Due to small energy difference between \( 2s \) and \( 2p \) orbitals, the interaction between them becomes quite large.

![Energy Level Diagram](image)

**Fig. 3.6** Energy Level Diagram of Molecular Orbitals
Fig. 3.7 Energy Level Diagram for B, C, and N Molecules

This results in loss of energy by $\sigma_{2s}$ and $\sigma^*_{2s}$, and thus $\sigma_{2s}$ and $\sigma^*_{2s}$ become more stable at the cost of $\sigma_{2p}$ and $\sigma^*_{2p}$, which get destabilized (higher energy). Hence the energy level diagram for such molecules is little modified as shown in Figure 3.7:

$$\sigma_{2s} < \sigma^*_{2s} < \sigma_{2p} < \sigma^*_{2p} < \pi_{2p} = \pi^*_{2p} < \sigma_{3p} < \sigma^*_{3p} < \sigma_{3p}$$

3.3.2 Electronic Configuration of Molecules and their Related Properties

For writing the electronic configuration of diatomic molecules, following two rules are to be applied:

(i) The number of electrons present in the two atoms are counted and then filled in the appropriate energy level diagram according to Aufbau’s rule.

(ii) The pairing in $\pi_{2p}$ & $\pi_{3p}$, or $\pi^*_{2p}$ & $\pi^*_{3p}$ will take place only when each molecular orbital of identical energy has one electron.

After writing the molecular orbital diagram for a molecule or ion, the under mentioned parameters about the molecule/ion may be predicted.

(i) **Bond order**: It is defined as the number of covalent bonds by which the two atoms are joined in the molecule. It is calculated as given below:

$$\text{Bond order} = \frac{1}{2}[\text{Number of electrons in bonding M.O i.e. } N_b - \text{Number of electrons in anti-bonding M.O i.e. } N_a]$$

\[ \therefore \text{Bond order} = \frac{1}{2}[N_b - N_a] \]
(ii) **Bond Angle:** A bond angle is the angle between two bonds originating from the same atom in a covalent species. By definition, “Bond angle is simply the angle between two bonds or two bonded electron pairs in a compound”. Geometrically, a bond angle is an angle between two converging lines. Following are examples of bond angles.

![Bond Angle Diagram]

For example in CH₄ the bond angle is 109 degrees.

A lone pair of electrons at the central atom always tries to repel the shared pair (bonded pair) of electrons. Due to this, the bonds are displaced slightly inside resulting in a decrease of bond angle. Electronegativity also effects bond angle. If the electronegativity of the central atom decreases, bond angle decreases.

(iii) **Bond length:** Bond length is the distance between the centres of two bonded nuclei. It is inversely proportional to bond order i.e. as bond order increases, bond length decreases.

\[
\text{Bond length} \propto \frac{1}{\text{Bond order}}
\]

<table>
<thead>
<tr>
<th>Bond order</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>1.43</td>
</tr>
<tr>
<td>O₂</td>
<td>1.21</td>
</tr>
<tr>
<td>N₂</td>
<td>1.10</td>
</tr>
</tbody>
</table>

(iv) **Stability of molecules:** Stability of molecules is directly proportional to bond order.
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Molecular Orbital Theory of Covalent Bonding

Stability $\propto$ Bond order of molecule
Higher the bond order of the molecule more will be the stability of molecule. When bond order is observed to be zero, the molecule does not exist at all.

(v) Dissociation energy: Bond dissociation energy is the energy required to separate the two atoms. It is directly proportional to bond order.

Bond dissociation energy $\propto$ Bond order
So, bond dissociation energy increases with increase of bond order as evident from the following data

<table>
<thead>
<tr>
<th>Bond order</th>
<th>Bond dissociation energy (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2$</td>
<td>1</td>
</tr>
<tr>
<td>151</td>
<td></td>
</tr>
<tr>
<td>$O_2$</td>
<td>2</td>
</tr>
<tr>
<td>493</td>
<td></td>
</tr>
<tr>
<td>$N_2$</td>
<td>3</td>
</tr>
<tr>
<td>940</td>
<td></td>
</tr>
</tbody>
</table>

(vi) Magnetic property of molecule: When all the electrons in molecular orbitals (bonding and anti-bonding) are paired, the molecule is repelled by the magnetic field. Such molecules are called diamagnetic. However, if molecular orbitals possess one or more unpaired electrons then the molecule is attracted by the magnetic field and termed as paramagnetic.

The magnetic moment shown by any atom, molecule or ion is calculated by the formula.

$$\mu = \sqrt{n} \mu_0$$

where $\mu =$ magnetic moment
$n =$ number of unpaired electrons

Check Your Progress
1. What are the two ways of linear combination of atomic orbitals?
2. What are molecular orbitals?

3.4 MOLECULAR ORBITAL DIAGRAM OF HOMONUCLEAR AND HETRONUCLEAR MOLECULES

Bonding in homonuclear and hetronuclear molecules may be understood by following molecular orbital diagrams.

3.4.1 Homonuclear Species

1. Hydrogen molecule: Hydrogen molecule is having two hydrogen atoms containing one electron each ($1s^2$). Its mod is as given in Figure 3.8.
Fig. 3.8 M.O Diagram of H₂ Molecule

(a) M.O configuration of H₂ = (σ₁)² (σ*₁)²

(b) Bond order = \frac{1}{2}[N_e - N_a] = \frac{1}{2}[2 - 0] = 1 (single bond)

(c) Stability = as bond order is one, the molecule is quite stable.

(d) It is diamagnetic in nature as all the electrons in molecular orbital are paired.

2. H₂⁺ ion: It is made up of H atom containing one electron and H⁺ ion containing no electron. M.O diagram for H⁺ ion is given in Figure 3.9.

Fig. 3.9 Energy level diagram of H⁺

(a) M.O configuration of H⁺ = (σ₁)² (σ*₁)²

(b) Bond order = \frac{1}{2}[N_e - N_a] = \frac{1}{2}[1 - 0] = \frac{1}{2}

(c) Stability. Its bond order is less than the bond order for H₂ molecule. Therefore, it is less stable than H₂ molecule.

(d) It is paramagnetic in behavior as it possess one unpaired electron (σ₁)².

3. H⁻ ion or H⁺ cation or H-He molecule: These species are having three electrons in all which are arranged in M.O. diagram as shown in Figure 3.10.

Fig. 3.10 M.O Energy Level Diagram of H⁻He
Molecular Orbital Theory of Covalent Bonding

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(a) M.O. configuration of H\(_2^+\) or He\(_2^+\) or H-He = (\(\sigma_n\)\(^2\)) \((\sigma^*\)\(^2\))

(b) Bond order = \(\frac{1}{2}[N_b - N_a] = \frac{1}{2}[2 - 2] = \frac{1}{2}\)

(c) Stability. Its stability is equal to H\(_2^+\) as in both cases the bond order is 0.5.

(d) It shows paramagnetic nature as it has one unpaired electron (\(\sigma^*\)\(^\downarrow\)).

<table>
<thead>
<tr>
<th>Properties of ions or molecule</th>
<th>H(_2^+)</th>
<th>H(_2)</th>
<th>H(_2^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond order</td>
<td>(\frac{1}{2})</td>
<td>1</td>
<td>(\frac{1}{2})</td>
</tr>
<tr>
<td>Bond length(^\uparrow)</td>
<td>H(_2^+) &gt; H(_2)</td>
<td>Minimum</td>
<td>H(_2^*) &gt; H(_2)</td>
</tr>
<tr>
<td>Stability</td>
<td>Somewhat stable</td>
<td>Quite stable</td>
<td>Somewhat stable</td>
</tr>
<tr>
<td>Magnetic character</td>
<td>Paramagnetic</td>
<td>Diamagnetic</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>Dissociation energy</td>
<td>H(_2^+) &lt; H(_2)</td>
<td>Maximum</td>
<td>H(_2^*) &lt; H(_2)</td>
</tr>
</tbody>
</table>

4. Helium molecule (He\(_2\)): Each helium atom contains 2 electrons. Therefore, He\(_2\) molecule will have 4 electrons. These 4 electrons will be arranged in M.O. diagram as given below in Figure 3.11.

![M.O. Energy Level Diagram of He\(_2\)](image)

(a) M.O. configuration of He\(_2\) = (\(\sigma_n\)\(^2\)) \((\sigma^*\)\(^2\))

(b) Bond order = \(\frac{1}{2}[N_b - N_a] = \frac{1}{2}[2 - 2] = 0\)

Bond order zero indicates that there is no linkage between two atoms. Hence the He\(_2\) molecule does not exist.

(c) Stability. The molecule is highly unstable and there is no experimental proof for its existence.

(d) It is diamagnetic in nature as all the electrons in M.O. are paired.

5. Lithium molecule (Li\(_2\)): Each lithium atom has electronic configuration of \(1s^2\) \(2s^2\) and so the Li\(_2\) molecule has total of six electrons. In the molecular orbital formation, the electrons of the inner shell (K shell) do not enter in bonding and so remain in their atomic orbitals. The orbitals which do not
enter into bonding are called nonbonding orbitals. Thus we infer that only
the valence electrons are involved in bond formation. The M.O. energy
level diagram of Li₂ is shown in Figure 3.12.

(a) M.O. configuration Li₂ = (KK)(σ₁g)²(σ*₁g)²

(b) Bond order = \( \frac{1}{2} |N_\sigma - N_\pi| = \frac{1}{2} |2 - 0| = 1 \)

(c) Stability. The σ bond in lithium molecule is comparatively longer and
weaker than that of H₂ molecule as being formed by overlapping of 2s
orbitals. Bond dissociation energy of Li₂ is kJ/mole which is less than
that of H₂ molecule (431.4 kJ/mole).

(d) It is diamagnetic in nature as all electrons in M.O. are paired.

6. Nitrogen molecule (N₂): Nitrogen molecule has 14 electrons and thus its
M.O. energy level diagram may be shown as in Figure 3.13.

(a) M.O. configuration of N₂ = (KK)(σ₁s)²(σ*₁s)²(π₁u)²(π*₁u)²(σ₁u)²

(b) Bond order = \( \frac{1}{2} |N_\sigma - N_\pi| = \frac{1}{2} |8 - 2| = 3 \)
i.e. a triple bond exists between two nitrogen atoms. 
(Note: Electrons of K shell do not involve in M.O. formation. 
Therefore, these electrons remain as nonbonding electrons. Hence 
these are neither considered as bonding nor as anti-bonding.)

(c) Stability. Since the bond order of $N_2$ molecule is 3, it is highly stable 
molecule. It is evident from its bond dissociation energy (940 kJ/mole).

(d) All the electrons in M.O. are paired so it is diamagnetic in nature. This 
has also been proved experimentally.

7. $N_2^+$: ion shows that it is formed by the loss of one electron from 
$N_2$ molecule.

Thus M.O. electronic configuration of $N_2^+$ ion will be

$$N_2^+ = KK \left( \sigma_{2s} \right)^2 \left( \sigma_{2s}^* \right)^2 \left( \pi_{2p_x} \right)^2 \left( \pi_{2p_y} \right)^2 \left( \pi_{2p_z} \right)^4$$

The characteristic properties of the cation will be:

(a) Bond order $= \frac{1}{2} [\text{Number of 2s} - \text{Number of 2s}^*] = \frac{1}{2} [7 - 2] = \frac{5}{2}$

(b) The bond order of cation is smaller than that of $N_2$ molecule. Therefore, 
it is less stable than $N_2$ molecule.

(c) It has one unpaired electron in its M.O. electronic configuration. So, 
it is paramagnetic in nature.

8. $N_2^-$: ion is formed when $N_2$ molecule gains one electron. This additional 
electron will enter the empty $\pi^{*}_{2p_z}$ or $\pi^{*}_{2p_y}$ orbital (see Fig.3.11). Following 
is the M.O. electronic configuration for $N_2^-$ anion.

$$N_2^- = KK \left( \sigma_{2s} \right)^2 \left( \sigma_{2s}^* \right)^2 \left( \pi_{2p_x} \right)^2 \left( \pi_{2p_y} \right)^2 \left( \pi_{2p_z} \right)^2 \left( \pi^{*}_{2p_z} \right)^1$$

Bond order $= \frac{1}{2} [\text{Number of 2s} - \text{Number of 2s}^*] = \frac{1}{2} [8 - 3] = 2.5$

So this ion is less stable than $N_2$ molecule. Furthermore, the $N_2^-$ anion has 
one unpaired electron ($\pi^{*}_{2p_z}$). So, it is paramagnetic in its behaviour.

9. $N_2^-$: anion: This anion is formed when two electrons are added to $N_2$ 
molecule. These two additional electrons will be taken, one each by two 
nitrogen atoms. According to Hand’s rule, these two electrons will occupy 
the empty $\pi^{*}_{2p_z}$ or $\pi^{*}_{2p_y}$ orbitals. So the M.O. electronic configuration will 
be

$$N_2^{--} = KK \left( \sigma_{2s} \right)^2 \left( \sigma_{2s}^* \right)^2 \left( \pi_{2p_x} \right)^2 \left( \pi_{2p_y} \right)^2 \left( \pi_{2p_z} \right)^2 \left( \pi^{*}_{2p_z} \right)^1 \left( \pi^{*}_{2p_y} \right)^1$$
The consequences of this M.O. electronic configuration are

(a) Bond order \( = \frac{1}{2} [N_0 - N_f] = \frac{1}{2} [8 - 4] = 2 \)

(b) Stability. Since the bond order for \( N_{1}^{+} \) is 2, which is less than \( N_{1}^{+} \), and \( N_{1}^{+} \) (bond order = 2.5 each) as well as \( N_{1}^{-} \) molecule (bond order = 3), its stability is least.

\[
N_{1}^{-} > N_{1}^{+} = N_{1} > N_{1}^{2+}
\]

(c) Bond length. Bond length is inversely proportional to the bond order so the relative bond length will be in the order

\[
N_{1}^{2+} > N_{1} > N_{1}^{-} > N_{1}^{+}
\]

These properties of \( N_{1}^{-} \), \( N_{1}^{+} \), \( N_{1}^{2+} \) and \( N_{1}^{-}^{2+} \) ions are compiled below.

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond order</th>
<th>Stability</th>
<th>Bond length</th>
<th>Magnetic nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_{1}^{-} )</td>
<td>2.5</td>
<td>Less stable</td>
<td>Medium value</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>( N_{1} )</td>
<td>3</td>
<td>Most stable</td>
<td>Minimum value</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>( N_{1}^{+} )</td>
<td>2.5</td>
<td>Less stable</td>
<td>Medium value</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>( N_{1}^{2+} )</td>
<td>2</td>
<td>Less stable</td>
<td>Maximum value</td>
<td>Paramagnetic</td>
</tr>
</tbody>
</table>

10. Oxygen molecule (\( O_{2} \)). Oxygen molecule has 16 electrons in all, in which each oxygen atom has contributed 8 electrons. The molecular orbital energy level diagram of \( O_{2} \) molecule is as given below in Figure 3.14.

![M.O. Energy Level Diagram for \( O_{2} \) Molecule]
(a) M.O. electronic configuration.

\[ \text{KK}(\sigma_a)^0(\sigma^*_{e_1})^0(\sigma^*_{e_2})^0(\pi_{e_1})^0(\pi_{e_2})^0(\pi^*_{e_1})^0(\pi^*_{e_2})^0 \]

(b) Bond order. From M.O. diagram of \( \text{O}_2 \), the \( N_b = 8 \) and \( N_s = 4 \).

Therefore, bond order \( = \frac{1}{2}(8-4) = 2 \) i.e. it has double bond.

(c) Stability. Since the bond order of \( \text{O}_2 \) molecule is 2, therefore the \( \text{O}_2 \) molecule is quite stable. It is confirmed by its high dissociation energy (443 kJ/mole).

(d) Magnetic character. From its M.O. diagram it is clear that the oxygen molecule has two unpaired electrons \( (\pi^*_{e_1})(\pi^*_{e_2}) \). So, it is paramagnetic in nature as confirmed by experiments.

11. \( \text{O}^+_2 \) cation: This cation is formed when one electron is ionized from the oxygen molecule. From the M.O. diagram of \( \text{O}_2 \) molecule (Figure 3.14), if one electron is ionized \( (e_{\pi^*}) \), then the M.O. electronic configuration will be:

\[ \text{O}^+_2 = \text{KK}(\sigma_a)^0(\sigma^*_{e_1})^0(\sigma^*_{e_2})^0(\pi_{e_1})^0(\pi_{e_2})^0(\pi^*_{e_1})^0(\pi^*_{e_2})^0 \]

(a) Bond order \( = \frac{1}{2}(8-4) = 2 \)

(b) Stability. The bond order of \( \text{O}^+_2 \) cation is higher than that of \( \text{O}_2 \) molecule. Therefore, its stability will be more than that of \( \text{O}_2 \) molecule (i.e. \( \text{O}_2 > \text{O}^+_2 \)).

(c) Bond length. Bond length being inversely proportional to bond order, it decreases with increase of bond order. Therefore, \( \text{O}^+_2 \) has lower bond length than \( \text{O}_2 \) molecule.

(d) Magnetic parameter. M.O. configuration has one unpaired electron \( (\pi^*_{e_1}) \). Thus, it is paramagnetic in nature.

12. \( \text{O}_2^- \) ion (Superoxide ion): This ion is formed when \( \text{O}_2 \) molecule gains one electron. This new electron pairs with either of the two half-filled antibonding orbitals \( \pi^*_{e_1} \) or \( \pi^*_{e_2} \). Therefore, its electronic configuration becomes

\[ \text{O}_2^- = \text{KK}(\sigma_a)^0(\sigma^*_{e_1})^0(\sigma^*_{e_2})^0(\pi_{e_1})^0(\pi_{e_2})^0(\pi^*_{e_1})^0(\pi^*_{e_2})^0 \]

(a) Bond order \( = \frac{1}{2}(8-4) = 2 \)

(b) Stability. As the bond order of superoxide ion is less than that of \( \text{O}_2 \) molecule, it is less stable than \( \text{O}_2 \) molecule (\( \text{O}_2 > \text{O}_2^- \)).
(c) Bond length. Higher the bond order, shorter is the bond length. Thus, the bond length of $\text{O}_2^+$ ion is more than $\text{O}_2$ molecule ($\text{O}_2 > \text{O}_2^+$).

(d) Magnetic nature. $\text{O}_2^+$ shows paramagnetic character due to the presence of one unpaired electron ($\pi^*$).

13. $\text{O}_2^-$ ion (Peroxide ion): Addition of two electrons (one each in $\pi^*$ and $\sigma^*$) to $\text{O}_2$ molecule gives $\text{O}_2^-$ ion. So, its M.O. electronic configuration will be:

$$\text{O}_2^- = \text{KK} (\pi^*_{\text{O}_2}) (\pi^*_{\text{O}_2}) (\sigma^*_{\text{O}_2}) (\sigma^*_{\text{O}_2}) (\pi^*_{\text{O}_2}) (\pi^*_{\text{O}_2})$$

(a) Bond order: $\frac{1}{2} |N_1 - N_2| = \frac{1}{2} |3 - 1| = 1$ (Single bond)

(b) Stability. It is less stable than $\text{O}_2$ molecule. The order of stability of $\text{O}_2$ and its various ionic species is $\text{O}_2^- < \text{O}_2 < \text{O}_2^+$

(c) Bond length. Bond length is inversely proportional to bond order its bond length will be greater than $\text{O}_2$ molecule $\text{O}_2^- > \text{O}_2$

(d) Magnetic effect. As expected $\text{O}_2^+$ shows diamagnetic behaviour when placed in a magnetic field. The compiled list of the properties of these ions and oxygen molecule is presented below.

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond order</th>
<th>Stability</th>
<th>Bond length</th>
<th>Magnetic nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2$</td>
<td>2.0</td>
<td>$\text{O}_2 &lt; \text{O}_2^- \text{ (Bond energy of } \text{O}_2 = 493.2 \text{ kJ/mole})$</td>
<td>$\text{O}_2^- &gt; \text{O}_2 &lt; \text{O}_2^+$ (1.21A)</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>$\text{O}_2^+$</td>
<td>1.5</td>
<td>$\text{O}_2^+ &gt; \text{O}_2 &gt; \text{O}_2^-$</td>
<td>$\text{O}_2^- &gt; \text{O}_2^+$</td>
<td>Paramagnetic</td>
</tr>
</tbody>
</table>

14. Fluorine molecule (F$_2$): When two fluorine atoms (each having 9 electrons) combine to give F$_2$ molecule then the total 18 electron occupy the molecular orbitals according to Aufbau’s rule. It results in the following M.O. electronic configuration (Refer Figure 3.15).
Fig. 3.15 M.O. Energy Level Diagram for F₂ Molecule

(a) M.O. configuration

\[ F_2 = KK \left( \sigma_{1s} \right)^2 \left( \sigma_{2s} \right)^2 \left( \pi_{1\sigma} \right)^2 \left( \pi_{2\sigma} \right)^2 \]

(b) **Bond Order** \(-\frac{1}{2}(N_e - N_\text{a}) = \frac{1}{2}\) (i.e. single bond between two fluorine atoms).

(c) Stability. Since the bond order of \( F_2 \) molecule is one, therefore, it is a stable molecule.

(d) **Magnetic Nature**: It shows diamagnetic behaviour as all the electrons in \( F_2 \) molecule are paired.

15. **Neon Molecule** (Ne₂): It shall have 20 electrons in its molecule, which will be occupying the M.O. in increasing energy level as shown below.

\[ \text{Ne}_2 = KK \left( \sigma_{1s} \right) \left( \sigma_{2s} \right) \left( \sigma_{1\sigma} \right) \left( \sigma_{2\sigma} \right) \left( \pi_{1\sigma} \right) \left( \pi_{2\sigma} \right) \left( \pi_{1\pi} \right) \left( \pi_{2\pi} \right) \]

This electronic configuration of Ne₂ molecule will indicate for the following inference.

(a) **Bond order** \(-\frac{1}{2}(N_e - N_\text{a}) = \frac{1}{2}8=0 = 0\) zero, i.e. no bond exists between two Ne atoms.

(b) Stability. As the bond order is zero, the molecule is highly unstable and exists only in atomic state.

(c) Magnetic character. All the electrons in Ne₂ molecule are paired. So, it is **diamagnetic in nature**.

3.4.2 **Heteronuclear Molecules**

In the foregoing discussion, we have studied the M.O. diagrams for homonuclear diatomic molecules and their related properties. We may now apply the same
method to heteronuclear diatomic species such as CO, *NO*, CN, NO. Due to difference in electronegativities of the two hetero atoms, the molecular orbitals become polarized. It results in higher stabilization of MO’s of more electronegative atom compared to other atom. This can best be illustrated taking the example of CO.

**Carbon Monoxide**: It possesses 10 valence electrons (4 contributed by carbon and 6 by oxygen atom) which may be accommodated in five M.O. The M.O. energy level diagram of CO is as given in Figure 3.16.

![M.O. Energy Level Diagram for Carbon Monoxide](image)

**Fig. 3.16** M.O. Energy Level Diagram for Carbon Monoxide

(a) Electronic configuration.
\[
\text{KK} \left\{ \sigma_2 \right\} \left\{ \sigma^* \right\} \left\{ \pi_2 \right\} \left\{ \pi^* \right\}
\]

(b) Bond order.
\[
\frac{1}{2} [N_e - N_a] - \frac{1}{2} [\Delta] = \frac{1}{2}
\]

(c) Stability. As the bond order is three, the CO molecule is highly stable molecule.

(d) Magnetic properties. All electrons in M.O. are paired. Hence CO is diamagnetic in nature.

**Nitric Oxide (NO)**: Nitric oxide has 11 valence electrons and so its M.O. electronic configuration will be

\[
\text{NO} = \text{KK} \left\{ \sigma_2 \right\} \left\{ \sigma^* \right\} \left\{ \sigma_2 \right\} \left\{ \pi_2 \right\} \left\{ \pi^* \right\}
\]

(a) Bond order.
\[
\frac{1}{2} [N_e - N_a] - \frac{1}{2} [\Delta] = \frac{1}{2}
\]

(b) Stability. It is less stable than NO⁺ ion (bond order = 3) because bond order of NO is smaller than that of NO⁺ ion. This is manifested by quick oxidation of NO to NO⁺ ion by the loss of one \( \pi^* \) electron.

(c) Magnetic nature. It is paramagnetic, as it possesses one \( \pi^* \) unpaired electron.
Check Your Progress

3. What is π-molecular orbitals?
4. What is bond order?
5. What is bond dissociation energy?

3.5 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Additive overlap and subtractive overlap are the two ways of linear combination of atomic orbitals.
2. The molecular orbitals which have cylindrical symmetry around the internuclear axis (bond axis) are termed as σ-molecular orbitals.
3. Molecular orbitals formed by the lateral or sidewise overlap of either two 2p_y orbitals or two 2p_z orbitals are designated as σ*-molecular orbitals.
4. Bond order is defined as the number of covalent bonds by which the two atoms are joined in the molecule.
5. Bond dissociation energy is the energy required to separate the two atoms.
   It is directly proportional to bond order.

3.6 SUMMARY

- Molecular orbital theory is based upon the effects of the various electron field upon each other and employs molecular orbitals rather than atomic orbitals. Each such orbitals characterizing the molecule as a whole is described by a definite combination of quantum numbers and possesses a relative energy value.
- Additive overlap and subtractive overlap are the two ways of linear combination of atomic orbitals.
- In additive overlap type of linear combination, the positive lobe (i.e., the lobe having + sign) of ψ_x overlaps with the positive lobe of ψ_y and a molecular orbital is formed.
- In subtractive overlap type of linear combination the positive lobe of ψ_x overlaps with the negative lobe (i.e., the lobe having - sign) of ψ_y and a molecular orbital is formed.
- The molecular orbitals which have cylindrical symmetry around the internuclear axis (bond axis) are termed as molecular orbitals.
• Molecular orbitals formed by the lateral or sidewise overlap of either two
  2p\textsubscript{x} orbitals or two 2p\textsubscript{y} orbitals are designated as \pi\text{-molecular orbitals.}
• Bond order is defined as the number of covalent bonds by which the two
  atoms are joined in the molecule.
• Bond length is the distance between the centres of two bonded nuclei. It is
  inversely proportional to bond order i.e. as bond order increases, bond
  length decreases.
• Bond dissociation energy is the energy required to separate the two atoms.
  It is directly proportional to bond order.

### 3.7 KEY WORDS

• **Bond Order.** It is defined as the number of covalent bonds by which the
  two atoms are joined in the molecule.
• **Bond Angles:** These are the angles between adjacent lines representing
  bonds.
• **Electronic Configuration:** It is the distribution of electrons of an atom or
  molecule in atomic or molecular orbitals.

### 3.8 SELF ASSESSMENT QUESTIONS AND EXERCISES

**Short Answer Questions**

1. Define the following terms.
   (i) Bond order
   (ii) Bond length
   (iii) Bond dissociation energy
   (iv) Bond angle
2. Compare and molecular orbitals.
3. What do you understand by electronic configuration of molecules?

**Long Answer Questions**

1. Write the postulates of molecular orbital theory.
2. Explain the various shapes of molecular orbitals.
3. Explain the two ways of linear combination of atomic orbitals or their wave
   functions forming bonding and anti-bonding molecular orbitals.
4. Draw the molecular orbital diagram of any five homonuclear molecule. Also,
   provide necessary explanation.
3.9 FURTHER READINGS


UNIT 4 INTERMOLECULAR FORCES AND LATTICE ENERGY

Structure
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4.2 Intermolecular Forces: Van der Waals Forces
   4.2.1 Types of Van der Waals Forces
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4.0 INTRODUCTION

It has been proved with many evidences that there exist forces of attraction between the molecules of polar as well as non-polar compounds. The magnitude of these forces is maximum in solids and decreases for liquid and gases. These forces of attraction are called intermolecular forces (IMF). These forces of attraction were first recognized van der Waals and hence these are also known van der Waals forces. The lattice energy of a crystalline solid is a measure of the energy released when ions are combined to make a compound. It is a measure of the cohesive forces that bind ions. You will also learn about the dipole moment and its applications. The degree of polarity in a polar molecule is expressed by its dipole moment which is equal to the product of charge and the distance between atoms.
In this unit, you will learn about the intermolecular forces, lattice energy and its calculations intermolecular forces, lattice energy, dipole moment in detail.

4.1 OBJECTIVES

After going through this unit, you will be able to:

- Explain the Van der Waals forces and its types
- Discuss the characteristics and various factors affecting the magnitude of Van der Waals forces
- Define lattice energy
- Calculate lattice energy using Born Lande, Born-Meyer, Born-Haber and Kapustinskii equations
- Explain dipole moment and its significance
- Discuss the applications of dipole moment

4.2 INTERMOLECULAR FORCES: VAN DER WAALS FORCES

The Van der Waals forces are very short lived intermolecular attractive forces which exist between all kind of atoms molecules and ions when they are sufficiently close to each other. These forces have nothing to do with valence electrons of the elements. In other words these forces exist in neutral molecules, ions and atoms of inert gases or solids.

The van der Waals forces are very weak compared to the normal valence forces: enthalpy of sublimation of Cl₂ (s) is only 21kJ mol⁻¹, while the bond strength of Cl-Cl bond is 240kJ mol⁻¹. The van der Waals forces are additive and cannot be saturated like the valence bond forces.

The atoms of the molecules like N₂, O₂, Cl₂, P₂, S₂ etc. in which the valence orbitals are either used in normal bonding or are occupied by non-bonding electrons, are rather firmly held together in the liquid or solid states by van der Waals forces or bonds. These forces are almost absent when the molecules of the gas are far apart and are in rapid kinetic motion. But as the atoms or molecules of the gas are brought nearer to each other by increasing the pressure and kinetic energy is withdrawn by cooling, van der Waals forces are capable of holding the molecules together to form the liquid or solid state. Thus a gas can be liquefied by allowing it to expand suddenly from high pressure. During expansion the gas does work in overcoming intermolecular forces of attraction. Thus the energy required for this purpose is obtained from the gas itself, thereby lowering the temperature and causing the liquefaction.
4.2.1 Types of Van der Waals Forces

There are four types of van der Waals forces discussed below:

1. **Dipole-dipole Interaction**: These interactions are present in polar molecules which have permanent polarity. For example, gases like NH₃, SO₂, HF, HCl etc. are polar molecules.

   It is known that a polar molecule has separate centers of positive and negative charge and possesses permanent dipole moment. When polar molecules are brought nearer to each other, they orient themselves in such a way that the positive end of one dipole (polar molecule) attracts the negative end of another dipole and vice-versa as shown in Figure 4.1. Due to this dipole-dipole interacting many molecules are held together. Dipole-dipole interactions between polar molecules are also called Keesom Forces and are the strongest of all other types of van der Waals forces. The intensity of these forces decreases by an increase in temperature.

   These forces are given by Eq. (4.1) where \( \mu_1 \) and \( \mu_2 \) are the dipole moments of the two molecules separated by a distance \( r \), \( \varepsilon_0 \) being the permittivity of vacuum. This effect is inversely proportional to \( T \).

\[
E_r = \frac{-2 \mu_1 \mu_2}{3(4\pi \varepsilon_0) r^3 kT}
\]

The dipole-dipole attractions are very weak and fall off as \( r^6 \), being only 1.4 \( \text{kJ mol}^{-1} \) for \( \mu = 1 \text{ D} \) and \( r = 300 \text{ pm} \).

![Fig 4.1 Dipole-dipole Interactions](image)

2. **Ion-dipole Interactions**: We know that polar molecules are attracted towards ions. The negative end of the dipole is attracted towards the cation and the positive end is directed towards the anion Figure 4.2. This type of interaction is known as ion-dipole interaction. For example, dissolution of NaCl in water. When NaCl is put in water, it dissolves in it, since the negative ends of water molecule dipoles aggregate around Na⁺ ions and the positive ends around Cl⁻ ions.
3. **Dipole-induced Dipole Interactions:** These forces are observed in a mixture of polar and non-polar molecules. When a non-polar molecule is brought near to a polar molecule the positive end of the polar molecule attracts the mobile electrons of non-polar molecule and thus polarity is induced in non-polar molecule as shown in Figure 4.3. Now both the molecules become dipoles and therefore the positive end of the polar molecule attracts the displaced electron cloud of non-polar molecule. Hence the two types of molecules are held together by forces which are also called Debye Forces.

\[
E_D = -\frac{2\alpha \mu^2}{4\pi \varepsilon_0 r^6}
\]

Where \( \alpha \) is the polarizability of the molecule. For a dipole moment of 1 D in a medium with polarizability \( \alpha \) \( 10 \times 10^{-30} \text{ cm}^3 \) (benzene), \( E_D \) comes out to be \( \alpha \) 0.8 \( \text{kJ mol}^{-1} \). \( E_D \) is called the Debye energy.

These are extremely weak forces, their importance being limited to the solutions of polar solutes in non-polar solvents.

4. **Instantaneous Dipole-induced Dipole Interactions:** These forces of attraction occur in monatomic noble gases like He, Ne, Ar etc. and non-polar molecules like H₂, O₂, Cl₂, I₂, N₂ etc. A non-polar atom may be considered as a positive center surrounded by a symmetrical electron cloud, both in equilibrium. But as the electron cloud oscillates, the electron cloud becomes denser on one side of the molecule than on the other side and thus the equilibrium gets disturbed for a moment.
The displacement of electron cloud creates an instantaneous dipole temporarily. Hence the non-polar molecule is momentarily self polarised and becomes temporarily polar (Figure 4.4 (b))

When this temporarily polar molecule is brought near to a non-polar molecule, it polarises the neighbouring molecule by disturbing its electronic distribution and an induced dipole is created in it, i.e., the non-polar molecule momentarily becomes polar (as shown in Figure 4.4(c)).

In similar fashion a large number of non-polar molecules become temporarily polar which are mutually attracted by weak attractive forces. Since the molecules are in rapid motion and are constantly departing from the site of temporary dipoles, the attractive forces acting between the polar molecules are very weak.

According to Frintz London (1930) the instantaneous formation and subsequent decay of dipoles in a gas due to temporary distortion of electron cloud may be shown in Figure 4.5.

![Diagram](Figure 4.5 Instantaneous Formation and Decay of d-poles in a Gas)

The weak inter-molecular forces operating in gases due to instantaneous polarization of non-polar molecule are also known as London Forces. These forces are very weak and are known to operate in all types of molecules. These forces are weaker in most cases than dipole-dipole or ion-dipole forces, but are responsible for bringing about condensation of gases, even of noble gases. These forces become stronger with the increase of number of electrons in molecules/atoms. The forces become stronger with the increase in boiling points of the molecules as shown below.
### Intermolecular Forces and Lattice Energy

<table>
<thead>
<tr>
<th>Molecules/Atoms:</th>
<th>He</th>
<th>H₂</th>
<th>Ne</th>
<th>N₂</th>
<th>O₂</th>
<th>Ar</th>
<th>F₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of electrons:</td>
<td>2</td>
<td>2</td>
<td>10</td>
<td>14</td>
<td>16</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Boiling point (°C):</td>
<td>-269</td>
<td>-253</td>
<td>-246</td>
<td>-196</td>
<td>-183</td>
<td>-186</td>
<td>-186</td>
</tr>
</tbody>
</table>

#### Direction of Strength of London forces

London, form quantum mechanics derived that electric field produced temporarily in any one atom due to the asymmetric distribution of the orbital charge density, produced a resultant energy in the molecules \( E_1 \) given by the equation (4.3)

\[
E_1 = -\frac{3I_1 I_2 \alpha_1 \alpha_2}{2(I_1 + I_2) \varepsilon_0 r^3}
\]  

Where \( I_1 \) and \( I_2 \) refer to the ionization energies of the two molecules, separated by a distance \( r \) and having polarizabilities \( \alpha_1 \) and \( \alpha_2 \), respectively.

Multiplying the Equations (4.1), (4.2) and (4.3) by Avogadro’s number \( N \) gives the energy of these interactions for one mole of compounds.

#### 4.2.2 Characteristics of Van der Waals forces

(i) These forces are only short range forces. In the simplest molecules they are in important only up to \( 10^{-7} \) cm.

(ii) These forces are much weaker than covalent and hydrogen bonds. The energies per molecule involved in a covalent bond, hydrogen bond and van der Waals attraction are 200-8400, 10-40 and 2-20 kJ respectively.

(iii) If two atoms or molecules approach each other both attractive and repulsive forces operate between their negative electrons and positive protons. These forces are in equilibrium at an inter nuclear distance approximately equal to 4 Å. However, at intermolecular distance between 4 Å to 10 Å, attractive forces predominate. It is these attractive forces which are acting between the molecules and are called van der Waals forces.

(iv) The experimental evidences for the existence of van der Waals forces are: The non-ideality of real gases; the Joule-Thompson effect and condensation of noble gases.

#### 4.2.3 Factors Affecting the Magnitude of Van der Waals Forces

1. **Condition of Temperature**: Lower the temperature, lesser would be the random movement of molecules and greater would be the chance of molecular interactions. At higher temperatures the condition would be somewhat the reverse. Hence at low temperatures van der Waals’ interactions would be relatively stronger.
2. **Effect of Pressure**: when the pressure increases, the molecules would become closer and greater would be the attraction.

3. **Molecular Size**: Larger the molecular size, roughly longer is the molar walls, the stronger the van der Waals forces.

The boiling points of a series of compounds which are having similar structures, increase with the increasing molecular weight. For example, boiling points of saturated hydrocarbons get increased from methane (CH\(_4\)) to ethane (C\(_2\)H\(_6\)) and so on.

The boiling point have been found to increase with increase in number of electrons and the size of the molecule in case of compounds with identical structure as given below.

<table>
<thead>
<tr>
<th>Substance</th>
<th>CH(_4)</th>
<th>SiH(_4)</th>
<th>GeH(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of electrons</td>
<td>10</td>
<td>18</td>
<td>36</td>
</tr>
<tr>
<td>Boiling point, °K</td>
<td>112</td>
<td>161</td>
<td>185</td>
</tr>
</tbody>
</table>

4. **The Number of Electrons Present in a Molecule**: The van der Waal’s forces have been found to increase with the number of electrons in the molecule. Greater the number of electrons, stronger would be the van der Waal’s forces and higher the boiling points. In case of halogens, the boiling points have been found to increase from fluorine to chlorine, bromine and iodine with progressive increase of electrons. Same has been found to be true of noble gases, i.e., the boiling points in these gases tend to increase from helium to radon with increase in number of electrons.

5. **Molecular Weight**: When the molecular weight of a substance (or atomic weight of inert gases) increases, its molecular size gets increased. Also its surface area tends to increase. Hence, these forces would be stronger.

Boiling point of octane (C\(_{\text{10}}\)H\(_{22}\)) has been found to be more than hexane (C\(_6\)H\(_{14}\)). Octane molecule is having large molecular weight (114), large size and large surface area than hexane (mol. Wt. 8). Because of large surface area, the van der Waal’s forces become stronger in octane than in hexane. Hence, boiling point of octane become more than hexane.

6. **Molecular Shape**: Certain molecules are having such a shape which offers maximum chances of attraction between them. These molecules are having high boiling point, e.g., normal pentane C\(_5\)H\(_{12}\) has zigzag shape and has boiling point, 36.1 °C. (Refer Figure 4.6 (a)). Certain molecules possess such a shape which provides minimum chances of attraction between them. These molecules have low boiling points, e.g., neo pentane, C\(_5\)H\(_{12}\) is having closely packed structure with boiling point 9.5 °C only (Refer Figure 4.6 (b)).
4.2.4 Applications of Van der Waals Forces

Van der Waals forces, although weak are used to explain many important phenomenon discussed below:

1. These forces account for different hardness in certain solids. For example, if atoms or molecules in any crystal are held by van der Waals forces, the crystals can be broken easily. Such crystals will be soft and possess low melting points.

2. These forces explains the deviation of the behaviors of gases at low temperature from that at ideal gases.

3. These forces are responsible for condensation and crystallization in the noble gases and halogens.

The actual crystal structures of the halogens are not all alike but they all consist of diatomic molecules. Iodine is typical in having a close packed structure very much like that of the inert gases. As with the inert gases, the strength of van der Waal’s forces increases with increasing atomic number so that the melting and boiling points of the halogens increase in passing from fluorine to iodine.

The inert gases are monoatomic and exist as single atoms in the gaseous state. In the solid state these atoms are arranged in a cubic close-packed structure; each atom being surrounded by 12 equidistant neighbours. The relative weakness of the van der Waal’s forces holding such a crystal together is shown by the low melting and boiling points of the inert gases. The melting and boiling points of inert gases increase as the atomic number or size of the atom increases, as shown in Table 4.1.

| Table 4.1 Melting and Boiling Point of Inert Gases |
|----------------|---|---|---|---|---|
| He  | Ne  | Ar | Kr | Xe | Rn |
| At. No | 2  | 10 | 18 | 36 | 54 | 86 |
| M.P. (*K) | 24.6 | 73.9 | 116 | 161 | 202 |
| B.P. (*K) | 4.2 | 27.2 | 83.3 | 120 | 165 | 211 |
Such a variation suggests that the strength of the van der Waal’s forces increases as the size of the particles linked together gets larger. These forces between helium atoms are so weak that helium cannot be solidified at atmospheric pressure.

**Check Your Progress**
1. Define Van der Waals forces.
2. How will the condition of temperature effect the Van der Waals forces?

### 4.3 Lattice Energy

The lattice energy (\(u\)) of a crystal is the energy evolved when one gram molecule of the crystal is formed from its gaseous atoms. The formation of a mole of an atomic solid \(C^+\) have the constituent gaseous ions may be represented as:

\[
C^+ (g) + a (g) \rightarrow C^+ a(s) + \text{Energy}
\]

The energy released in the above equation is known as lattice energy. It is usually denoted by \(u\). As per the connections of laws of thermodynamics lattice energy has a negative sign.

From first law of thermodynamics we know that the energy released in the formation of one mole of an ionic solid from its constituent gaseous ions in numerically equal to the energy that will be needed to convert one mole of the same ionic solid into the gaseous ions. So, lattice energy may also be defined as the energy required to overcome ions of one gram mole of an ionic solid from their equilibrium position in the crystal to infinity. This may be represented as

\[
C^- a^- + \text{Energy} \rightarrow C^+ (g) + a (g)
\]

From above equation it is clear that the stability of an ionic solid is measured in terms of its lattice energy.

#### 4.3.1 Calculation of Lattice Energy

The lattice energy of an ionic crystal is determined by coulombic interaction between all its ions carried the formation of an ionic crystal from its constituent ions.

When the ions approach each other to form the ionic crystal, the only force at first acting between them is the electrostatic attraction due to the opposite charges which varies inversely with distance, \(r\) between the two ions.

\[
P.E_{\text{ionic}} = \frac{Z_1 Z_2 (\pm e) (\pm e) A}{r} = \frac{Z_1 Z_2 e^2 A}{r}
\]

Where \(Z_1\) and \(Z_2\) are the number of charges on cations (+e) and anions (−e) respectively. \(A\) is known as Madelung constant which depends on the geometric arrangement of the ions in the lattice. Since the value of this constant depends only on the geometry of the crystal, the value will be the same for all other solids which exhibit the sodium chloride structure or some other structure.
As the ions approach close to one another, however, this attractive force given by equation (4.4) is opposed by the repulsive force due to the electron systems of the two ions which is given by equation (4.5)

\[
P.E. = \frac{Be^2}{r^n} \quad \text{... (4.5)}
\]

Where \( e \) is the electronic charge, \( n \) is called the Born exponent and \( B \) is a repulsion coefficient which measures the strength of the repulsive force and depends upon the particular ion present. The value of \( n \) depends upon the types of electronic configuration which are present in the ions of the crystal; \( n \) generally has a value between 9 and 12.

When the ions are brought together from infinite distance, the net potential energy for ions is obtained by adding Equations (4.4) and (4.5).

\[
P.E. = \frac{Z_+ Z_- e^2}{r} + \frac{Be^2}{r^n} \quad \text{... (4.6)}
\]

Equation (4.6) is known as Born equation. This equation gives the potential energy for a cation carrying \( Z_+ \), as integral charge and potential energy for an anion carrying \( Z_- \), as integral charge. From Eq. (3) it is also evident that the repulsion term, \( (Be^2/r^n) \), increases more rapidly than the first term with decrease in the value of \( r \). Born equation (4.6) is mainly used for calculating the energy released if a cation and an anion, which are separated by an infinite distance in gaseous state, are put together in a crystal at a distance \( r \) from each other.

### 4.3.2 Born-Lande Equation

Consider the equation (4.6) again. At the equilibrium distance, \( r_0 \), the attractive and the repulsive forces are exactly balanced and the potential energy becomes minimum at \( r_0 \). In order to calculate this, different equation (4.6) with respect to \( r \)

and then putting \( \frac{d(P.E.)}{dr} = 0 \) for \( r = r_0 \)

\[
\frac{d(P.E.)}{dr} = -Z_+ Z_- e^2 (-1)r^{-2} \frac{A}{r^n} + Be^2 (-n)(r^{-1})^{-n-1} = 0
\]

or

\[
\left[ \frac{d(P.E.)}{dr} \right]_{r=r_0} = -Z_+ Z_- e^2 (-1)r_0^{-2} \frac{A}{r^n} + Be^2 (-n)(r_0^{-1})^{-n-1} = 0
\]

or

\[
B = \frac{AZ_+ Z_- e^2}{n} r_0^{n-1} \quad \text{... (4.7)}
\]
Substituting equation (4.7) into (4.6), we get

\[
(P.E.)_o = \frac{Ae^2 Z_1 Z_2 \left( \frac{1}{n} - 1 \right)}{r_o} \quad \ldots(4.8)
\]

The lattice energy, \( U_o \), is the amount of energy released when one mole of sodium chloride crystals is formed from gaseous ions which are at infinite separation. Thus, by definition

\[
U_o = -(P.E.)_o \times N
\]

\[
= -\frac{NAe^2 Z_1 Z_2 \left( \frac{1}{n} - 1 \right)}{r_o}
\]

\[
= \frac{NAe^2 Z_1 Z_2 \left( 1 - \frac{n}{1} \right)}{r_o} \quad \ldots(4.9)
\]

Where \( N \) is the Avogadro’s number. Equation (4.9) is known as Born Lande equation.

From Born lande equation following conclusions can be drawn:

(i) The lattice energy \( U_e \) depends upon the changes of the ions, multiple charged ions giving more lattice energy than simply charged ions.

(ii) The lattice energy \( U_e \) depends upon the value of \( r_o \), the smaller the value of \( r_o \) the more negative being the value of lattice energy.

(iii) The lattice energy depends on the value of mode lung constant, which depends on the geometrical arrangement of the ions in the lattice.

(iv) The lattice energy depends upon the value of the born exponent \( \beta \), which may be determined from measurement of the compressibilities of ionic crystals.

### 4.3.3 Born-Mayer Equation

The Born mayer equation is used to calculate the lattice energy of an ionic solid. It is an improved version of Born lande equation. It is given by the equation,

\[
U = \frac{N M Z_1 Z_2 e^2}{4\pi \varepsilon_0 r_o} \left( 1 - \frac{D}{r_o} \right) \quad \ldots(4.10)
\]

Where:

- \( N_a \) = Avogadro’s constant
- \( M \) = Madelung Constant
- \( Z_1 \) = Charge number of cation
- \( Z_2 \) = Charge number of anion
Intermolecular Forces and Lattice Energy

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4.3.4 Kapustinskii’s Equation

The Russian chemist A.F. Kapustinskii noticed that if the Madelung constants for a number of structures are divided by the number of ions per formula unit, approximately the same value is obtained for them all. Moreover, he also noticed that the order of values so obtained increases with the coordination number. Therefore, since as we have seen, the ionic radius also increases with co-ordination number. The variation in A from one structure to another can be expected to be quite small. This led him to propose that there exists a hypothetical rock-salt structure that is energetically equivalent to the true structure of any ionic solid. That being so, the lattice enthalpy can be calculated by using the Madelung constant and the appropriate ionic radii for (6, 6) co-ordination. The resulting expression is called the Kapustinskii equation.

\[ U_s = \frac{125200vZ}{r_s}\left(1 - \frac{34.5}{r_s}\right) \quad \ldots (4.11) \]

Where:

- \( v \) = The number of the ions per molecule i.e., 3 for \( \text{BeCl}_2, \text{Li}_2\text{O} \), etc.
- \( r_s \) = The sum of the ionic radii of the ions.

4.3.5 Born-Haber Cycle (Experimental Determination of Lattice Energy)

Born Haber in 1919 derived a cycle that relates the lattice energy of a crystal to other thermodynamics data. The values of lattice energy can be obtained indirectly by means of an energy cycle, consisting of ionic solids, the gaseous ions and the elements in their standard states. This cycle is based on following assumptions:

(i) The reactants are vaporized and converted into gaseous atoms.
(ii) The gaseous atoms are converted into ions and
(iii) The gaseous ions are combined to give the product.

For a single substance such as an alkali metal halide (MX), such a process might be formulated.
\[ MX(s) \leftrightarrow \frac{-U_i}{-\Delta H_f} \quad \leftarrow M^+(g) + X^-(g) \]

\[ -\Delta H_f \quad + I \quad - E \]

\[ M(s) + \frac{1}{2} X_2(g) \xrightarrow{+s+1/2e} M(g) + X(g) \]

Each step being denoted by an energy quantity. They have the following significances:

(i) \( S \) – It is the sublimation energy of the metal \( M(s) \rightarrow M(g) \)

As the energy is required for the process (endothermic), its value is reported as a positive quantity.

(ii) \( D \) – It is the dissociation energy of \( X_2 \) (gas) into atoms.

\[
\frac{1}{2} X_2(g) \xrightarrow{+1/2e} X(g)
\]

This process is also endothermic and its value is considered to be a positive quantity.

(iii) \( I \) – It represents ionization energy, i.e., energy required for the removal of an electron from an isolated gaseous atom, \( M \). This process is endothermic and its value is reported as positive quantity. \( M(g) \rightarrow M^+(g) + e^- \)

(iv) \( E \) – It represents electron affinity, i.e., amount of energy released when a neutral gaseous atom gains an electron. The process is exothermic and its value is given as a negative quantity. \( X(g) + e^- \rightarrow X^+(g) \)

(v) \( U_i \) – It represents lattice energy, i.e., the amount of energy released when one mole of gaseous positive and negative ions condense to form an ionic solid.

\[
M^+(g) + X^-(g) \xrightarrow{-U_i} MX(s)
\]

This process is exothermic and its value is always negative.

(vi) \( \Delta H_f \) – It is the heat of formation which is equal to the amount of energy released when one more of a substance is formed from its elements.

\[
M(s) + \frac{1}{2} X_2(g) \xrightarrow{-\Delta H_f} MX(s)
\]
This is single step reaction. Energy is released in the process and its value is reported as a negative quantity. As the same product is obtained from the same reactants by either path, the total energy changes must be equal in the two paths. It follows that

\[-\Delta H_f = S + \frac{1}{2} D + I - E - U_f\]  

...(4.12)

Solving for \(U_f\), that

\[U_f = \Delta H_f + S + \frac{1}{2} D + I - E\]  

...(4.13)

Thus, lattice energy can be calculated if other thermochemical quantities are known.

### 4.4 DIPOLE MOMENT

We know that two atoms differing is electronegativity in a molecule produces a dipole with positive at one end and negative at the other end. The degree of polarity in a polar molecule is expressed by its dipole moment which is equal to the product of charge and the distance between atoms.

Mathematically- Dipole moment,

\[\mu = e \times d\]  

...(4.14)

Where

\[e = \text{electronic charge and is of the order of } 10^{-19}\]  
es.u. and

\[d = \text{distance and is of the order } 10^{-8} \text{ cm.}\]

\(\mu\) is, therefore, of the order of \(10^{-36}\) e.s.u. per cm. and this unit is known as Debye (D).

Dipole moment is a vector quantity having both direction and magnitude and is often indicated by an arrow pointing towards the negative end e.g., \(\vec{\mu}\). The molecular dipole moment of molecules having one polar bond is the same as that of the individual bonds while in case of molecules containing more than one polar bonds, the molecular dipole moment is the sum of the dipole moments of all the individual bonds. Dipole moment can be applied to find out the shape of the molecules, i.e., whether symmetrical or unsymmetrical.

In general a polar bond is formed between two atoms of different radii and different electronegativities. It should be remembered that greater the value of the dipole moment, greater will be the polarity of Bond.
4.4.1 Dipole Moment of Diatomic Molecules

In case of diatomic molecules, the dipole moment is the same as that of individual bonds. This is a molecular dipole moment for example, the molecular dipole moment of HCl is the same as that of the simple HCl bond, i.e., 1.03 D.

\[
\begin{align*}
\hat{H} & \quad \text{and} \quad \hat{Cl} \\
\mu & = 1.03 \text{ D}
\end{align*}
\]

4.4.2 Dipole Moment of Polyatomic Molecules

In molecules containing more than two atoms i.e. having more than one polar bond, the molecular dipole moment is made up of the dipole moments of all the individual bonds. Its magnitude depends not only on the values of individual dipole moments but also on the arrangement of the polar bonds in space. This can be understood by the following examples:

(i) **Carbon Dioxide Molecule**: As the electronegativity of oxygen is more than that of carbon, it means that carbon-oxygen bonds in carbon dioxide are polar, i.e., each shared electron pair lies closer to each oxygen atom than to the central carbon atom, as shown below:

\[
\begin{align*}
\hat{C} & : \hat{O} : \hat{C} \quad \text{or} \quad O = C = O \\
\end{align*}
\]

Experimentally, it has been proved that the molecule is non-polar and its dipole moment is zero. These facts reveal that carbon dioxide molecule is linear because the dipole moment on one side of the molecule is cancelled by that on the other side.

(ii) **Carbon Disulphide Molecule**: As the electronegativity of sulphur is more than that of carbon, it means that each shared electron pair lies closer to each sulphur atom than to the central atom and therefore both the carbon-sulphur bonds are polar.

\[
\begin{align*}
\hat{S} : \hat{C} : \hat{S} \\
\end{align*}
\]

Experimentally, it has been proved that the molecule is non-polar and its dipole moment is zero. These facts reveal that carbon dioxide molecule is linear because the dipole moment on one side of the molecule is cancelled by that on the other side of the molecule.
(iii) **Water Molecule**: As each shared electron pair lies closer to oxygen atom than to hydrogen atom, it means that both the oxygen-hydrogen bonds are polar

\[ \text{H} - \overset{\delta}{\text{O}} - \overset{\delta}{\text{H}} \]

Experimentally, it has been proved that the molecule is polar and its dipole moment is 1.84 D. Therefore, the water molecule is non-linear. In other words, the water molecule has an unsymmetrical or bent structure. The angle between two bonds in H\(_2\)O should be 104.5\(^\circ\) to explain that the dipole moment of each O–H bond is 1.60 D and the net dipole moment is 1.4 D. The bond angle of 104.5\(^\circ\) has been confirmed by the X – Ray analysis.

(iv) **Sulphur Dioxide Molecule**: Its dipole moment is 1.60 D. It reveals that the molecule has a bent structure because the two oxygen atoms are not lying symmetrically with respect to the sulphur atom as O = S = O.

\[ \text{O} = \overset{\delta}{\text{S}} = \overset{\delta}{\text{O}} \]

(v) **Ammonia Molecule**: Its dipole moment is 1.46D. This value is indicative of the fact that the three hydrogen atoms are not lying symmetrical with respect to the nitrogen atom. It means that the NH\(_3\) molecule is highly polar. The high polarity of NH\(_3\) molecule has been explained by assigning a triangular pyramidal structure to the molecule in which nitrogen atom lies at the apex of the pyramid while the three hydrogen atoms are lying at the other three corners. Similarly, the molecules of PCl\(_3\) and AsCl\(_3\) have triangular pyramidal structures with P or As atom at the apex.

(vi) **BF\(_3\), CH\(_4\) and CCl\(_4\) Molecules**: In BF\(_3\), there are three B – F bonds which are oriented at an angle of 120\(^\circ\) to one another. The three B – F bonds lie in one plane and cancel the dipole moment of one another. Hence, the dipole moment of BF\(_3\) would be zero. Similarly, the dipole moments of methane (CH\(_4\)) and carbon tetrachloride (CCl\(_4\)) molecules would be zero due to their symmetrical tetrahedral shape (see Figure 4.8).
4.4.3 Significance of Dipole Moment

1. Knowledge of Shape of Molecules: (a) Molecules possessing regular geometry are having zero dipole moment. e.g. carbon tetrachloride (CCl₄), methane (CH₄) etc. are having zero dipole moment. Their shape would be regular tetrahedral.

2. Knowledge of Polar and Non-polar Molecules
    (a) If a molecule is having some dipole moment, it is a polar molecule. H₂O (µ = 1.84 D) and NH₃ (µ = 1.46 D) are polar molecules.
    (b) If a molecule is having zero dipole moment, it is a non-polar molecule. e.g. H₂N₂D₂ (each has µ = 0) etc. are non-polar molecules.

3. Knowledge of Degree of Polarity of Molecules: If the dipole moment of a molecule is having a high value, its degree of polarity would be high, e.g. HF (µ = 1.91 D). Thus, HF is more polar than HCl (µ = 1.03 D). Thus, HF is more polar than HCl.

4. Knowledge of Polarity in Polyatomic Molecules: Polyatomic molecules have been of two types.
    (i) Molecules with symmetrical shape.
    (ii) Molecules with unsymmetrical shape.

   (i) **Symmetric Molecules:** Such molecules are said to be non-polar. In such cases, the polarity of one bond would be able to cancel the polarity of other bond. Such molecules have zero dipole moment.
   (i) CO, i.e. O = C = O

Fig. 4.9 Shape Molecules  Fig. 4.10 Non-Polar Molecules

Intermolecular Forces and Lattice Energy

Self-Instructional Material
(ii) \( \text{CCl}_4 \) i.e.
(iii) \( \text{CS}_2 \) i.e. \( S = \text{C} = \text{S} \)

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(i) **Unsymmetric Molecules**
Such molecules are said to be polar. In such cases, the polarity of one bond fails to cancel the polarity of other bond, for example.

(i) \( \text{H}_2\text{O} \)
(ii) \( \text{NH}_3 \)

\[ \text{Fig. 4.11 Water} \quad \text{Fig. 4.12 Ammonia} \]

4.4.4 Dipole Moment and Percentage Ionic Character

The concept of dipole moment has been found to be quite useful for finding the percentage ionic character in a molecule. It is demonstrated as follows.

The relation between dipole moment \( (\mu) \) and percent ionic character \( (P) \) is as follows:

\[ \mu = \frac{Pd}{100} \]

The above relation is quite useful for knowing the percent ionic character of a bond from dipole moment \( (\mu) \) and bond length \( (d) \) as shown in Table 4.2.

**Table 4.2 Ionic Character of the \( H \) – \( X \) Bonds**

<table>
<thead>
<tr>
<th>Example of the molecule</th>
<th>Dipole moment (D)</th>
<th>Bond length (( \mu ))</th>
<th>Percent Ionic Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HI} )</td>
<td>0.38</td>
<td>171</td>
<td>5</td>
</tr>
<tr>
<td>( \text{HBr} )</td>
<td>0.78</td>
<td>141</td>
<td>17</td>
</tr>
<tr>
<td>( \text{HCl} )</td>
<td>1.03</td>
<td>127</td>
<td>12</td>
</tr>
<tr>
<td>( \text{HF} )</td>
<td>1.91</td>
<td>92</td>
<td>45</td>
</tr>
</tbody>
</table>

4.4.5 Measurement of Dipole Moment

It is possible to measure dipole moment from the relative dielectric constant, \( \varepsilon \) of the molecules. The total molar polarization \( P_n \) may be given by the following Clausius and Mosotti equation:
\[ P_n = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \frac{M}{\rho} \]

\( M \) and \( \dot{\varepsilon} \) are molecular weight and density of the compound respectively.

It is possible to obtain values of \( \varepsilon \) and \( \mu \) from the measurements of the dielectric constants of the compound at different temperatures. Debye deduced the following relation:

\[ P_n = \frac{N}{3} \left( \alpha + \frac{\mu^2}{3kT} \right) \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \frac{M}{\rho} \text{ (in SI units)} \]

\[ P_n = \frac{4\pi N}{3} \left( \alpha + \frac{\mu^2}{3kT} \right) \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \frac{M}{\rho} \text{ (in C.G.S. units)} \]

### 4.4.6 Applications of Dipole Moment

The various applications of dipole moments are as follows:

1. **Bond Polarity**: By using equations as given above it is possible to determine the electronegativity difference of the bonded atoms from the dipole moment measurements. When dipole moment is referred a bond in a molecule, it is known as the bond moment. Some typical values for bond moments in bye are given in Table 4.3.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond moment (Debye)</th>
<th>Bond</th>
<th>Bond moment (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H − C</td>
<td>0.40</td>
<td>C − F</td>
<td>1.39</td>
</tr>
<tr>
<td>H − N</td>
<td>1.33</td>
<td>C − Cl</td>
<td>1.47</td>
</tr>
<tr>
<td>N − O</td>
<td>1.36</td>
<td>N − F</td>
<td>0.17</td>
</tr>
<tr>
<td>H − P</td>
<td>0.36</td>
<td>C = N</td>
<td>0.90</td>
</tr>
<tr>
<td>H − S</td>
<td>0.68</td>
<td>C = O</td>
<td>2.3</td>
</tr>
<tr>
<td>C − N</td>
<td>0.23</td>
<td>C = N</td>
<td>3.5</td>
</tr>
<tr>
<td>C − O</td>
<td>0.74</td>
<td>N = C</td>
<td>3.0</td>
</tr>
<tr>
<td>C − S</td>
<td>0.90</td>
<td>N¹ · B²</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N¹ · O²</td>
<td>4.3</td>
</tr>
</tbody>
</table>

2. **Cis and Trans Isomers**: Dipole moment has been used to characterize cis and trans isomers for example. The cis isomer of a square planar complex has dipole moment whereas the trans isomer does not have.

3. **Structure Equilibria of Complexes**: Measurement of dipole moments have been used for the determination of concentration of tetrahedral and
square planar complexes at equilibria. These two forms have different dipole moments, due to different stereochemistries.

### Check Your Progress

3. What is lattice energy?
4. What is dipole moment?
5. Write the mathematical expression for dipole moment.

### 4.5 ANSWERS TO CHECK YOUR PROGRESS

1. The van der Waals forces are very short lived intermolecular attractive forces which exist between all kind of atoms molecules and ions when they are sufficiently close to each other. These forces have nothing to do with valence electrons of the elements.

2. Lower the temperature, lesser would be the random movement of molecules and greater would be the chance of molecular interactions. At higher temperatures the condition would be somewhat the reverse. Hence at low temperatures van der Waals interactions would be relatively stronger.

3. The lattice energy (u) of a crystal is the energy evolved when one gram molecule of the crystal is formed from its gaseous atoms.

4. The degree of polarity in a polar molecule is expressed by its dipole moment which is equal to the product of charge and the distance between atoms.

5. Mathematically dipole moment is expressed as:  \( \mu = e \times d \)

Where  
\[ e = \text{electronic charge and is of the order of } 10^{-10} \text{ e.s.u.} \]
\[ d = \text{distance and is of the order } 10^{-8} \text{ cm.} \]

### 4.6 SUMMARY

- The magnitude of forces of attraction between the molecules of polar as well as non-polar compounds is maximum in solids and decreases for liquid and gases. These forces of attraction are called intermolecular forces (IMF).

- The Van der Waals forces are very short lived intermolecular attractive forces which exist between all kind of atoms molecules and ions when they are sufficiently close to each other. These forces have nothing to do with valence electrons of the elements.

- There are four types of van der Waals forces i.e. Dipole-dipole interaction, Ion-dipole interactions, Dipole-induced dipole interactions and Instantaneous dipole-induced dipole interactions.
• Dipole-dipole interactions are present in polar molecules which have permanent polarity.
• We know that polar molecules are attracted towards ions. The negative end of the dipole is attracted towards the cation and the positive end is directed towards the anion. This type of interaction is known as ion-dipole interaction.
• Dipole-induced dipole interactions are observed in a mixture of polar and non-polar molecules.
• Instantaneous dipole-induced dipole interactions occur in monoatomic noble gases like He, Ne, Ar etc. and non-polar molecules like H$_2$, O$_2$, Cl$_2$, I$_2$, N$_2$ etc.
• The lattice energy (u) of a crystal is the energy evolved when one gram molecule of the crystal is formed from its gaseous atoms.
• The lattice energy of an ionic crystal is determined by coulombic interaction between all its ions carried the formation of an ionic crystal from its constituent ions.
• The Born Mayer equation is used to calculate the lattice energy of an ionic solid.
• The degree of polarity in a polar molecule is expressed by its dipole moment which is equal to the product of charge and the distance between atoms.
• Dipole moment can be applied to find out the shape of the molecules, i.e., whether symmetrical or unsymmetrical.
• In case of diatomic molecules, the dipole moment is the same as that of individual bonds.
• In molecules containing more than two atoms i.e. having more than one polar bond, the molecular dipole moment is made up of the dipole moments of all the individual bonds. Its magnitude depends not only on the values of individual dipole moments but also on the arrangement of the polar bonds in space.
• It is possible to measure dipole moment from the relative dielectric constant, 
  \( \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \) of the molecules.

4.7 **KEY WORDS**

- **Enthalpy**: It is a property of a thermodynamic system which is equal to the system’s internal energy plus the product of its pressure and volume.
- **Lattice Energy**: It is a measure of the energy released when ions are combined to make a compound or it is a measure of the cohesive forces that bind ions.
• Madelung constant: It is used in determining the electrostatic potential of a single ion in a crystal by approximating the ions by point charges.

4.8 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions
1. What are the different types of Van der Waals forces?
2. Discuss the characteristics of Van der Waals forces.
3. What are the various applications of Van der Waals forces?
4. Write a short note on lattice energy.
5. What is dipole moment?

Long Answer Questions
1. What are the various factors affecting the Van der Waals forces? Explain.
2. Explain the born lande and born-Meyer equation to calculate the lattice energy.
3. How will you calculate the lattice energy using kapustinskii equation?
4. Explain the born-Haber cycle.
5. Explain the significance and applications of dipole moment.

4.9 FURTHER READINGS

UNIT 5  PROPERTIES OF IONIC COMPOUNDS

Structure
5.0 Introduction
5.1 Objectives
5.2 Ionic Compounds
5.3 Factors Affecting the Formation of Ionic Bond
5.4 Properties of Ionic Compounds
5.5 Energetics of Dissolution of Ionic Compounds
5.5.1 Applications
5.6 Answers to Check Your Progress Questions
5.7 Summary
5.8 Key Words
5.9 Self Assessment Questions and Exercises
5.10 Further Readings

5.0 INTRODUCTION

In chemistry, an ionic compound is a chemical compound composed of ions held together by electrostatic forces termed ionic bonding. The compound is neutral overall, but consists of positively charged ions called cations and negatively charged ions called anions. Individual ions within an ionic compound usually have multiple nearest neighbours, so are not considered to be part of molecules, but instead part of a continuous three-dimensional network, usually in a crystalline structure. Ionic compounds containing hydrogen ions (H\(^+\)) are classified as acids, and those containing basic ions hydroxide (OH\(^-\) or oxide (O\(^2-\)) are classified as bases. Ionic compounds without these ions are also known as salts and can be formed by acid-base reactions. Ionic compounds can also be produced from their constituent ions by evaporation of their solvent, precipitation, freezing, a solid-state reaction, or the electron transfer reaction of reactive metals with reactive non-metals, such as halogen gases.

Ionic compounds typically have high melting and boiling points, and are hard and brittle. As solids they are almost always electrically insulating, but when melted or dissolved in water they become highly conductive, because the ions are mobilized.

In this unit, you will study about the properties of ionic compounds, factors affecting the formation of ionic bond, ionization energy, electron affinity, lattice energy and Salvation energy. You will also study about the applications of ionic compounds and energetics of dissolution of ionic compounds.
5.1 OBJECTIVES

After going through this unit, you will be able to:

- Explain properties of ionic compounds
- Describe electrical conductivity
- Define ionization energy, electron affinity, lattice energy and Salvation energy
- Understand energetics of dissolution of ionic compounds
- Discuss applications of ionic compounds

5.2 IONIC COMPOUNDS

Ionic bonding is a form of chemical bonding that involves the electrostatic attraction between oppositely charged ions. It is the primary interaction that occurs in ionic compounds. Characteristically, it is one of the main bonds along with Covalent bond and Metallic bond. Ions are atoms that have gained one or more electrons (known as anions, which are negatively charged) and atoms that have lost one or more electrons (known as cations, which are positively charged). This transfer of electrons is known as electrovalence. Fundamentally, the cation is a metal atom and the anion is a non-metal atom, but these ions can be of a more complex nature, for example the molecular ions like NH₅⁺ or SO₃²⁻. Therefore, an ionic bond is the transfer of electrons from a metal to a non-metal in order to obtain a full valence shell for both atoms.

Each atom is unique because it is made of a specific number of protons, neutrons, and electrons. Usually, the number of protons and electrons is the same for an atom. When an atom gains or loses an electron, we get an ion. Since electrons themselves have a net negative charge, adding or removing electrons from an atom changes the charge of the atom. This is because the number of electrons is no longer in balance with the number of protons, which have a positive charge.

Compounds consist of ions and are known as ionic compounds. Atoms can gain or lose electrons and are called ions. The ions may have a negative charge or positive charge. Atoms that gain electrons and therefore have a net negative charge are known as anions. Conversely, atoms that lose electrons and therefore have a net positive charge are called cations. Cations tend to be metals, while anions tend to be non-metals. Ions may also be single atoms or multiple, complex groups of atoms.

 Principally, the non-metals lose electrons to gain negative charge and form anions, whereas metals lose electrons to gain positive charge and form cations. Anions are ions that have negative charge and cations are ions that tend to have a positive charge. Ionic bonds are generally between metals and non-metals.
The opposite negative and positive charges of the ions hold together in ionic bonds, forming ionic compounds, which are just what they sound like: compounds made of ions. The loss or gain from one atom matches the loss or gain of the other, so one atom essentially ‘donates’ an electron to the other atom it pairs up with.

Following are the some significant properties of ionic compounds:

- The electrostatic forces of attraction between oppositely charged ions lead to the formation of ions.
- They form crystals. Ionic compounds form crystal lattices rather than amorphous solids.
- They have higher enthalpies of fusion and vaporization than molecular compounds.
- They are hard.
- They are brittle.
- Ionic compounds have high boiling and melting points as they are very strong and require a lot of energy to break.
- They conduct electricity but only when they are dissolved in water, i.e., ionic compounds do not conduct electricity in a solid state but they do conduct electricity in the molten state.
- Electrovalent compounds usually dissolve in water and are insoluble in solvents like oil, petrol, kerosene, etc.
- In comparison to molecular compounds, ionic compounds have higher enthalpies of fusion and vaporization.

Ionic bond is formed by the transference of one or more electrons from one atom to the other. Characteristically, this type of bond typically comes into existence between a metal (electropositive) and a non-metal (electronegative) atom. If any metal atom loses its valence electrons it will change into a positive ion (cation) while if any non-metal atom gains an electron it will change into a negative ion (anion) and expand in size. Thus, they become stable by attaining 8 (or 2) electrons in the outermost shell. The oppositely charged ions are held together by electrostatic force of attraction. Thus, ionic bond may be defined as the electrostatic force of attraction which holds both the positively charged (cation) and negatively charged (anion) together, i.e., when a cation and an anion come close to each other, they are held by electrostatic force of attractions and the bond established between them is known as an ionic or electrovalent bond.

In simple words, an ionic bond involves the transference of a certain number of electrons to another dissimilar atom which has a tendency to gain electrons, so that both acquire stable inert gas configuration. The electrostatic always tends to decrease the potential energy. Hence the potential energy of the compound is much less than it was before the formation of an ionic bond. This can be explained with the help of example for the formation of NaCl molecule.
Formation of Sodium Chloride (NaCl)

Sodium atom, Na (2, 8, 1) has only 1 electron in its valence shell. In order to acquire the configuration of nearest noble gas Ne (2, 8) it has to lose its valence electron, while the Chlorine atom, Cl (2, 8, 7), has seven electrons in its valence shell. It can acquire the configuration of nearest noble gas, Ar (2, 8, 8) by gaining one electron. Thus, Sodium atom transfers its valence electron to Chlorine atom resulting in the formation of sodium ion (Na⁺) and chloride ion (Cl⁻), respectively (Refer Figure 5.1). The electrostatic force of attraction holds these oppositely charged ions together. These changes are represented below by using Lewis Symbols.

![Ionic Bond Formation for Sodium Chloride](image)

*Fig. 5.1 Ionic Bond Formation for Sodium Chloride*

The number of electrons which an atom loses or gains while forming an ionic bond is termed as the ‘Electrovalency’. The atom which loses electrons is called electropositive atom while the atom which gains electrons is called electronegative atom. The positive (+) sign is put before the valency of electropositive atom while negative (-) sign is put before the valency of electronegative atom, for example electrovalency of Na is +1 and of Cl is -1. Alternatively, electrovalency is equal to the unit charges on the ion.

The common monoatomic ions of some groups of the representative elements are given below:

<table>
<thead>
<tr>
<th>Group</th>
<th>1</th>
<th>2</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N⁰</td>
<td>F⁻</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Mg²⁺</td>
<td>Al³⁺</td>
<td>P⁰</td>
<td>S⁰</td>
<td>Cl⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K⁺</td>
<td>Ca²⁺</td>
<td></td>
<td></td>
<td>Br⁻</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb⁺</td>
<td>Sr²⁺</td>
<td></td>
<td></td>
<td>I⁻</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs⁺</td>
<td>Ba²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Let us now write the Lewis structures of the ionic compounds formed by: K and O; Ca and F; Na and S; Na and P, and Al and F.
2K + Cl₂ → K⁺[Cl]⁻ + K⁺ or KCl
Ca + 2[Cl]⁻ → [Ca⁺][Cl]⁻ or CaCl₂
2Na + Br₂ → [Na⁺][Br]⁻ or NaBr
2Na + F⁻ → Na⁺[F]⁻ or Na⁺F⁻
Al⁺ + 3[Cl]⁻ → [Al⁺][Cl]⁻ or AlCl₃

It may be noted that ion has a uniform field of influence around it, hence, ionic bond is non-directional in nature.

5.3 FACTORS AFFECTING THE FORMATION OF IONIC BOND

An ionic bond is formed by the complete transference of one or more electrons from the outer energy shell (valency shell) of one atom to the outer energy shell of the other atom. Hence, both the atoms acquire the stable electronic configurations of the nearest noble atom. The atom from which the electrons are transferred, i.e., the atom which loses the electrons, acquires a positive charge and becomes cation. The various factors that affect the formation of ionic bond are as follows:

1. Ionization Energy: Ionization energy is required in the formation of ionic bond when a metal atom loses electron to form cation. This process required energy equal to the ionization energy. Lesser the value of ionization energy, greater is the tendency of the atom to form cation. For example, alkali metals form cations quite easily because of the low values of ionization energies. Hence, either of the two atoms forming ionic bond should have a low ionization energy, i.e., a smaller amount of energy is required to pullout an electron from its outer energy level it means that the lower the value of ionization potential, the greater will be the case of formation of cations and hence the electrovalent bond.

\[ M \rightarrow M^+ + e^- \ [E_1 = \text{First Ionization Energy}] \]
\[ M^+ \rightarrow M^{2+} + e^- \ [E_2 = \text{Second Ionization Energy}] \]

The alkali metals (Group I) have low ionization energies. Therefore, they can readily lose an electron from their valency shells. On the other hand, the alkaline earth metals, do so less readily. The reason is that atoms of alkaline earth metals have to lose two electrons from their outer energy level so as to acquire stable configuration of nearest inert gas.

Once an electron has been lost from an atom, the remaining electrons are held more firmly and are not lost so easily. Thus Second Ionization Energy...
Properties of Ionic Compounds

NOTES

(E_f) is very high as compared with the First Ionization Energy (E_i). Therefore to remove two electrons, the required energy must be equal to E_f + E_{f-2}.

Because of this reason alkaline earth metals with two electrons in the outermost energy level form positive ions less readily.

The removal of three or more electrons needs large energies. Therefore positive ions with three or four units are rarely formed.

2. **Electron Affinity**: Electron affinity is defined as the change in energy (in kJ/mole) of a neutral atom (in the gaseous phase) when an electron is added to the atom to form a negative ion or there is possibility that the neutral atom is capable of gaining an electron. Principally, the term ‘Electron Affinity’ refers to the energy released when gaseous atom accepts electron to form a negative ion.

When an electron is added to a neutral atom (i.e., first electron affinity) energy is released; thus, the first electron affinities are **negative**. However, more energy is required to add an electron to a negative ion (i.e., second electron affinity) which overwhelms any the release of energy from the electron attachment process and hence, second electron affinities are **positive**.

- **First Electron Affinity**: This is the negative energy because energy is released.

\[ X(g) + e^- \rightarrow X^-(g) \]

- **Second Electron Affinity**: this is the positive energy because energy needed is more than energy gained.

\[ X^- (g) + e^- \rightarrow X^{2-} (g) \]

Thus, the value of electron affinity gives the tendency of an atom to form anion. Now greater the value of electron affinity more is the tendency of an atom to form anion. For example, halogens having highest electron affinities within their respective periods to form ionic compounds with metals very easily. One of the two atoms forming an ionic bond should have high electron affinity, i.e., it should be able to accept the electron readily. The elements of Group 17 (halogens) possess the highest electron affinities of all the elements hence they are early connected into anions, hence can form ionic bond readily.

The elements of Group 16 have quite high electron affinities and form ionic bonds but less readily than those of Group 17 elements because they accept two electrons to achieve stable configuration of nearest inert gas. The reason for this is that the addition of one electron to the atom is accompanied by release of energy to form a singly charged negative ion. The negative ion so formed repels the new coming electron and energy has to be supplied to add electron to overcome the strong repulsion from the already negatively charged ion.
X + e⁻ → X⁻ (Electron Affinity)

Singly Charged Ion

X⁻ + e⁻ + Energy Supplied → X²⁻

Singly Charged Ion

Consequently, the formation of doubly-charged negative ion is not an easy process. Therefore, formation of oxides or sulphides is not that easy as compared to the formation of fluorides or chlorides. Thus, it may be concluded that the ionic bonds are generally formed between the atoms of the elements of the left of the periodic table.

3. **Lattice Energy:** Lattice energy is defined as the amount of energy released when cations and anions are brought from infinity to their respective equilibrium sites in the crystal lattice to form one mole of the ionic compound. The higher the lattice energy, the greater is the tendency of the formation of an ionic bond. The higher the charges on the ions and smaller the distance between them, the greater is the force of attraction between them. The formation of an ionic bond depends upon the lattice energy. For lattice energies to be high, the force of electrostatic attraction between the constituent ions should be high.

### Check Your Progress

1. What is ionic bond? How is it formed?
2. Define ionization energy giving suitable example.
3. Explain the term electron affinity with the help of an example.
4. How does the formation of an ionic bond depend upon the lattice energy?

### 5.4 PROPERTIES OF IONIC COMPOUNDS

Compounds containing ionic bond are known as ionic compounds. These are polar in nature and on dissolution is water they split into two oppositely charged ions. The characteristic properties of ionic compounds are:

1. **Crystalline Nature:** Ionic compounds usually exist in the form of crystalline solids. X-ray analysis have shown that these solids do not exist as molecules but exist in the form of ions. These ions are arranged in a well defined geometric pattern to form ionic crystal, for example, in sodium chloride crystal each sodium ion (Na⁺) is surrounded by six chloride (Cl⁻) ions and each chloride (Cl⁻) ion is surrounded by six sodium ions as shown in Figure 5.2. It may be noted that pattern of arrangement of ions depends on the size of the ions and also on magnitude of charge on the ions.
2. **High Melting and Boiling Points**: Ionic compounds possess high melting and boiling points. Their relative high melting and boiling points are due to electrostatic forces of attraction and considerable amount of energy is needed to break up their crystal lattices. The closer the ions in a crystal, the stronger will be the electrostatic attraction forces and consequently higher will be the melting points as shown below.

<table>
<thead>
<tr>
<th>Melting Points of Some Sodium Salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
</tr>
</tbody>
</table>

3. **Electrical Conductivity**: Ionic compounds conduct electricity when molten (liquid) or in aqueous solution (dissolved in water), because their ions are free to move from place to place. Ionic compounds cannot conduct electricity when solid, as their ions are held in fixed positions and cannot move, i.e., in solid state the ions occupy fixed positions and hence are not able to have free movement. Thus, ionic compounds are bad conductors of electricity in the solid state but are good conductors of electricity in the aqueous state. By definition, “Ionic compounds are conductors of electricity when molten or in solution, and insulators when solid”.

However, a few solids like MAgI$_4$ (M = K, NH$_3$, Rb) are able to conduct similar to those of the ions is solutions due to the high mobility of Ag$^+$ ions in an unusual crystal lattice.

4. **Solubility**: Ionic compounds are quite soluble in solvents of high dielectric constant and of polar nature. It is because the high dielectric constant of the solvent that lowers the attractive forces between the ions of the lattice. Also, because of the polar nature the solvent interacts highly with the ions and the energy of solution is sufficient to overcome the attractive forces between the ions. Non-polar solvents like benzene, carbon tetrachloride, etc., which have low dielectric constants do not solvate the ions. Hence ionic compounds are soluble in polar solvents but insoluble in non-polar solvents.
5. **Ionic Reactions:** Chemical reactions of an ionic compound are the reactions of its constituent ions. These are usually rapid.

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \text{ (Neutralisation Reaction)} \]
\[ \text{Acid} \quad \text{Base} \]
\[ \text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \text{ (Precipitation Reaction)} \]

6. **Space-Isomerism:** The linkage between the two oppositely charged atoms is simply due to the electrostatic attraction between them and is, therefore, non-rigid and non-direction. They are incapable of exhibiting any type of space-isomerism.

7. **Isomorphism:** Mitscherlich’s law could not explain the isomorphism of compounds like sodium fluoride and magnesium oxide or potassium sulphide and calcium chloride. However, the electronic theory of valency offers explanation of suggesting that compounds showing isomorphism have similar electronic structures as shown below:

   (i) Sodium Fluoride and Magnesium Oxide
   
   Na\(^+\) F  
   2, 8 2, 8 
   Mg\(^{2+}\) O\(^-\)  
   2, 8 2, 8

   (ii) Potassium Sulphide and Calcium Chloride
   
   K\(^+\) S\(^2-\) K\(^+\)  
   2,8,8 2,8,8 2,8,8  
   Ca\(^{2+}\) Cl\(^-\)  
   2,8,8 2,8,8 2,8,8

8. **Hardness and Britteness:** Ionic compounds are hard because the positive and negative ions are strongly attracted to each other and difficult to separate, however when pressure is applied to an ionic crystal then ions of like charge are forced to come closer to each other. The electrostatic repulsions can be enough to split the crystal, so ionic solids are brittle. Figure 5.3 illustrates the ionic properties of NaCl in original state and Figure 5.4 is showing repulsion of like ions.

![Salt in the Solid State](image)

*Fig. 5.3 Ionic Properties of NaCl in Original State*
5.5 ENERGETICS OF DISSOLUTION OF IONIC COMPOUNDS

It is found that different ionic solids tend to dissolve in different extent in a solvent. This dissolution of ionic solvents is governed by the following factors:

1. Dielectric Constant of a Solvent

According to Coulomb’s law of electrostatic forces of attraction ($F$) we have,

$$F = \frac{q_1 q_2}{r^2 D}$$

where, $D =$ Dielectric Constant of Solvent

For $\text{H}_2 \text{O}$, $D = 80$

For $\text{C}_2 \text{H}_5 \text{OH}$, $D = 25$

As the dielectric constant of water has been very high as compared to that of $(\text{C}_2 \text{H}_5 \text{OH})$, the forces of attraction between $\text{Na}^+$ and $\text{Cl}^-$ ions in the crystal get reduced to minimum. Thus, $\text{NaCl}$ is having more solubility in water than in ethyl alcohol $(\text{C}_2 \text{H}_5 \text{OH})$. Its $\text{Na}^+$ and $\text{Cl}^-$ ions are hydrated and a lot of hydration energy gets released. The system thus, tends to attain minimum energy and maximum stability.

2. Lattice Energy

The cations and anions in an ionic solid are held together by strong ionic attractive forces. So as to dissolve the ionic solids, these forces must be cut off. For this purpose, energy has to be supplied to separate the ions. The energy required to separate the ions in one mole of the ionic solid is termed as its Lattice Energy. Smaller the lattice energy, greater the tendency of an ionic solid to dissolve.

Hence,

$$\text{Lattice Energy} \propto \frac{1}{\text{Tendency of an ionic solid dissolve}}$$

<table>
<thead>
<tr>
<th>Na$^+$</th>
<th>Cl$^-$</th>
<th>Lattice Energy</th>
<th>Na$^+$ (g) + Cl$^-$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One Mole</td>
<td>766 50 k cals</td>
<td>One Mole</td>
<td>One Mole</td>
</tr>
</tbody>
</table>
We know that PbSO₄ is sparingly soluble while Na₂SO₄ is highly soluble in water. The reason is that, the lattice energy of PbSO₄ is very high as compared to Na₂SO₄.

3. Solvation of Ions (Solvation Energy)

When we add an ionic solid to a solvent, the cations and anions present in this solid are respectively surrounded by the negative and positive ends of the solvent molecules (Refer Figure 5.5). Surrounding solvent molecules, partly tend to neutralize the charge of the ions and also act as an insulating sphere. The insulating effect is termed as Dielectric Effect.

![Fig. 5.5 Ionization of KCl in Water](image)

Thus ion-dipole interaction which causes loose combination between the ion and solvent molecules is termed as solvation. If the solvent has been water, it is termed as hydration. During solvation (hydration), energy always gets released which is termed as solvation energy (hydration energy).

Thus, solvation (hydration) energy refers to the energy released when one mole of the ions are solvated (hydrated).

\[
\text{K}^+ (\text{g}) + \text{Water} \rightarrow \text{K}^+ (\text{aq}) + \text{Hydration Energy} \\
(\text{One Mole}) \\
(\text{One Mole of Hydrated Ions})
\]

Higher the hydration energy, higher the solubility of the ionic solid. Ions with small size and high charge are heavily hydrated and are having maximum hydration energy, e.g., the hydration energy of Li⁺ ion has been more than that of Na⁺ ion which in turn has been greater than that of K⁺ ion.

Therefore, the lattice energy and hydration energy have been mainly responsible for dissolution of an ionic solid. The overall energy change due to these energies is termed as heat of solution, \(\Delta H\).

Thus, \(\Delta H\) (Solution) = Hydration Energy – Lattice Energy
When hydration energy has been greater than lattice energy, the system will acquire minimum energy and maximum stability. Hence, the solubility of the ionic solid would tend to increase.

It is to be noted that the magnitude of lattice energy and hydration energy depends upon the same factors. However, with increase in charge and decrease in size of ions, increase in lattice energy has been more as compared to hydration energy. Thus, with increase in charge and decrease in size of the ions, solubility of electrolytes tend to decrease. For instance Na\(^+\) Cl\(^-\) has been more soluble in water than Mg\(^{2+}\) O\(^2-\).

AlCl\(_3\) has been covalent compound in the dry state while it has been completely ionic in the aqueous solution.

The reason is that if aluminium chloride, AlCl\(_3\) (dry) is treated with water, it is easily hydrated. Due to hydration, energy is released which is termed as Hydration Energy. This energy is sufficient for removing three electrons to from Al\(^{3+}\) ion.

\[
\text{AlCl}_3 (s) + 6\text{H}_2\text{O} \rightarrow \text{AlCl}_3 \cdot 6\text{H}_2\text{O} + \text{Hydration Energy}
\]

\[
\uparrow
\]

[Al(H\(_2\)O)\(_3\)]\(^{3+}\) + 3Cl\(^-\)

Ionic solids are not soluble in non-polar solvents (benzene, carbon tetrachloride, etc.) since the ions of ionic solids do not interact with the solvent molecules due to non-polar nature of the solvent, to form the hydrated ions and hence no hydration energies are obtained.

Common examples of dissolution of ionic solids are:

(a) LiCl, LiBr, NaCl, NaBr, etc., are the examples of ionic solids which are soluble in water, since their hydration energies are greater than their lattice energies as shown below. The values are given in kJ/mole.

Hydration Energies: LiCl = 883, LiBr = 854, NaCl = 775, NaBr = 741
Lattice Energies: LiCl = 840.1, LiBr = 781.2, NaCl = 770.3, NaBr = 728.4

(b) The ionic solids like KCl, KBr and KI are insoluble in water, since their hydration energies are less than their lattice energies as shown below. The values are given in kJ/mole.

Hydration Energies: KCl = 686, KBr = 657, KI = 619
Lattice Energies: KCl = 701.2, KBr = 671.1, KI = 632.2

Similarly, AgCl, BaSO\(_4\), CaF\(_2\) and AlF\(_3\) are also insoluble in water, since their hydration energies are less than their lattice energies.

High value of dielectric constant of the solvent also favours the dissolution of the ionic solids, because it weakens the electrostatic force of attraction existing between the oppositely charged ions present in the ionic solids.
5.5.1 Applications

1. **Low Solubilities of Silver Halides:** The lattice energy of silver halides, AgCl, AgBr, and AgI in water is almost of the same order, yet the solubilities of these halides differs a lot. This unusual behaviour could be explained on the basis of the outer electronic configurations of the cations under study. The outer electronic configuration of Ag⁺ ion may be put as follows:

\[(n - 1) d^{10} ns^2 np^6\]

Here, \(n = 5\)

The outer electron configuration of alkali metal ions like Na⁺, K⁺, etc., would be ns² np⁶. We know that the d electrons are able to screen the nucleus from outer electrons less effectively than s and p electrons. The Ag⁺ ion is having d electrons whereas alkali metal ions do not have. Thus, the nucleus of Ag⁺ ion will attract its outer electrons more strongly as compared to alkali metal ions. Because of this silver halides undergo appreciable polarization and hence appreciable change from ionic to covalent character. Thus silver halides have been less soluble in water.

2. **Comparison between the Solubilities of Halides of a Given Metal:**

Compare the solubilities of halides given by Li-metal. We know that higher is the magnitude of lattice energy, lesser is the solubility of the ionic solid in water. Now since the lattice energies of the halides of Li decrease from LiF to LiI, the solubility of these halides is in the increasing order. Thus,

<table>
<thead>
<tr>
<th>Halides of Li</th>
<th>LiF</th>
<th>LiCl</th>
<th>LiBr</th>
<th>LiI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values of Lattice Energy (kJ/mole)</td>
<td>1034</td>
<td>840.1</td>
<td>781.1</td>
<td>718.2</td>
</tr>
</tbody>
</table>

- Decreasing
- Increasing

Thus, we see that LiF is insoluble in water while LiI is soluble in this solvent. In general we can say that the order of the solubility of the halides of a given metal can be written as fluoride < chloride < bromide < iodides.

3. **Comparison between the Solubility of Hydroxides and Fluorides of Alkaline Earth Metals:** Since the size of the divalent alkaline earth metal cations (M²⁺ ions) increase on moving down the group from Be²⁺ to Ba²⁺, the magnitude of the lattice energy of the hydroxides and fluorides of these metals decrease in the same direction. With the decrease in the lattice energy value, the solubility of these compounds increases. Thus Be(OH)₂ and Mg(OH)₂ are almost insoluble in water and hydroxides of other alkaline earth metals are slightly soluble. Similarly MgF₂ and CaF₂ are also insoluble in water.
4. Comparison between the Solubility of M⁺ - Salts with Polyvalent Ions (SO₄²⁻, C₂O₄²⁻, PO₄³⁻, etc.) and that of M³⁺ - Salts with the Same Ions: Due to the smaller size of alkaline earth metal ions (M⁺ ions) as compared to those of alkali metal cations (M⁺ ions) of the same period, the lattice energies of M⁺ salts with polyvalent ions (e.g., SO₄²⁻, C₂O₄²⁻, PO₄³⁻, etc.) are higher than those of the corresponding to M⁺ salts. Consequently M⁺ salts are less soluble than M⁺ salts, for example CaCO₃ is less soluble in water than K₂CO₃.

5. Why a few solids like MAgI₂ (M = k, NH₄, Rb) are able to conduct electricity? 6. What is salvation and hydration? 7. Define heat of solution.

Check Your Progress

5. Why a few solids like MAgI₂ (M = k, NH₄, Rb) are able to conduct electricity?
6. What is salvation and hydration?
7. Define heat of solution.

5.6 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Ionic bond is formed by the transference of one or more electrons from one atom to the other. Characteristically, this type of bond typically comes into existence between a metal (electropositive) and a non-metal (electronegative) atom. If any metal atom loses its valence electrons it will change into a positive ion (cation) while if any non-metal atom gains an electron it will change into a negative ion (anion) and expand in size. Thus, they become stable by attaining 8 (or 2) electrons in the outermost shell. The oppositely charged ions are held together by electrostatic force of attraction. Thus, ionic bond may be defined as the electrostatic force of attraction which holds both the positively charged (cation) and negatively charged (anion) together, i.e., when a cation and an anion come close to each other, they are held by electrostatic force of attractions and the bond established between them is known as an ionic or electrovalent bond.

2. Ionization energy is required in the formation of ionic bond when a metal atom loses electron to form cation. This process required energy equal to the ionization energy. Lesser the value of ionization energy, greater is the tendency of the atom to form cation. For example, alkali metals form cations quite easily because of the low values of ionization energies. Hence, either of the two atoms forming ionic bond should have a low ionization energy,
i.e., a smaller amount of energy is required to pull out an electron from its outer energy level it means that the lower the value of ionization potential, the greater will be the ease of formation of cations and hence the electrovalent bond.

\[ M \rightarrow M^+ + e^- \] \[ \text{[E}_1\text{ = First Ionization Energy]} \]
\[ M^+ \rightarrow M^{2+} + e^- \] \[ \text{[E}_2\text{ = Second Ionization Energy]} \]

3. Electron affinity is defined as the change in energy (in kJ/mole) of a neutral atom (in the gaseous phase) when an electron is added to the atom to form a negative ion or there is possibility that the neutral atom is capable of gaining an electron. Principally, the term 'Electron Affinity' refers to the energy released when gaseous atom accepts electron to form a negative ion. Thus, the value of electron affinity gives the tendency of an atom to form anion. Now greater the value of electron affinity more is the tendency of an atom to form anion. For example, halogens having highest electron affinities within their respective periods to form ionic compounds with metals very easily. One of the two atoms forming an ionic bond should have high electron affinity, i.e., it should be able to accept the electron readily. The elements of Group 17 (halogens) possess the highest electron affinities of all the elements hence they are early connected into anions, hence can form ionic bond readily.

4. The higher the value of lattice energy of resulting ionic compound, the greater will be its ease of formation. For lattice energies to be high, the force of electrostatic attraction between the constituent ions should be high.

5. A few solids like \( \text{M} \text{Ag}_2 \) (\( \text{M} = \text{K, NH}_3, \text{Rb} \)) are able to conduct electricity similar to those of the ions is solutions due to the high mobility of \( \text{Ag}^+ \) ions in an unusual crystal lattice.

6. The ion-dipole interaction which causes loose combination between the ion and solvent molecules is termed as solvation. If the solvent has been water, it is termed as hydration. During solvation (hydration), energy always gets released which is termed as solvation energy (hydration energy).

7. The lattice energy and hydration energy have been mainly responsible for dissolution of an ionic solid. The overall energy change due to these energies is termed as heat of solution, \( \Delta H \).

Thus, \( \Delta H \) (Solution) = Hydration Energy – Lattice Energy

When hydration energy has been greater than lattice energy, the system will acquire minimum energy and maximum stability. Hence, the solubility of the ionic solid would tend to increase.
5.7 SUMMARY

- Ionic bonding is a form of chemical bonding that involves the electrostatic attraction between oppositely charged ions. It is the primary interaction that occurs in ionic compounds. Characteristically, it is one of the main bonds along with Covalent bond and Metallic bond.
- Ions are atoms that have gained one or more electrons (known as anions, which are negatively charged) and atoms that have lost one or more electrons (known as cations, which are positively charged). This transfer of electrons is known as electrovalence.
- Principally, the non-metals lose electrons to gain negative charge and form anions, whereas metals lose electrons to gain positive charge and form cations.
- The electrostatic forces of attraction between oppositely charged ions lead to the formation of ions.
- Ionic compounds form crystal lattices rather than amorphous solids, have higher enthalpies of fusion and vaporization than molecular compounds.
- Ionic compounds have high boiling and melting points as they are very strong and require a lot of energy to break.
- Ionic bond is formed by the transference of one or more electrons form one atom to the other. Characteristically, this type of bond typically comes into existence between a metal (electropositive) and a non-metal (electronegative) atom.
- If any metal atom loses its valence electrons it will change into a positive ion (cation) while if any non-metal atom gains an electron it will change into a negative ion (anion) and expand in size. Thus, they become stable by attaining 8 (or 2) electrons in the outermost shell.
- The oppositely charged ions are held together by electrostatic force of attraction. Thus, ionic bond may be defined as the electrostatic force of attraction which holds both the positively charged (cation) and negatively charged (anion) together, i.e., when a cation and an anion come close to each other, they are held by electrostatic force of attractions and the bond established between them is known as an ionic or electrovalent bond.
- The number of electrons which an atom loses or gains while forming an ionic bond is termed as the ‘Electrovalency’.
- The atom which loses electrons is called electropositive atom while the atom which gains electrons is called electronegative atom.
- The positive (+) sign is put before the valency of electropositive atom while negative (-) sign is put before the valency of electronegative atom, for example electrovalency of Na is +1 and of Cl is -1. Alternatively, electrovalency is equal to the unit charges on the ion.
An ionic bond is formed by the complete transference of one or more electrons from the outer energy shell (valency shell) of one atom to the outer energy shell of the other atom. Hence, both the atoms acquire the stable electronic configurations of the nearest noble atom.

Ionization energy is required in the formation of ionic bond when a metal atom loses electron to form cation. This process required energy equal to the ionization energy. Lesser the value of ionization energy, greater is the tendency of the atom to form cation.

The lower the value of ionization potential, the greater will be the case of formation of cations and hence the electrolvalent bond.

\[ M \rightarrow M^+ + e^- \quad [E_1 = \text{First Ionization Energy}] \]
\[ M^+ \rightarrow M^{2+} + e^- \quad [E_2 = \text{Second Ionization Energy}] \]

Electron affinity is defined as the change in energy (in kHz/mole) of a neutral atom (in the gaseous phase) when an electron is added to the atom to form a negative ion or there is possibility that the neutral atom is capable of gaining an electron. Principally, the term ‘Electron Affinity’ refers to the energy released when gaseous atom accepts electron to form a negative ion.

Lattice energy is defined as the amount of energy released when cations and anions are brought from infinity to their respective equilibrium sites in the crystal lattice to form one mole of the ionic compound.

The higher the lattice energy, the greater is the tendency of the formation of an ionic bond. The higher the charges on the ions and smaller the distance between them, the greater is the force of attraction between them.

The formation of an ionic bond depends upon the lattice energy. For lattice energies to be high, the force of electrostatic attraction between the constituent ions should be high.

Compounds containing ionic bond are known as ionic compounds. These are polar in nature and on dissolution is water they split into two oppositely charged ions.

Ionic compounds conduct electricity when molten (liquid) or in aqueous solution (dissolved in water), because their ions are free to move from place to place.

Ionic compounds cannot conduct electricity when solid, as their ions are held in fixed positions and cannot move, i.e., in solid state the ions occupy fixed positions and hence are not able to have free movement.

By definition, ‘Ionic compounds are conductors of electricity when molten or in solution, and insulators when solid’.

Chemical reactions of an ionic compound are the reactions of its constituent ions. These are usually rapid.
Ionic compounds are hard because the positive and negative ions are strongly attracted to each other and difficult to separate, however when pressure is applied to an ionic crystal then ions of like charge are forced to come closer to each other. The electrostatic repulsions can be enough to split the crystal, so ionic solids are brittle.

The ion-dipole interaction which causes loose combination between the ion and solvent molecules is termed as solvation. If the solvent has been water, it is termed as hydration. During solvation (hydration), energy always gets released which is termed as solvation energy (hydration energy).

The lattice energy and hydration energy have been mainly responsible for dissolution of an ionic solid. The overall energy change due to these energies is termed as heat of solution, ΔH.

\[ \Delta H \text{ (Solution)} = \text{Hydration Energy} - \text{Lattice Energy} \]

When hydration energy has been greater than lattice energy, the system will acquire minimum energy and maximum stability. Hence, the solubility of the ionic solid would tend to increase.

Ionic solids are not soluble in non-polar solvents (benzene, carbon tetrachloride, etc.) since the ions of ionic solids do not interact with the solvent molecules due to non-polar nature of the solvent, to form the hydrated ions and hence no hydration energies are obtained.

5.8 KEY WORDS

- **Electrovalency**: The number of electrons which an atom loses or gains while forming an ionic bond is termed as the ‘Electrovalency’.
- **Ionic compound**: An ionic compound is a chemical compound composed of ions held together by electrostatic forces termed ionic bonding.
- **Electron affinity**: Electron affinity is defined as the change in energy (in kJ/mole) of a neutral atom (in the gaseous phase) when an electron is added to the atom to form a negative ion.
- **Salvation of ions**: The ion-dipole interaction which causes loose combination between the ion and solvent molecules is called salvation of ions.

5.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

**Short Answer Questions**

1. What are ionic compounds?
2. How is ionic bond formed?
3. Define the term electrical conductivity.
4. Explain the significance of electron affinity.
5. What are the significant properties of ionic compounds?
6. What are polar and non-polar solvents?
7. Write applications of ionic compounds.

**Long Answer Questions**

1. Discuss the various properties of ionic compounds giving appropriate example.
2. Explain briefly that how ionic bond transfer of electrons from a metal to a non-metal in order to obtain a full valence shell.
3. Describe the factors affecting the formation of ionic bond briefly.
4. Give a detailed account of energetics of dissolution of ionic compounds.
5. Why are ionic compounds hard and brittle? Give reasons and examples.
6. Discuss the ion-dipole interaction property of ions with regard to solvation energy and hydration energy. What will be the effect if the hydration energy is higher?
7. Explain the properties of ionic compounds with the help of examples.

### 5.10 Further Readings


UNIT 6 BRONSTED CONCEPT OF ACIDS AND BASES

Structure
6.0 Introduction
6.1 Objectives
6.2 Bronsted Concept
6.3 Bronsted-Lowry Concept of the Proton-Donor Acceptor System
   6.3.1 Conjugate Acid-Base Pairs
   6.3.2 Amphoteric Substances
6.4 Relative Strength of Bronsted Acids and Bronsted Bases in Aqueous Medium
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   6.6.1 Variation of Basicity in a Period
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   6.6.4 Variation of Acidic Strength in a Group
6.7 Relative Order of Acidic Strength of Oxyacids
6.8 Advantages and Limitation of Bronsted-Lowry Concept
6.9 Answers to Check Your Progress Questions
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6.0 INTRODUCTION

The Bronsted–Lowry theory is an acid–base reaction theory which was proposed independently by Johannes Nicolaus Bronsted and Thomas Martin Lowry in 1923. The fundamental concept of this theory is that when an acid and a base react with each other, the acid forms its conjugate base, and the base forms its conjugate acid by exchange of a proton (the hydrogen cation, or H⁺). This theory is a generalization of the Arrhenius theory. In the Arrhenius theory, acids are defined as substances that dissociate in aqueous solution to give H⁺ (hydrogen ions) and the bases are defined as substances that dissociate in aqueous solution to give OH⁻ (hydroxide ions). Principally, according to the Bronsted–Lowry scheme a substance can function as an acid only in the presence of a base; similarly, a substance can function as a base only in the presence of an acid.
In this unit, you will study the Bronsted-Lowry and Arrhenius concept of acids and bases, conjugate acid-base pairs, amphiprotic substances, relative strength of Bronsted acids and Bronsted bases in aqueous medium, levelling and differentiating solvents, and advantages and limitation of Bronsted-Lowry concept.

6.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand Bronsted-Lowry and Arrhenius concept of acids and bases
- Describe conjugate acid-base pairs and amphiprotic substances
- Discuss relative strength of Bronsted acids and Bronsted bases in aqueous medium
- Interpret levelling and differentiating solvents
- Explain advantages and limitation of Bronsted-Lowry concept of acids and bases

6.2 BRONSTED CONCEPT

The Bronsted-Lowry theory is an acid–base reaction theory which was proposed independently by Johannes Nicolaus Bronsted and Thomas Martin Lowry in 1923. The fundamental concept of this theory is that when an acid and a base react with each other, the acid forms its conjugate base, and the base forms its conjugate acid by exchange of a proton (the hydrogen cation, or H⁺). This theory is a generalization of the Arrhenius theory.

Principally, according to the Bronsted-Lowry scheme a substance can function as an acid only in the presence of a base; similarly, a substance can function as a base only in the presence of an acid. Furthermore, when an acidic substance loses a proton, it forms a base, called the conjugate base of an acid, and when a basic substance gains a proton, it forms an acid called the conjugate acid of a base. Thus, the reaction between an acidic substance, such as hydrochloric acid, and a basic substance, such as ammonia, may be represented by the equation:

\[ \text{HCl} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{Cl}^- \]

In the above equation the ammonium ion (NH₄⁺) is the acid conjugate to the base ammonia, and the chloride ion (Cl⁻) is the base conjugate to hydrochloric acid.

The Bronsted–Lowry theory enlarges the number of compounds considered to be acids and bases to include not only the neutral molecules, for example sulfuric, nitric, and acetic acids, and the alkali metal hydroxides, but also certain atoms and molecules with positive and negative electrical charges (cations and anions). The ammonium ion, the hydronium ion, and some hydrated metal cations are considered...
acids. The acetate, phosphate, carbonate, sulfide, and halogen ions are considered base.

The concept of acidity originated from the ancient Greeks who defined sour tasting substances as ‘Acids’. These substances were also found to change the colour of litmus paper and corrode metals. On the other hand bases were defined and studied by their ability to counteract acids. Acids and bases possess the characteristics that are opposite to each other. With the availability of large experimental data, the need for proper definition and classification arose from time to time. The concepts of acids and bases developed one after another tend to make the definitions more and more broad based.

In the Arrhenius theory, acids are defined as substances that dissociate in aqueous solution to give H+ (hydrogen ions) and the bases are defined as substances that dissociate in aqueous solution to give OH− (hydroxide ions). But in the Bronsted–Lowry theory, the acids and bases are defined by the way they react with each other, which allows for greater generality. The definition is expressed in terms of an equilibrium expression as follows.

\[
\text{Acid} + \text{Base} \rightleftharpoons \text{Conjugate Base} + \text{Conjugate Acid}
\]

With an acid, HA, the equation can be written symbolically as:

\[
\text{HA} + \text{B} \rightleftharpoons \text{A}^{-} + \text{HB}^{+}
\]

The equilibrium sign, \(\rightleftharpoons\), is used because the reaction can occur in both forward and backward directions. The acid, HA, can lose a proton to become its conjugate base, A-. The base, B, can accept a proton to become its conjugate acid, HB+. Most acid-base reactions are fast so that the components of the reaction are usually in dynamic equilibrium with each other.

Arrhenius defined acids as any species that gives H+ ions (or H2O+ ions) in water and base as a substance which furnishes OH− ions in water. Thus according to this concept, the substances like HCl, HNO3, H2SO4, CH3COOH, etc., are acids, since they give H+ ions when dissolved in water.

\[
\text{HCl} \rightleftharpoons \text{H}^{+} + \text{Cl}^{-} \quad \text{...(6.1)}
\]

H+ ion produced in Equation (6.1), gets hydrated by one molecule of water (H2O) and gives hydronium ion H3O+.

\[
\text{H}^{+} + \text{H}_{2}\text{O} \rightleftharpoons \text{H}_{3}\text{O}^{+} \quad \text{...(6.2)}
\]

On adding the Equations (6.1) and (6.2), we get Equation (6.3) which represents the acidic behaviour of HCl in water.

\[
\text{HCl} + \text{H}_{2}\text{O} \rightleftharpoons \text{H}_{3}\text{O}^{+} + \text{Cl}^{-} \quad \text{...(6.3)}
\]

Equation (6.3) can also be written as:

\[
\text{HCl} + \text{Water} \rightleftharpoons \text{H}^{+} (\text{aq}) + \text{Cl}^{-} (\text{aq})
\]
Some chemists believe that H⁺ produced in Equation (6.1) gets associated with four molecules of water and gives [H(H₂O)₄]⁺ or [H₂O]⁺ ion.

\[
H^+ + 4H₂O \rightarrow [H(H₂O)₄]⁺ [H₂O]⁺
\]

The substances like NaOH, KOH, Ca(OH)₂, etc., are bases, since they give OH⁻ ions in water.

\[
\text{NaOH} \quad \xrightarrow{\text{H₂O}} \quad \text{Na}^+ + \text{OH}^-
\]

\[
\text{NaOH} + \text{Water} \quad \xrightarrow{\text{aq}} \quad \text{Na}^-(\text{aq}) + \text{OH}^-(\text{aq})
\]

**Acid-Base Neutralisation Reaction in Water:** According to this concept, the acid-base neutralisation reaction in water consist of available H₂O⁺ or H⁺ ions (acid) which combines with a compound containing OH⁻ ions (base) to form the salt and water.

\[
\begin{align*}
\text{HCl} + \text{NaOH} & \quad \xrightarrow{\text{H₂O}} \quad \text{NaCl} + \text{H}_2\text{O} \\
\text{Acid} & \quad \text{Base} & \quad \text{Salt} & \quad \text{Water}
\end{align*}
\]

The above reaction occurs in following steps:

\[
\begin{align*}
\text{HCl} & \quad \xrightarrow{\text{H₂O}} \quad \text{H}^+ + \text{Cl}^- \\
\text{NaOH} & \quad \xrightarrow{\text{H₂O}} \quad \text{Na}^+ + \text{OH}^-
\end{align*}
\]

Or

\[
\begin{align*}
\text{HCl} + \text{NaOH} & \quad \xrightarrow{\text{H₂O}} \quad \text{Na}^+ \text{Cl}^- + \text{H}^+ [\text{OH}^-]
\end{align*}
\]

The formation of salt (NaCl) and H₂O can also be shown as follows:

\[
\begin{align*}
\text{HCl} & \quad \xrightarrow{\text{H₂O}} \quad \text{H}^+ + \text{Cl}^- \\
\text{H}^+ + \text{H}_2\text{O} & \quad \xrightarrow{\text{H₂O}} \quad \text{H}_3\text{O}^+ \\
\text{NaOH} & \quad \xrightarrow{\text{H₂O}} \quad \text{Na}^+ + \text{OH}^-
\end{align*}
\]

Or

\[
\begin{align*}
\text{HCl} + \text{H}_2\text{O} + \text{NaOH} & \quad \xrightarrow{\text{H₂O}} \quad \text{Na}^+ \text{Cl}^- + [\text{H}_3\text{O}^+] [\text{OH}^-]
\end{align*}
\]

Or

\[
\begin{align*}
\text{HCl} + \text{H}_2\text{O} + \text{NaOH} & \quad \xrightarrow{\text{H₂O}} \quad \text{NaCl} + 2\text{H}_2\text{O}
\end{align*}
\]

Or

\[
\begin{align*}
\text{HCl} + \text{NaOH} & \quad \xrightarrow{\text{H₂O}} \quad \text{NaCl} + \text{H}_2\text{O}
\end{align*}
\]

Due to the formation of a salt, acid-base neutralisation reaction is also called salt formation reaction. This shows that in neutralisation reaction, H₂O is produced by the combination of H⁺ and OH⁻. Thus we can say that neutralisation reaction, according to Arrhenius concept of acids and bases, is the combination of H⁺ OH⁻ ions, which are produced by the dissociation of the acid and base, respectively in aqueous medium.
Advantages

(i) Arrhenius concept has been invaluable in elucidating the behaviour of aqueous solutions. The constant heat of neutralization of a strong acid by a strong base can be readily explained in the light of this concept.

(ii) The theory correlated the catalytic action of acids with the concentration of hydrogen ions.

(iii) Aqueous solution of non-metallic oxides (e.g., CO₂, SO₂, SO₃, N₂O₅, N₂O₄, P₂O₅, P₂O₆, etc.) is acidic, since it gives H⁺ ions in water.

\[ \text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+ + \text{SO}_4^{2-} \]

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightleftharpoons 2\text{HNO}_3 \rightleftharpoons 2\text{H}^+ + \text{NO}_3^- \]

(iv) Aqueous solution of metallic oxides (e.g., CaO, Na₂O, etc.) and the compounds like NH₃, N₂H₄, NH₂OH, etc., are bases, since these substances give OH⁻ ions in water.

\[ \text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca(OH)}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^- \]

\[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]

\[ \text{N}_2\text{H}_4 + \text{H}_2\text{O} \rightleftharpoons [\text{N}_2\text{H}_5]^+\text{[OH]} \rightleftharpoons \text{N}_2\text{H}_5^+ + \text{OH}^- \]

\[ \text{NH}_2\text{OH} + \text{H}_2\text{O} \rightleftharpoons [\text{NH}_2\text{OH}]^+\text{[OH]} \rightleftharpoons \text{NH}_2\text{OH}^- + \text{OH}^- \]

(v) The strength of an acid (HA) and a base (BOH) can be expressed quantitatively in terms of the ionization (or dissociation) constant of the acid and base in aqueous solution.

\[ \text{HA}_{\text{Acid}} \rightleftharpoons \text{H}^+ + \text{A}^- \quad \text{K}_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \]

\[ \text{BOH}_{\text{Base}} \rightleftharpoons \text{B}^+ + \text{OH}^- \quad \text{K}_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} \]

Limitations

(i) Arrhenius concept lacks in generality.

(ii) This theory deals with dissociation and acid-base reactions in aqueous medium only and does not explain their behaviours in non-aqueous solvents in dissociation of acids and bases.

(iii) This concept restricts bases to hydroxides only.

(iv) According to this concept, acid-base neutralization reactions take place only in water and hence cannot explain such reactions occurring in other solvents or in the gas phase, for example, the formation of NH₄Cl(s) by

\[ \text{NH}_3 + \text{HCl} \rightleftharpoons \text{NH}_4^+ + \text{Cl}^- \]
the combination of NH₃ (g) and HCl (g) cannot be explained by Arrhenius concepts.

\[ \text{NH}_3 (g) + \text{HCl} (g) \rightarrow \text{NH}_4 \text{Cl} (s) \]

(v) According to this concept, acids and bases undergo dissociation only in water (aqueous solvent). Thus, it cannot explain the dissociation of acids and bases in non-aqueous solvents like liq. NH₃, liq. SO₂, etc.

### 6.3 BRONSTED-LOWRY CONCEPT OF THE PROTON-DONOR ACCEPTOR SYSTEM

Bronsted-Lowry in 1923 proposed a new concept of acids and bases which is independent of solvent. According to this concept, an acid is a species (molecule or ion) that can lose a proton (H⁺) and base is a species (molecule or ion) that can accept a proton. In other words an acid is a proton donor and base is a proton acceptor.

(i) HCl can lose a proton (H⁺) to give Cl⁻ ion, so HCl is an acid according to Bronsted-Lowry concept.

\[ \text{HCl} \xrightarrow{\text{H}^+} \text{Cl}^- \]  \hspace{1cm} \text{(Bronsted Acid)} \hspace{1cm} \text{(6.4)}

Similarly, since Cl⁻ ion can accept a proton (H⁺) to form HCl, so it is a base.

\[ \text{Cl}^- \xrightarrow{\text{H}^+} \text{HCl} \]  \hspace{1cm} \text{(Bronsted Base)} \hspace{1cm} \text{(6.5)}

On combining Equations (6.4) and (6.5), we get,

\[ \text{HCl} \xrightarrow{\text{H}^+} \text{Cl}^- \]  \hspace{1cm} \text{Bronsted Acid} \hspace{1cm} \text{Bronsted Base}

(ii) The following reaction shows that NH₃ acts as a Bronsted base and NH₄⁺ ion acts as a Bronsted acid.

\[ \text{NH}_3 \xrightarrow{\text{H}^+} \text{NH}_4^+ \]  \hspace{1cm} \text{Bronsted Base} \hspace{1cm} \text{Bronsted Acid}

Examples of Bronsted Acids and Bronsted Bases
Table 6.1 illustrates some examples of Bronsted acids and Bronsted bases.

<table>
<thead>
<tr>
<th>Bronsted Acids (These can lose one or more protons)</th>
<th>Bronsted Bases (These can accept one or more protons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HX ( \xrightarrow{-H^+} ) ( +H^+ )</td>
<td>X^−</td>
</tr>
<tr>
<td>NH₄⁺ ( \xrightarrow{-H^+} ) ( +H^+ )</td>
<td>NH₃</td>
</tr>
<tr>
<td>H₂S ( \xrightarrow{-H^+} ) ( +H^+ )</td>
<td>HS⁻</td>
</tr>
<tr>
<td>H₂S ( \xrightarrow{-2H^+} )</td>
<td>S²⁻</td>
</tr>
<tr>
<td>COOH ( \xrightarrow{-2H^+} )</td>
<td>COO⁻</td>
</tr>
<tr>
<td>COOH</td>
<td>COO⁻</td>
</tr>
<tr>
<td>H₂O⁻ ( \xrightarrow{-H^+} ) ( +H^+ )</td>
<td>H₂O</td>
</tr>
<tr>
<td>H₂SO₄ ( \xrightarrow{-2H^+} ) ( +H^+ )</td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>H₂SO₄⁻ ( \xrightarrow{-H^+} ) ( +H^+ )</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>H₃PO₄ ( \xrightarrow{-3H^+} ) ( +H^+ )</td>
<td>PO₄³⁻</td>
</tr>
<tr>
<td>H₂CO₃ ( \xrightarrow{-H^+} ) ( +H^+ )</td>
<td>HCO₃⁻</td>
</tr>
<tr>
<td>H₂O ( \xrightarrow{-H^+} ) ( +H^+ )</td>
<td>OH⁻</td>
</tr>
<tr>
<td>CH₃COOH ( \xrightarrow{-H^+} ) ( +H^+ )</td>
<td>CH₃COO⁻</td>
</tr>
<tr>
<td>NH₂CONH₂ ( \xrightarrow{-H^+} ) ( +H^+ )</td>
<td>H₂N. CO. NH¹</td>
</tr>
<tr>
<td>NH₂CONH₂⁺ ( \xrightarrow{-H^+} ) ( +H^+ )</td>
<td>NH₂CONH₂</td>
</tr>
<tr>
<td>HNO₃ ( \xrightarrow{-H^+} ) ( +H^+ )</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>H₂NO₃⁺ ( \xrightarrow{-H^+} ) ( +H^+ )</td>
<td>HNO₃</td>
</tr>
</tbody>
</table>
6.3.1 Conjugate Acid-Base Pairs

Conjugate means related. To understand the concept of conjugate acid-base pairs, consider the reaction between HCl(ag) and NH₃((ag).

\[ \text{HCl} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{Cl}^- \]  \hspace{1cm} \ldots(6.6)

The above reaction occurs through the following two steps:

(i) \[ \text{HCl} \rightleftharpoons \text{Cl}^- + \text{H}^+ \]  \hspace{1cm} \text{Acid} \hspace{1cm} \text{Base}

Here HCl (acid) – Cl⁻ (base) pair is called conjugate acid-base pair.

(ii) The proton lost by HCl in step (i) is accepted by NH₃, so that NH₄⁺ ion is obtained.

\[ \text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+ \]  \hspace{1cm} \text{Base} \hspace{1cm} \text{Acid}

Here, NH₄⁺ (acid) – NH₃ (base) pair is also called conjugate acid-base pair.

On adding the above two equations,

\[ \text{HCl} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{Cl}^- \]  \hspace{1cm} \ldots(6.7)

This Equation (6.7) is same as Equation (6.6).

Equation (6.6) shows that it consists of two conjugate acid-base pairs, which are HCl – Cl⁻ and NH₄⁺ – NH₃. Thus, if in HCl – Cl⁻ pair, HCl is designated as Acid₁, then its conjugate base Cl⁻ may be designated as Base₁. Similarly, if in NH₄⁺ – NH₃ pair, NH₄⁺ is designated as Acid₂, then NH₃ may be represented as Base₂. Thus, Equation (6.6) can be written as:

Hence, the general equation representing acid-base reaction can be written as:

\[ \text{Acid₁} + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1 \]

It also indicates that in order to get the conjugate base from a given acid, one proton has to be removed from that acid, i.e.,

\[ \text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^- \]
Similarly in order to get a conjugate acid from a given base one proton has to be added to that base, i.e.,

\[
\text{Base} + \text{H}^+ \rightarrow \text{Conjugate acid}
\]

**Examples of Conjugate Acid-Base Pairs**

Some examples of conjugate acid-base pairs are given in Table 6.2.

**Table 6.2 Examples of Conjugate Acid-Base Pairs**

<table>
<thead>
<tr>
<th>Acid (_i)</th>
<th>Base (_j)</th>
<th>Acid (_i) (Conjugate Acid to Base (_j))</th>
<th>Base (_j) (Conjugate Base to Acid (_i))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO(_3^-) + H(_2)O</td>
<td>(\rightleftharpoons) H(_3)O(^+) + CO(_3^{2-})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCN + H(_2)O</td>
<td>(\rightleftharpoons) H(_3)O(^+) + CN(^-)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2)S + H(_2)O</td>
<td>(\rightleftharpoons) H(_3)O(^+) + HS(^-)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2)O + CO(_3^{2-})</td>
<td>(\rightleftharpoons) HCO(_3^-) + OH(^-)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2)O + H(_2)O</td>
<td>(\rightleftharpoons) H(_3)O(^+) + OH(^-)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH(_3) + H(_2)O</td>
<td>(\rightleftharpoons) H(_3)O(^+) + NH(_4^+)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl + CH(_3)COOH</td>
<td>(\rightleftharpoons) CH(_3)COO(^-) + Cl(^-)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO(_3^-) + H(_2)SO(_4)</td>
<td>(\rightleftharpoons) H(_2)SO(_4^+) + ClO(_3^-)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCOOH + H(_2)NCO.NH(_2)</td>
<td>(\rightleftharpoons) H(_2)NCONH(_2^+) + HCOO(^-)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**6.3.2 Amphoteric Substances**

The substances which can act as Bronsted acids (loss of proton) as well as Bronsted bases (gain of proton) are called amphoteric substances, consider the example,

\[
\text{Acid} + \text{Base} \rightleftharpoons \text{Acid} + \text{Base}
\]

In reaction (a), H\(_2\)O molecule loses a proton (H\(_2\)O \(\rightarrow\) H\(^+\) + OH\(^-\)) and hence acts as an acid while in reaction (b) this molecule gains a proton from HCl.
(H₂O ⇌ H⁺ + H₂O⁻) and hence behaves as a base. Thus since H₂O can lose as well as gain a proton, it behaves as an acid as well as a base. In other words, we can say that H₂O is an amphoteric substance.

Examples of amphoteric species (molecules and ions) are given in acid-base reactions, shown in Table 6.3. These substances have been shown in a rectangle.

Table 6.3 Acid-base Reactions in which the Species Shown in Rectangle Behave as Amphoteric Substances

<table>
<thead>
<tr>
<th>Acid₁</th>
<th>Base₂</th>
<th>Acid₃</th>
<th>Base₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) (a) CH₃COOH</td>
<td>+ H₂O</td>
<td>→ H₂O⁻</td>
<td>+ CH₃COO⁻</td>
</tr>
<tr>
<td>(b) HF</td>
<td>+ CH₃COOH</td>
<td>→ CH₃COOH⁻</td>
<td>+ F⁻</td>
</tr>
<tr>
<td>(ii) (a) H₂SO₄</td>
<td>+ 2H₂O</td>
<td>→ 2H₂O⁻</td>
<td>+ SO₄²⁻</td>
</tr>
<tr>
<td>(b) HF</td>
<td>+ H₂SO₄</td>
<td>→ H₂SO₄⁻</td>
<td>+ F⁻</td>
</tr>
<tr>
<td>(iii) (a) H₂N₂CO.NH₃</td>
<td>+ NH₃</td>
<td>→ NH₄⁺</td>
<td>+ H₂N₂CO.NH₃⁻</td>
</tr>
<tr>
<td>(b) H₂SO₄</td>
<td>+ H₂N₂CO.NH₃</td>
<td>→ H₂N₂CO.NH₄⁺</td>
<td>+ HSO₄⁻</td>
</tr>
<tr>
<td>(iv) (a) HNO₃</td>
<td>+ H₂O</td>
<td>→ H₂O⁻</td>
<td>+ NO₃⁻</td>
</tr>
<tr>
<td>(b) HF</td>
<td>+ HNO₃</td>
<td>→ H₁NO₃⁻</td>
<td>+ F⁻</td>
</tr>
</tbody>
</table>

Check Your Progress

1. What do you understand by the Bronsted-Lowry concept?
2. Define the Bronsted-Lowry and Arrhenius concepts.
3. Give the equilibrium expression for acid and base.
4. Why acid-base neutralisation reaction is called salt formation reaction?
5. What is amphoteric substances?

6.4 RELATIVE STRENGTH OF BRONSTED ACIDS AND BRONSTED BASES IN AQUEOUS MEDIUM

Relative strength of Bronsted acids and Bronsted bases can be determined by treating these substances with water. When an acid reacts with H₂O, water acts as a base and when a base reacts with H₂O, water acts as an acid. Consider the following examples,
(i) **Reaction of HCl (Strong Acid) with H₂O (Base):** Since HCl is a strong acid, it is nearly 100% ionized in water and hence this reaction proceeds almost completely towards right. This state has been shown by a longer half arrow, pointing towards right. Thus the reaction of HCl with H₂O can be depicted as:

![Reaction Diagram](attachment:reaction_diagram.png)

In the above reaction the two acids viz., HCl and H₂O⁻ are competing for donating a proton to the base (HCl → H⁺ + Cl⁻, H₂O → H⁺ + H₂O⁻). Since the equilibrium of this reaction lies towards right, HCl donates the proton more strongly than does H₂O⁻ ion. Thus HCl is a stronger acid than H₂O⁻ ion. In other words, we can say that HCl is a strong acid and H₂O⁻ ion is a weak acid.

In this reaction the two bases namely H₂O and Cl⁻ are competing for the gain of a proton from the acid (H₂O → H⁺ + H₂O⁻, Cl⁻ → Cl⁺ + H₂O). Since the reaction proceeds towards right, H₂O molecule gains the proton more strongly than does Cl⁻ ion. Thus H₂O is stronger base than Cl⁻ ion, i.e., H₂O is a strong base and Cl⁻ ion is a weak base.

(ii) **Reaction of CH₃COOH (Weak Acid) with H₂O (Base):** Since CH₃COOH is a weak acid, it is less than 1% ionised in H₂O and hence this reaction proceeds mostly towards left. This state of affairs is represented by using a longer half arrow, pointing towards left. Thus, the reaction of CH₃COOH with H₂O can be shown as:

![Reaction Diagram](attachment:reaction_diagram.png)

6.5 **LEVELLING AND DIFFERENTIATING SOLVENTS**

The apparent strength of a protic acid has been found to depend upon the solvent in which the acid is dissolved. Let us consider the ionization of HCl, HBr and HI in two different solvents like water and acetic acid (CH₃COOH).

(i) **Ionisation in H₂O:** When these acids are dissolved in water, they get ionized to the same extent and hence appear to be almost equally strong in this
solvent. H\(^+\) ion lost by these acids is accepted by H\(_2\)O (which acts as a base) to form H\(_3\)O\(^+\) ion.

\[
\text{HX (X = Cl, Br, I) + H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + X^-
\]

Thus, we find that water (solvent) brings all the three acids to the same level of their acidic strength and hence is called a leveling solvent for these acids. The phenomenon due to which the leveling solvent makes all the acids behave equally strong is called leveling effect. It is due to the leveling effect that the relative acid strength of the above acids cannot be measured in aqueous medium.

(ii) Ionization in CH\(_3\)COOH: When the above said acids are dissolved in CH\(_3\)COOH, they are ionized to different extents and hence show different acidic strength in this solvent.

\[
\text{HX (X = Cl, Br, I) + CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COOH}^+ + X^-
\]

Since CH\(_3\)COOH (solvent) brings the acids to different level of their acid strength, this solvent is called a differentiating solvent for these acids.

The above two examples show that water acts as levelling solvent for HCl, HBr and HI but CH\(_3\)COOH acts as a differentiating solvent for the same acids.

Other solvents may have their own levelling effects too, for example the benzoic acid is a very weak acid in aqueous solution, but in liquid ammonia it acts as a very strong acid.

### 6.6 PERIODIC TRENDS, BASIC STRENGTH OR BASICITY OF A BRONSTED BASE

The basic strength of a Bronsted base is defined as its proton accepting power. For example, since F\(^-\) ion has greater power to accept a proton to form its conjugate acid, HF, while Cl\(^-\) ion has a lesser power to do so to form HCl (conjugate acid), F\(^-\) ion has higher basic strength (i.e., proton accepting power) than Cl\(^-\) ion. (F \(>\) Cl).

#### 6.6.1 Variation of Basicity in a Period

Let us consider the anions namely CH\(_3\)\(^+\), NH\(_2\)\(^-\), OH\(^-\) and F\(^-\). These anions have been derived from the hydrides of 2nd period CH\(_4\), NH\(_3\), H\(_2\)O and HF.
respectively. These anions act as Bronsted bases, since they can accept a proton to give their corresponding conjugate acids.

It has been found that the basicity of the given anions decreases as we move from left to right in the period, i.e., the basicity is in the order \( \text{CH}_3^- > \text{NH}_3^- > \text{OH}^- > \text{F}^- \). This order can be explained as follows:

<table>
<thead>
<tr>
<th>Base (Hydride Ion)</th>
<th>Conjugate Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3^- )</td>
<td>( \text{CH}_4 )</td>
</tr>
<tr>
<td>( \text{NH}_3^- )</td>
<td>( \text{NH}_4^+ )</td>
</tr>
<tr>
<td>( \text{OH}^- )</td>
<td>( \text{OH}_2^+ )</td>
</tr>
<tr>
<td>( \text{F}^- )</td>
<td>( \text{HF} )</td>
</tr>
</tbody>
</table>

(i) We know that in the formation of the given anions, H-atom overlaps with the negatively-charged central atom and hence some volume of the central atom is occupied by H-atoms and the remaining volume of the central atom is occupied by the electron due to which the central atom is carrying negative charge on it. Since the number of H-atoms overlapping the central atom is decreasing from \( \text{CH}_3^- \) to \( \text{F}^- \) ions, the volume occupied by H-atoms is also decreasing from \( \text{CH}_3^- \) to \( \text{F}^- \) ions and hence the volume occupied by the electron is increasing. In case of \( \text{F}^- \) ion, since no H-atom is present, the whole volume of this ion is occupied by the electron. Thus,

<table>
<thead>
<tr>
<th>Ions:</th>
<th>( \text{CH}_3^- )</th>
<th>( \text{NH}_3^- )</th>
<th>( \text{OH}^- )</th>
<th>( \text{F}^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of H-Atoms:</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>Zero</td>
</tr>
<tr>
<td>Volume occupied by H-Atoms:</td>
<td>( \frac{3}{4} \times \frac{3}{3} = \frac{3}{4} )</td>
<td>( \frac{2}{3} \times \frac{2}{3} = \frac{4}{9} )</td>
<td>( \frac{1}{2} \times \frac{1}{2} = \frac{1}{4} )</td>
<td>Zero</td>
</tr>
</tbody>
</table>

Volume occupied by the Electron:

\[
\text{Volume occupied by the Electron: } \left(1 - \frac{3}{4}\right) = \frac{1}{4} \quad \left(1 - \frac{2}{3}\right) = \frac{1}{3} \quad \left(1 - \frac{1}{2}\right) = \frac{1}{2} \quad \text{(Whole Number)}
\]

The increase in the volume occupied by the electron produces an increase in the delocalisation of the electron and hence the electron density round the central atom decreases from \( \text{CH}_3^- \) to \( \text{F}^- \). The decrease in the electron density round the central atom increases the delocalisation and thereby the volume occupied by the electron also increases.
density decreases the tendency of the anion to accept the proton and hence
the basicity of the anion decreases from CH$_4$ to F$^-$ . Thus we see that the
basicity of the given anions decreases as CH$_4$ > NH$_3$ > OH$^-$ > F$^-$ . In
general we can say that the basicity of the anions derived from the
hydrides of the elements of the same period decreases as we move from
left to right in the period.

(ii) We know that in a given conjugate acid-base pair, if the acid is strong, its
conjugate base will be weak and vice versa. Thus since the acidic strength
of CH$_4$, NH$_3$, H$_2$O and HF which are conjugate acids of CH$_4^-$, NH$_3^-$,
OH$^-$ and F$^-$ ions respectively increases as CH$_4$ < NH$_3$ < H$_2$O < HF, the
basic strength of the given bases should decrease in the same direction, i.e.,
the basic strength of the hydride anions should be in the order CH$_4^-$ > NH$_3^-$
> OH$^-$ > F$^-$ .

6.6.2 Variation of Basicity in Groups

The hydride anions of the elements of these groups are NH$_3^-$, PH$_3^-$, AsH$_3^-$,
SbH$_5^-$, BiH$_3^-$ (Group VA), OH$^-$, SH$^-$, HSe$^-$, HP$^-$, (Group of VIA) and F$^-$, Cl$^-$(Group of VIIA). These anions have a tendency to accept a proton and hence, according to Bronsted-Lowry concept of bases, act as Bronsted bases.

After accepting the proton they give their corresponding conjugate acids.

It has been found that the basicity of the hydride anions of the elements of a
given group decreases as we move down the group. This progressive decrease
can be explained by using the same argument that has been used in explaining the
successive decrease in the basicity of the hydride anions of the non-metals along
the period (e.g., CH$_4$ > NH$_3$ > OH$^-$ > F$^-$ ). Thus the basicity of the hydride anions of the elements of Groups VA, VIA and VIIA decreases in the following given order:

- Group VA: NH$_3^-$ > PH$_3^-$ > AsH$_3^-$ > SbH$_5^-$ > BiH$_3^-$
- Group VIA: OH$^-$ > SH$^-$ > HSe$^-$ > HP$^-$
- Group VIIA: F$^-$ > Cl$^-$ > Br$^-$ > I$^-$

Thus it can be concluded that:

(i) From moving left to right in a given period, the basicity of the hydride anions of the non-metal decreases.

(ii) On moving down the group, the basicity of hydride anions of the element decreases.
So, we can say that the basicity of the hydride ions decreases on moving from left to right in a period as well as while moving down the group.

### 6.6.3 Variation of Acidic Strength or Acidity in a Period

According to Bronsted-Lowry theory, Bronsted acid is defined as the tendency to lose (release) a proton (H⁺) to form its conjugate base. So, acidity of Bronsted acid is its proton releasing power. Consider the hydrides of the non-metals of the second period of the periodic table namely CH₄, NH₃, H₂O and HF. These hydrides have a tendency to release a proton (H⁺) and after losing the proton they give their conjugate bases as shown below:

<table>
<thead>
<tr>
<th>Acid (Hydride Molecule)</th>
<th>Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>CH₄⁻</td>
</tr>
<tr>
<td>NH₃</td>
<td>NH₄⁻</td>
</tr>
<tr>
<td>H₂O</td>
<td>OH⁻</td>
</tr>
<tr>
<td>HF</td>
<td>F⁻</td>
</tr>
</tbody>
</table>

The acidity of CH₄, NH₃, H₂O and HF molecules increases as we move from left to right in the period, i.e., the acidity is in the order: CH₄ < NH₃ < H₂O < HF. This can be explained as, since CH₄, NH₃, H₂O, and HF molecules, after losing a proton, give CH⁺₄, NH₄⁺, OH⁻ and F⁻ ions which are conjugate bases, CH₄⁻ (acid) - CH₄⁺ (base), NH₃⁻ (acid) - NH₄⁺ (base), H₂O⁻ (acid) - OH⁻ (base) and HF⁻ (acid) - F⁻ (base) are conjugate acid-base pairs. We have already stated that the basicity of CH₄⁻, NH₄⁺, OH⁻ and F⁻ ions increases as CH₄⁻ > NH₄⁺ > OH⁻ > F⁻. Again we know that, according to Bronsted-Lowry concept, in a given conjugate acid-base pair, if the acid is strong, its conjugate base would be weak and vice versa. Thus since the basicity of CH₄⁻, NH₄⁺, OH⁻ and F⁻ ions is in the decreasing order (CH₄⁻ > NH₄⁺ > OH⁻ > F⁻), the acidity of their conjugate acids (viz., CH₄, NH₃, H₂O, and HF, respectively) would be in the increasing order (CH₄ < NH₃ < H₂O < HF).

### 6.6.4 Variation of Acidic Strength in a Group

Consider the hydrides of Group 14, H₂O, H₂S, H₂Se and H₂Te. It has been observed that their acidic strength (i.e., proton releasing power) increases as we move down the group from H₂O to H₂Te. Thus the acidic strength is in the order H₂O < H₂S < H₂Se < H₂Te. This increasing order is also confirmed by the fact that the values of dissociation constant (Kₐ) for the given molecules also increase in the same order (H₂O = 1.0 x 10⁻¹⁴, H₂S = 1.0 x 10⁻⁷, H₂Se = 1.7 x 10⁻⁴, H₂Te = 2.3 x 10⁻²). This order can be explained as, since the given hydride molecules,
after losing a proton (H⁺), give OH⁻, SH⁻, HSe⁻ and HTe⁻ ions, respectively, which are their conjugate bases. H₂O (acid) – OH⁻ (base), H₂S (acid) – HS⁻ (base), H₂Se (acid) – HSe⁻ (base) and H₂Te (acid) – HTe⁻ (base) are conjugate acid-base pairs. We have already stated that since the basic strength (i.e., proton accepting power) of OH⁻, SH⁻, SeH⁻ and TeH⁻ ions (which are conjugate bases of H₂O, H₂S, H₂Se and H₂Te molecules respectively) decreases as OH⁻ < SH⁻ < HSe⁻ < TeH⁻, the acidic strength (i.e., proton releasing power) of H₂O, H₂S, H₂Se and H₂Te which are conjugate acids of OH⁻, SH⁻, SeH⁻ and TeH⁻ ions, respectively should increase as H₂O < H₂S < H₂Se < H₂Te.

6.7 RELATIVE ORDER OF ACIDIC STRENGTH OF OXYACIDS

1. Consider the oxyacids of Cl-atom, i.e., HClO, HClO₂, HClO₃ and HClO₄. It has been shown earlier that the acidic strength of the given acids increases, as we move from HClO to HClO₄, (HClO < HClO₂ < HClO₃ < HClO₄). This order can be explained in any of the following ways:

(i) Explanation Based on Oxidation Number of Central Atom

The structures of these acids can be written as:

\[
\begin{align*}
\text{HClO} & : \quad \overset{\text{O}}{\underset{\text{H}}{\text{O}}}, \\
\text{HClO}_2 & : \quad \overset{\text{O}}{\underset{\text{O}}{\text{O}}}, \\
\text{HClO}_3 & : \quad \overset{\text{O}}{\underset{\text{O}}{\text{O}}}, \\
\text{HClO}_4 & : \quad \overset{\text{O}}{\underset{\text{O}}{\text{O}}},
\end{align*}
\]

These structures show that each acid has Cl – O – H bond. It may also be noted that the oxidation number of the central atom viz, Cl-atom increases from +1 to +7 as we move from HClO to HClO₄, (HClO = +1, HClO₂ = +3, HClO₃ = +5, HClO₄ = +7). As the oxidation number of Cl-atom increases from +1 (in HClO) to +7 (in HClO₄), the tendency of Cl-atom to attract the electron pair of Cl–O bond towards itself increases and hence the rupture of O – H bond becomes easier, i.e., with the increase in the oxidation number of Cl-atom, the possibility of getting H-atom as H⁺ ion by the rupture of O – H bond increases. In other words we can say that the acidic character of the given acids increases from HClO to HClO₄, (HClO < HClO₂ < HClO₃ < HClO₄).

(ii) Explanation Based on Bronsted-Lowry Concept of Acids and Bases

According to this concept ClO⁻, ClO₂⁻, ClO₃⁻ and ClO₄⁻ are the conjugate bases of HClO, HClO₂, HClO₃ and HClO₄, respectively.
We know that the basicity of ClO$_3^-$, ClO$_2^-$, ClO$_4^-$, and ClO$_7^-$ ions decreases as we move from ClO$_7^-$ to ClO$_4^-$ (ClO$_7^-$ > ClO$_6^-$ > ClO$_5^-$ > ClO$_4^-$). Again according to this concept, since the basicity of the anions decreases from ClO$_7^-$ to ClO$_4^-$ (ClO$_7^-$ > ClO$_6^-$ > ClO$_5^-$ > ClO$_4^-$), the acidity of their conjugate acids (viz., HClO, HClO$_2$, HClO$_3$, and HClO$_4$) will increase from HClO to HClO$_4$, i.e., the acidity of HClO, HClO$_2$, HClO$_3$, and HClO$_4$ increases as HClO < HClO$_2$ < HClO$_3$ < HClO$_4$.

2. Consider the halic acids of Cl, Br, and I, viz., HClO, HBrO, and HIO$_3$, the acidic strength of these acids is found to decrease as we move down the halogen group from Cl to I (HClO$_3$ > HBrO$_3$ > HIO$_3$). This order can be explained as follows.

All these acids have the same structure, i.e.,

```
  O
 /|
X—O—H
 /|
  O
```

(X = Cl, Br, I) and the oxidation number of the central atoms in each molecule is the same (+7). The acidity order is explained on the basis of the electronegativity of the central atom. As the electronegativity of the central atom (X) decreases as we move from Cl to I, the tendency of the central atom to attract the electron pair of X—O bond towards itself decreases and hence the possibility of the rupture of O—H bond also decreases, i.e., H-atoms are not obtained as H$^+$ ions quite easily. In other words we can say that the acid having the central atom with maximum electronegativity value will give H$^+$ ions quite easily while that having the central atom with minimum value of electronegativity will do so with great difficulty and hence acidic strength will decrease with the decrease in the electronegativity of the central atom (HClO$_3$ > HBrO$_3$ > HIO$_3$).

So, we can conclude that the acidic strength of oxyacids of the elements of the same group and in the same oxidation state, decreases as the electronegativity of the central atom decreases on moving down the group.

3. Acidic strength of H$_2$PO$_4$, H$_3$PO$_4$, and H$_5$PO$_4$ acids have been found as HPO$_4^-$ > H$_2$PO$_4$ and H$_3$PO$_4$. This order is explained on the basis of the number of OH groups attached directly with P-atom. These acids are monobasic, dibasic and tribasic and hence contain one, two and three OH groups, respectively.
6.8 ADVANTAGES AND LIMITATION OF BRONSTED-LOWRY CONCEPT

Advantages

(i) This concept is superior to Arrhenius concept, since Arrhenius concept can explain the acidic/basic character of a substance only in aqueous medium (H₂O) while Bronsted-Lowry concept can explain the acidic/basic nature of a substance in aqueous (H₂O) as well as in other protic solvents like liq. NH₃, liq. HF. For example, since H₂N·CO·NH₂ (urea) loses a proton in liq. NH₃, it behaves as a Bronsted acid in this solvent. On the other hand, HNO₃ gains a proton in liq. HF, it behaves as a Bronsted base in this solvent.

\[
\begin{array}{c|c|c}
\text{Acid} & \text{Base} & \text{Acid} \\
H₂N·CO·NH₂ & NH₃ & H₂N·CO·NH⁺ \\
HF & +HNO₃ & H₁NO₃⁻ + F⁻
\end{array}
\]

(ii) Acid-Base reactions taking place in gaseous phase can also be explained by Bronsted-Lowry concept for example in the reaction between HCl (g) and NH₃ (g), HCl (g) acts as an acid and NH₃ (g) behaves as a base.

\[
\begin{array}{c|c|c|c}
\text{Acid} & \text{Base} & \text{Acid} & \text{Base} \\
HCl (g) & NH₃ (g) & NH₄⁺ & Cl⁻ or NH₃⁺ Cl⁻
\end{array}
\]

Limitations

The most important limitation of this concept is that it cannot explain the Acid-Base reactions taking place in non-protic solvents, like liq. SO₂, liq. BF₃, BrF₃, AlCl₃, POCl₃, etc., in which no transfer of protons take place.

\[
\begin{array}{c|c|c|c}
\text{Acid} & \text{Base} & \text{Acid} & \text{Base} \\
SO₂ & SO₂ & SO²⁻ & SO₄²⁻ \\
BrF₃ & BrF₃ & BrF⁺ & Br⁻
\end{array}
\]
Check Your Progress

1. How will you determine the relative strength of Bronsted acids and Bronsted bases?
2. Why CH3COOH is called a differentiating solvent?
3. Define basic strength of a Bronsted base.
4. When the basicity of the given anions decreases?
5. Define acidity of Bronsted acid.
6. How the acidity of CH4, NH3, H2O and HF molecules increases?
7. What is the limitation of Bronsted-Lowry concept?

6.9 Answers to Check Your Progress Questions

1. The Bronsted–Lowry theory is an acid–base reaction theory which was proposed independently by Johannes Nicolaus Bronsted and Thomas Martin Lowry in 1923. The fundamental concept of this theory is that when an acid and a base react with each other, the acid forms its conjugate base, and the base forms its conjugate acid by exchange of a proton (the hydrogen cation, or H+). This theory is a generalization of the Arrhenius theory. Principally, according to the Bronsted–Lowry scheme a substance can function as an acid only in the presence of a base; similarly, a substance can function as a base only in the presence of an acid. Furthermore, when an acidic substance loses a proton, it forms a base, called the conjugate base of an acid, and when a basic substance gains a proton, it forms an acid called the conjugate acid of a base.

2. In the Arrhenius theory, acids are defined as substances that dissociate in aqueous solution to give H+ (hydrogen ions) and the bases are defined as substances that dissociate in aqueous solution to give OH− (hydroxide ions). But in the Bronsted–Lowry theory, the acids and bases are defined by the way they react with each other, which allows for greater generality.

3. The equilibrium expression for acid and base is expressed as follows.
   Acid + Base  $\rightleftharpoons$ Conjugate Base + Conjugate Acid

   With an acid, HA, the equation can be written symbolically as:
   HA + B $\rightarrow$ A− + HB+

   The equilibrium sign, $\rightleftharpoons$, is used because the reaction can occur in both forward and backward directions. The acid, HA, can lose a proton to become its conjugate base, A−. The base, B, can accept a proton to become its conjugate acid, HB+. Most acid-base reactions are fast so that the
components of the reaction are usually in dynamic equilibrium with each other.

4. Due to the formation of a salt, acid-base neutralisation reaction is also called salt formation reaction.

5. The substances which can act as Bronsted acids (loss of proton) as well as Bronsted bases (gain of proton) are called amphoteric substances.

6. Relative strength of Bronsted acids and Bronsted bases can be determined by treating these substances with water. When an acid reacts with H₂O, water acts as a base and when a base reacts with H₂O, water acts as an acid.

7. Since CH₃COOH (solvent) brings the acids to different level of their acid strength, this solvent is called a differentiating solvent for these acids.

8. The basic strength of a Bronsted base is defined as its proton accepting power. For example, since F⁻ ion has greater power to accept a proton to form its conjugate acid, HF, while Cl⁻ ion has a lesser power to do so to form HCl (conjugate acid), F⁻ ion has higher basic strength (i.e., proton accepting power) than Cl⁻ ion. (F > Cl⁻).

9. The basicity of the given anions decreases as we move from left to right in the period, i.e., the basicity is in the order CH₃ > NH₃ > OH⁻ > F⁻.

10. According to Bronsted-Lowry theory, Bronsted acid is defined as the tendency to lose (release) a proton (H⁺) to form its conjugate base. So acidity of Bronsted acid is its proton releasing power. Consider the hydrides of the non-metals of the second period of the periodic table namely CH₄, NH₃, H₂O and HF. These hydrides have a tendency to release a proton (H⁺) and after losing the proton they give their conjugate bases.

11. The acidity of CH₄, NH₃, H₂O and HF molecules increases as we move from left to right in the period, i.e., the acidity is in the order : CH₄ < NH₃ < H₂O < HF.

12. The most important limitation of this concept is that it cannot explain the acid-base reactions taking place in non-protonic solvents, like liq. SO₃, liq. BF₃, BrF₅, AICl₅, POCl₃ etc., in which no transfer of protons takes place.

### 6.10 SUMMARY

- The Bronsted-Lowry theory is an acid-base reaction theory which was proposed independently by Johannes Nicolaus Bronsted and Thomas Martin Lowry in 1923.
- The fundamental concept of this theory is that when an acid and a base react with each other, the acid forms its conjugate base, and the base forms
its conjugate acid by exchange of a proton (the hydrogen cation, or H⁺). This theory is a generalization of the Arrhenius theory.

- Principally, according to the Bronsted–Lowry scheme a substance can function as an acid only in the presence of a base; similarly, a substance can function as a base only in the presence of an acid.
- When an acidic substance loses a proton, it forms a base, called the conjugate base of an acid, and when a basic substance gains a proton, it forms an acid called the conjugate acid of a base.
- The reaction between an acidic substance, such as hydrochloric acid, and a basic substance, such as ammonia, may be represented by the equation:

\[
\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Cl}^-
\]

In the above equation the ammonium ion (NH₄⁺) is the acid conjugate to the base ammonia, and the chloride ion (Cl⁻) is the base conjugate to hydrochloric acid.

- The Bronsted–Lowry theory enlarges the number of compounds considered to be acids and bases to include not only the neutral molecules, for example sulfuric, nitric, and acetic acids, and the alkali metal hydroxides, but also certain atoms and molecules with positive and negative electrical charges (cations and anions).

- The ammonium ion, the hydronium ion, and some hydrated metal cations are considered acids. The acetate, phosphate, carbonate, sulfide, and halogen ions are considered base.

- The concept of acidity originated from the ancient Greeks who defined sour tasting substances as ‘Acids’. These substances were also found to change the colour of litmus paper and corrode metals. On the other hand bases were defined and studied by their ability to counteract acids.

- In the Arrhenius theory, acids are defined as substances that dissociate in aqueous solution to give H⁺ (hydrogen ions) and the bases are defined as substances that dissociate in aqueous solution to give OH⁻ (hydroxide ions).

- The Bronsted–Lowry theory, the acids and bases are defined by the way they react with each other, which allows for greater generality. The definition is expressed in terms of an equilibrium expression as follows:

\[
\text{Acid} + \text{Base} \rightleftharpoons \text{Conjugate Base} + \text{Conjugate Acid}
\]

With an acid, HA, the equation can be written symbolically as:

\[
\text{HA} + \text{B} \rightleftharpoons \text{A}^- + \text{HB}^+
\]

- The equilibrium sign, \(\rightleftharpoons\), is used because the reaction can occur in both forward and backward directions. The acid, HA, can lose a proton to become its conjugate base, A⁻. The base, B, can accept a proton to become
its conjugate acid, HBF$_4$. Most acid-base reactions are fast so that the components of the reaction are usually in dynamic equilibrium with each other.

- Arrhenius defined acids as any species that gives H$^+$ ions (or H$_2$O $^+$ ions) in water and base as a substance which furnishes OH$^-$ ions in water. Thus according to this concept, the substances like HCl, HNO$_3$, H$_2$SO$_4$, CH$_3$COOH, etc., are acids, since they give H$^+$ ions when dissolved in water.
- Acid-base neutralisation reaction in water is defined according to the concept that the acid-base neutralisation reaction in water consist of available H$_2$O or H$^+$ ions (acid) which combines with a compound containing OH-ions (base) to form the salt and water.
- Due to the formation of a salt, acid-base neutralisation reaction is also called salt formation reaction. This shows that in neutralisation reaction, H$_2$O is produced by the combination of H$^+$ and OH$^-$ ions. Thus we can say that neutralisation reaction, according to Arrhenius concept of acids and bases, is the combination of H$^+$ OH$^-$ ions, which are produced by the dissociation of the acid and base, respectively in aqueous medium.
- Bronsted-Lowry concept of the proton-donor acceptor system specified a new concept of acids and bases which is independent of solvent. According to this concept, an acid is a species (molecule or ion) that can lose a proton (H$^+$) and base is a species (molecule or ion) that can accept a proton. In other words an acid is a proton donor and base is a proton acceptor.
- The substances which can act as Bronsted acids (loss of proton) as well as Bronsted bases (gain of proton) are called amphoteric substances.
- Relative strength of Bronsted acids and Bronsted bases can be determined by treating these substances with water. When an acid reacts with H$_2$O, water acts as a base and when a base reacts with H$_2$O, water acts as an acid.
- The CH$_3$COOH (solvent) brings the acids to different level of their acid strength, this solvent is called a differentiating solvent for these acids.
- The basic strength of a Bronsted base is defined as its proton accepting power. For example, since F$^-$ ion has greater power to accept a proton to form its conjugate acid, HF, while Cl$^-$ ion has a lesser power to do so to form HCl (conjugate acid), F$^-$ ion has higher basic strength (i.e., proton accepting power) than Cl$^-$ ion. (F$^-$ > Cl$^-$).
- The hydride anions of the elements of the groups, namely NH$_3^-$, PH$_3^-$, AsH$_3^-$, SbH$_3^-$, BiH$_3^-$ (Group VA), OH$^-$, SH$^-$, HSe$^-$, HPO$_4$$^{2-}$ (Group of VIA) and F$^-$, Cl$^-$, Br$^-$, I$^-$ (Group of VIIA) have a tendency to accept a proton and hence, according to Bronsted-Lowry concept of bases, act as...
Bronsted Concept of Acids and Bases

NOTES

Bronsted bases. After accepting the proton they give their corresponding conjugate acids.

- According to Bronsted-Lowry theory, Bronsted acid is defined as the tendency to lose (release) a proton (H⁺) to form its conjugate base. So acidity of Bronsted acid is its proton releasing power. Consider the hydrides of the non-metals of the second period of the periodic table namely CH₄, NH₃, H₂O and HF. These hydrides have a tendency to release a proton (H⁺) and after losing the proton they give their conjugate bases.

- The acidity of CH₄, NH₃, H₂O and HF molecules increases as we move from left to right in the period, i.e., the acidity is in the order: CH₄ < NH₃ < H₂O < HF.

- The acidic strength of oxyacids of the elements of the same group and in the same oxidation state, decreases as the electronegativity of the central atom decreases on moving down the group.

- Acidic strength of H₃PO₄, H₂PO₄⁻ and HPO₄²⁻ acids have been found as HPO₄²⁻ > H₂PO₄⁻ and H₃PO₄. This order is explained on the basis of the number of OH groups attached directly with P-atom. These acids are monobasic, dibasic and tribasic and hence contain one, two and three OH groups, respectively.

- The most important limitation of this concept is that it cannot explain the acid-base reactions taking place in non-protonic solvents, like liq. SO₂, liq. BF₃, BrF₅, AlCl₃, POCl₃ etc., in which no transfer of protons take place.

6.11 KEY WORDS

- **Bronsted acids**: According to Bronsted-Lowry theory, Bronsted acid is defined as the tendency to lose (release) a proton (H⁺) to form its conjugate base.

- **Bronsted bases**: These can accept one or more protons.

- **Amphiprotonic substances**: The substances which can act as Bronsted acids (loss of proton) as well as Bronsted bases (gain of proton) are called amphiprotonic substances.

- **Basic strength**: The basic strength of a Bronsted base is defined as its proton accepting power.

- **Acid-Base neutralisation reaction in water**: According to this concept, the acid-base neutralisation reaction in water consist of available H₂O⁺ or H⁺ ions (acid) which combines with a compound containing OH⁻ ions (base) to form the salt and water.
6.12 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions
1. Define the Bronsted-Lowry concept of acids and bases.
2. What is Arrhenius concept of acids and bases?
3. Why is equilibrium sign used in the reaction?
4. Define the acid-base neutralisation reaction in water.
5. What is acid-base neutralisation reaction?
6. Give examples of Bronsted acids and Bronsted bases.
7. List the advantages and limitation of Bronsted-Lowry concept of acids and bases.

Long Answer Questions
1. Give a detailed account of Bronsted–Lowry theory and concept of acids and bases reaction giving appropriate example.
2. Correlate the acid-base theories given by Bronsted-Lowry and Arrhenius.
3. Discuss the advantages and disadvantages of Arrhenius concept of acids and bases giving appropriate examples.
4. Briefly explain the Bronsted-Lowry concept of the proton-donor acceptor system with the help of examples.
5. Discuss the concept of relative strength of Bronsted acids and Bronsted bases in aqueous medium giving examples.
6. Describe the various levelling and differentiating solvents for acid-base reactions.
7. Explain the periodic trends, basic strength or basicity of a Bronsted base giving suitable examples.
8. Write short notes on the following giving examples:
   (i) Variation of Basicity in Groups
   (ii) Variation of Acidic Strength or Acidity in a Period
   (iii) Variation of Acidic Strength in a Group
   (iv) Relative Order of Acidic Strength of Oxyacids

6.13 FURTHER READINGS

NOTES


UNIT 7 LEWIS CONCEPT OF ACIDS AND BASES

Structure
7.0 Introduction
    7.1 Objectives
7.2 Lewis Acids and Bases
    7.2.1 Neutralisation Reaction for Lewis Acid with a Lewis Base
7.3 Lewis Acids
    7.3.1 Variation of Lewis Acid Strength of Simple Cations
7.4 Lewis Bases
    7.4.1 Relative Variation in Basic Strength of NH₃, H₂O, HF and Ne Period
    7.4.2 Variations of Basic Strength in a Group
7.5 Comparative Assessment of Arrhenius, Bronsted-Lowry and Lewis Acids and Bases
7.6 Advantages and Limitations of Lewis Concept
7.7 Answers to Check Your Progress Questions
7.8 Summary
7.9 Key Words
7.10 Self Assessment Questions and Exercises
7.11 Further Readings

7.0 INTRODUCTION

In 1923, Gilbert N. Lewis suggested another way of looking at the reaction between H⁺ and OH⁻ ions. In the Bronsted model, the OH⁻ ion is the active species, in this reaction it accepts an H⁺ ion to form a covalent bond. In the Lewis model, the H⁺ ion is the active species, it accepts a pair of electrons from the OH⁻ ion to form a covalent bond. In the Lewis theory of acid-base reactions, bases donate pairs of electrons and acids accept pairs of electrons. A Lewis acid is therefore any substance, such as the H⁺ ion, that can accept a pair of nonbonding electrons. In other words, a Lewis acid is an electron-pair acceptor. A Lewis base is any substance, such as the OH⁻ ion, that can donate a pair of nonbonding electrons. A Lewis base is therefore an electron-pair donor. Principally, a Lewis acid is a chemical species that contains an empty orbital which is capable of accepting an electron pair from a Lewis base to form a Lewis adduct. A Lewis base, then, is any species that has a filled orbital containing an electron pair which is not involved in bonding but may form a dative bond with a Lewis acid to form a Lewis adduct. For example, NH₃ is a Lewis base, because it can donate its lone pair of electrons. Trimethylborane (Me₃B) is a Lewis acid as it is capable of accepting a lone pair. In a Lewis adduct, the Lewis acid and base share an electron pair furnished by the Lewis base, forming
a dative bond. In the context of a specific chemical reaction between NH₃ and Me₃B, the lone pair from NH₃ will form a dative bond with the empty orbital of Me₃B to form an adduct NH₃•Me₃B.

In this unit you will study about the neutralisation reaction, Lewis acids and bases, variation of Lewis acid strength of simple cations and variation in Lewis acid strength of Boron halides, variation in basic strength of NH₃, H₂O, HF and Ne period; and a comparative study of Arrhenius, Bronsted-Lowry and Lewis acids and bases concepts.

7.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand neutralisation reaction
- Describe Lewis acids and bases
- Discuss variation of Lewis acid strength of simple cations
- Interpret relative variation in basic strength of NH₃, H₂O, HF and Ne period
- Describe comparative assessment of Arrhenius, Bronsted-Lowry and Lewis acids and bases
- Explain advantages and limitations of Lewis concept

7.2 LEWIS ACIDS AND BASES

In 1923, Gilbert N. Lewis suggested another way of looking at the reaction between H⁺ and OH⁻ ions. In the Bronsted model, the OH⁻ ion is the active species, in this reaction it accepts an H⁺ ion to form a covalent bond. In the Lewis model, the H⁺ ion is the active species, it accepts a pair of electrons from the OH⁻ ion to form a covalent bond.

\[
\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}
\]

In the Lewis theory of acid-base reactions, bases donate pairs of electrons and acids accept pairs of electrons. A Lewis acid is therefore any substance, such as the H⁺ ion, that can accept a pair of nonbonding electrons. In other words, a Lewis acid is an electron-pair acceptor. A Lewis base is any substance, such as the OH⁻ ion, that can donate a pair of nonbonding electrons. A Lewis base is therefore an electron-pair donor.

Principally, a Lewis acid is a chemical species that contains an empty orbital which is capable of accepting an electron pair from a Lewis base to form a Lewis adduct. A Lewis base, then, is any species that has a filled orbital containing an electron pair which is not involved in bonding but may form a dative bond with a Lewis acid to form a Lewis adduct. For example, NH₃ is a Lewis
base, because it can donate its lone pair of electrons. Trimethylborane (Me₃B) is a Lewis acid as it is capable of accepting a lone pair. In a Lewis adduct, the Lewis acid and base share an electron pair furnished by the Lewis base, forming a dative bond. In the context of a specific chemical reaction between NH₃ and Me₃B, the lone pair from NH₃ will form a dative bond with the empty orbital of Me₃B to form an adduct NH₃•Me₃B.

An ‘adduct’ (from the Latin adductus, ‘drawn toward’ alternatively, a contraction of “addition product”) is a product of a direct addition of two or more distinct molecules, resulting in a single reaction product containing all atoms of all components. The resultant is considered a distinct molecular species. Examples include the addition of sodium bisulfite to an aldehyde to give a sulfonate. Adducts often form between Lewis acids and Lewis bases. A good example is the formation of adducts between the Lewis acid borane and the oxygen atom in the Lewis bases, tetrahydrofuran (THF): BH₃O(CH₂)₂ or diethyl ether: BH₃O(CH₂CH₂)₂.

Although the Bronsted-Lowry theory was more general than Arrhenius theory of acid and bases but it could not explain acid or bases reactions which do not involve transfer of protons. Gilbert N. Lewis proposed a broader concept of acids and bases from the proton. Although Lewis first proposed his system in 1923, he did little to develop it until 1938. Lewis defined an acid as a molecule or an ion that can accept an electron pair from some other substance and a base as a molecule or an ion which can donate an electron pair (lone pair of electrons) to some other substance. In other words, a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor. Since Lewis acid is an electron pair acceptor, it is an electron-deficient species. Similarly, since Lewis base is an electron pair donor, it is an electron pair rich species. Lewis acid should contain one or more vacant orbitals into which electron pair(s) donated by the Lewis base can be accommodated.

7.2.1 Neutralsation Reaction for Lewis Acid with a Lewis Base

According to Lewis concept of acids and bases, the neutralization reaction is that in which a Lewis acid reacts with a Lewis base and forms a compound which is called an adduct or complex compound. This compound contains (Lewis Base → Lewis Acid) co-ordinate bond. For example,

<table>
<thead>
<tr>
<th>Lewis Acid</th>
<th>Lewis Base</th>
<th>Adduct</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF₃</td>
<td>NH₃</td>
<td>[H₂N→BF₃]</td>
</tr>
</tbody>
</table>

(Lewis Base → Lewis Acid) co-ordinate bond result by the overlap of the filled orbital on the Lewis base with the vacant orbital on the Lewis acid.

7.3 LEWIS ACIDS

Lewis definition of an acid does not attribute acidity to any particular element but rather, to a unique atomic arrangement. Lewis acid is often considered as an...
Lewis Concept of Acids and Bases

NOTES

1. Molecules whose central atom has vacant p-orbitals or incomplete octet of electrons in its valence shell.

For example, BeF₆, BX₆ (X = H, F, Cl, Me), etc., the valence shell of Be-atom (central atom) in BeF₂ molecule (F – Be – F) has only 4 electrons (incomplete octet of electrons). Similarly, the valence shell of B-atom is BX₆ molecule has only 6 electrons (incomplete octet). The central atom of these molecules contains four orbitals namely 2s, 2p₁, 2p₂ and 2p₃ but all these orbitals are not filled, e.g., in BeF₆ molecule two orbitals viz., 2p₁ and 2p₂ are vacant while in BX₆, molecule one orbital namely 2p₃ is vacant. Thus these molecules are electron-deficient molecules. Due to the presence of vacant p-orbitals in the valence-shell of the central atom of these molecules, these molecules can accept one or more electron pairs from Lewis bases, since Lewis bases are electron pair donor species and hence act as Lewis acids. By accepting the electron pair(s) the central atom of the Lewis acid molecules completes its octet. Following Lewis Acid–Lewis Base reaction illustrates this point.
2. Molecules whose central atom has vacant d-orbitals in its valence shell. Such type of molecules include AlIF₃, AlCl₃, GaCl₃, SiX₄, GeX₄, SnX₄, PX₄, PF₅, AsF₅, SbF₅, BiF₅, TeCl₅, XeF₅, etc. Due to the presence of vacant d-orbitals these molecules can accept the electron pair(s) donated by Lewis bases. This is explained in following Lewis acid-Lewis base reactions.

<table>
<thead>
<tr>
<th>Lewis acid</th>
<th>Lewis base</th>
<th>Adduct</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlF₃ + 3F⁻</td>
<td>COCl₂</td>
<td>[COCl]⁺ [AlCl₃]⁻</td>
</tr>
<tr>
<td>AlCl₃ + Cl⁻</td>
<td></td>
<td>GaCl₄⁻</td>
</tr>
<tr>
<td>SnCl₅ + 2F⁻</td>
<td>SiF₆⁵⁺</td>
<td></td>
</tr>
<tr>
<td>SnCl₄ + 2Cl⁻</td>
<td>SnCl₆⁴⁺</td>
<td></td>
</tr>
<tr>
<td>AsF₅ + XeF₂</td>
<td>[XeF₆]⁺ [AsF₅]⁻</td>
<td></td>
</tr>
<tr>
<td>AsF₃ + XeF₃</td>
<td>[XeF₅]⁺ [AsF₃]⁻</td>
<td></td>
</tr>
<tr>
<td>SbF₅ + 2F⁻</td>
<td>SbF₆⁵⁺</td>
<td></td>
</tr>
<tr>
<td>SbF₃ + F⁻</td>
<td>SbF₄⁴⁺</td>
<td></td>
</tr>
<tr>
<td>SbF₅ + XeF₄</td>
<td>[XeF₆]⁺ [SbF₅]⁻</td>
<td></td>
</tr>
<tr>
<td>XeF₆ + 2Cl⁻</td>
<td>Cs₂[XeF₆]⁴⁺</td>
<td></td>
</tr>
<tr>
<td>XeF₅ + 2NO⁺</td>
<td>[NO]⁺ [XeF₅]⁻</td>
<td></td>
</tr>
<tr>
<td>HF + XeF₆</td>
<td>XeF₇⁺ [HF]⁻</td>
<td></td>
</tr>
</tbody>
</table>

3. Molecules whose central atom is linked with more electronegative atom by double bonds. For example, molecules like CO₂, CS₂, etc., in CO₂, the oxygen atoms are more electronegative than the carbon atom. As a result the electron density due to π-electrons is displaced away from the central atom carbon and towards oxygen atoms. The carbon atom is electron deficient and can accept electrons from a Lewis base, such as OH. This can be illustrated as follows.
Lewis Concept of Acids and Bases

Lewis acid + Lewis base → Adduct

\[
\begin{align*}
\text{H}_2\text{O} + \text{H}^+ &\rightarrow \text{H}_2\text{O}^+ \\
\text{CO}_2 + \text{H}^+ &\rightarrow \text{HCO}_2^- \\
\text{SO}_2 + \text{Ca}^{2+} &\rightarrow \text{Ca}^{2+}\text{O}_2^{2-}
\end{align*}
\]

4. Cations. This class of Lewis acids is made up of positively charged heavy metal ions with incomplete stable orbitals. Theoretically, all cations are potential Lewis acids because they are electron deficient. This property is negligible for alkali metal cations and is weak for the alkaline earth metal cations. Examples of some Lewis acid–Lewis base reactions, in which metal cations act as Lewis acids are given below.

\[
\begin{align*}
\text{Ag}^+ &+ 2\text{NH}_3 \rightarrow \text{H}_2\text{N}^-\text{Ag}^-\text{NH}_3^- \text{ or } [\text{Ag}^+\text{NH}_3]^+ \\
\text{Cu}^{2+} &+ 4\text{NH}_3 \rightarrow \text{Cu}^+\text{NH}_3^+ \text{ or } [\text{Cu}^+\text{NH}_3]^+ \\
\text{Ca}^{2+} &+ 4\text{NH}_3 \rightarrow [\text{Ca}^+\text{NH}_3]^2^+
\end{align*}
\]

Since \(H^+\) ion has empty 1s orbital, it is able to accommodate an electron pair donated by the electron pair donors. Thus, in the following reactions \(H^+\) ion acts as a Lewis acid.

\[
\begin{align*}
\text{H}^+ &+ \text{NH}_3 \rightarrow [\text{H}^+\text{NH}_3]^+ \text{ or } \text{NH}_4^+ \\
\text{H}^+ &+ \text{PH}_3 \rightarrow [\text{H}^+\text{PH}_3]^+ \text{ or } \text{PH}_4^+ \\
\text{H}^+ &+ \text{OH}_2 \rightarrow [\text{H}^+\text{OH}_2]^+ \text{ or } \text{H}_2\text{O}^+
\end{align*}
\]

5. Elements which have extent of electron in their valence shell. Oxygen and Sulphur atoms contain six electron in their valence shells and therefore, act as Lewis acids.
7.3.1 Variation of Lewis Acid Strength of Simple Cations

Lewis acid strength is defined as the tendency to accept electron pair(s). The Lewis strength acid of a cation depends on the following properties of the cation.

(i) **Size of the Cation**: Smaller the size of the cation, greater is its tendency to accept the electron pair(s) and hence stronger is the Lewis acid. So, the Lewis strength of cations decreases on moving down the group and increases on moving left to right in a period.

For example,

$\text{H}^+ > \text{Na}^+ > \text{K}^+$ (Cations of the same group)

$\text{Li}^+ < \text{Be}^{2+}$ (Cations of the same period)

(ii) **Oxidation State of the Cation**: Lewis strength of the cations of the same metal atom increases with the increase in oxidation number. For example, the Lewis acid strength of $\text{Fe}^{3+} < \text{Fe}^{4+}$.

7.3.2 Variation in Lewis Acid Strength of Boron Halides

All trihalides of boron namely $\text{BF}_3$, $\text{BCl}_3$, $\text{BBr}_3$, and $\text{BI}_3$ are obtained by $sp^2$ hybridization of central atom $\text{B}(2s^2, 2p_1^1, 2p_2^1, 2p_3^1)$. B-atom in its excited state uses only one $2s$ and two $2p$ orbitals in $sp^2$ hybridization, $2p$ remains vacant and thus can accept electron pair donated by the donor molecules (ROH, $\text{NH}_3$, $\text{H}_2\text{O}$ etc.) or ions ($\text{OH}^-$, $\text{F}^-$, $\text{Cl}^-$ etc.). So, trihalides of boron acts as Lewis acids. This can be illustrated as follows.
**Relative Order of Lewis Acid Character of Boron Halides**

Experimentally, the Lewis acid character of Boron trihalides is found to be in the order $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$. This means that BBr$_3$ will give more stable adducts than BBCl$_3$ and BCl$_3$ will yield more stable adducts than BF$_3$.

The above order can be explained on the basis of Boron-Halogen $\pi$-back bonding. We know that each of the given molecules has a trigonal planar geometry which arises due to $sp^3$ hybridisation of B-atom in its excited state. In $sp^3$ hybridisation, one 2p orbital, say 2p$_y$, of B-atom remains unhybridised and vacant. The halogen atom has valence-shell configuration as ns$^2$np$^5$. The singly filled np$_y$ orbital of halogen atom overlaps with the singly-filled $sp^3$ hybrid orbital of B-atom and forms a $\pi$-X-$\pi$ bond, while each of the remaining three orbitals of halogen atom contains one lone pair of electrons. Thus, the structure of BF$_3$ molecule can be shown, as depicted below in Figure 7.1. Now the filled 2p$_y$ orbital of F-atom makes a lateral overlap with the vacant 2p$_y$ orbital of B-atom and gives rise to the formation of an additional F $\rightarrow$ B $\pi$ bond, called $\pi$-$\pi$ back bond. Figure 7.2 illustrates the formation of $\pi$-$\pi$ back bond in BF$_3$ molecule by the lateral overlap between the filled 2p$_y$ orbital of F-atom and vacant 2p$_y$ orbital on B-atom.

![Fig. 7.1 Structure of BF$_3$ Molecule](image1)

![Fig. 7.2 Formation of $\pi$-$\pi$ Back Bond in BF$_3$ Molecule](image2)

The formation of $\pi$-$\pi$ back bonding results in the following:

$$\begin{align*}
\text{F} & \equiv \text{B} \\
\text{F} & \equiv \text{B} \\
\text{F} & \equiv \text{B} \\
\text{F} & \equiv \text{B}
\end{align*}$$
Due to the formation of extra F → B π-bond, B–F bond acquires some double bond character. Thus B–F bond should be shown as B≡F. Since any one of the three F-atoms can take part in the formation of B≡F bond, the structure of BF$_3$ can be supposed to be a resonance hybrid of the following three equivalent resonating structures.

On similar lines the resonating structures of BC1$_3$, BBr$_3$, and BI$_3$ molecules can also be written. It is because of the resonance that all the three B–X bond lengths in a given trihalide are equal.

The tendency of back bonding is maximum in BF$_3$ molecule. This tendency falls rapidly on passing from BC1$_3$ to BI$_3$. This means that the tendency of BF$_3$ molecule to accept electron pair given by Lewis base (e.g., NH$_3$, PH$_3$, F, etc.) is minimum and this tendency increases as we move from BF$_3$ to BI$_3$, i.e., the Lewis acid character of BX$_3$ molecules is in the order:

BF$_3$ < BC1$_3$ < BBr$_3$ < BI$_3$

### 7.4 LEWIS BASES

Lewis bases are the substances which can donate a pair of elections. Lewis bases are broadly classified as:

1. Molecules whose central atom has lone pair of elections.
   - These include hydrides of Group 15(NH$_3$, PH$_3$, AsH$_3$, etc.), Group 16(H$_2$O, H$_2$S, etc.) and Group 17 (HF, HCl, etc.).
2. Almost all negative ions.
   - Typical examples are F, Cl, I, OH, O$^-$, etc. These can be illustrated as follows.

<table>
<thead>
<tr>
<th>Lewis acid</th>
<th>Lewis base</th>
<th>Adduct</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF$_3$</td>
<td>$\cdot$</td>
<td>BF$_3$ or BF$_4$</td>
</tr>
<tr>
<td>H$^+$</td>
<td>Cl$^-$</td>
<td>HCl$^+$ or Cl$^-$</td>
</tr>
<tr>
<td>AXCl$_3$</td>
<td>$\cdot$</td>
<td>AXCl$_3$</td>
</tr>
<tr>
<td>I$_2$</td>
<td>I$^-$</td>
<td>I$_2$</td>
</tr>
<tr>
<td>H$^+$</td>
<td>$\cdot$</td>
<td>H$^+$</td>
</tr>
<tr>
<td>2H$^+$</td>
<td>$\cdot$</td>
<td>H$^+$</td>
</tr>
</tbody>
</table>

3. Molecules containing C=C double bond.
   - The donation of an electron pair from a π-band to a Lewis acid like metal ion, BF$_3$, AlF$_3$, etc., results in the formation of π-complexes. In complexes

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NOTES

Self-Instructional Material
of ethane with Ag, Pt and Rh, the metal atoms are bonded not to any simple carbon atom but to the \( \pi \)-bond directly.

4. Halides.

The halides that can make halide ion available behave like Lewis bases. For example, halides like XeF\(_2\), XeF\(_3\), CsF, NOF, COCl\(_2\), etc. The reactions can be illustrated as follows.

<table>
<thead>
<tr>
<th>Lewis acid</th>
<th>Lewis base</th>
<th>Adduct</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsF(_5)</td>
<td>XeF(_2)</td>
<td>[AsF(_5)]([\text{XeF}_2])</td>
</tr>
<tr>
<td>SnF(_4)</td>
<td>XeF(_2)</td>
<td>[SnF(_4)]([\text{XeF}_2])</td>
</tr>
<tr>
<td>AsF(_3)</td>
<td>XeF(_2)</td>
<td>[AsF(_3)]([\text{XeF}_2])</td>
</tr>
<tr>
<td>HF</td>
<td>XeF(_2)</td>
<td>[HF]([\text{XeF}_2])</td>
</tr>
<tr>
<td>XeF(_6)</td>
<td>CsF</td>
<td>Cs(_2)([\text{XeF}_6])</td>
</tr>
<tr>
<td>AlCl(_3)</td>
<td>COCl(_2)</td>
<td>[COCl(_3)]([\text{AlCl}_2])</td>
</tr>
</tbody>
</table>

7.4.1 Relative Variation in Basic Strength of NH\(_3\), H\(_2\)O, HF and Ne Period

The basic strength an electron releasing power of the substances depend upon the number of lone pairs in them. Greater the number of Lewis pairs, lesser is the tendency of the substance to donate the electron pair and hence lesser in its basic strength.

Since the number lone pairs in these substances increases as we move from NH\(_3\) to Ne (NH\(_3\)=1, H\(_2\)O=2, HF=3, Ne=4) the basic strength decreases as NH\(_3\)> H\(_2\)O > HF > Ne.

7.4.2 Variations of Basic Strength in a Group

Consider the hydrides of group 15 NH\(_3\), PH\(_3\), AsH\(_3\), SbH\(_3\) and BiH\(_3\). We know that the central atom in each of the hydrides has one lone pair of electrons. These molecules can donate this lone pair to the molecule (Lewis acid) and hence act as Lewis base.

<table>
<thead>
<tr>
<th>Lewis Base</th>
<th>Lewis Acid</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH(_3)</td>
<td>H(^+)</td>
<td>H(_3)N(^+) → H(_3)N(^+) or NH(_4^+)</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>F(^-)</td>
<td>H(_3)N(^-) → BF(_3)</td>
</tr>
</tbody>
</table>

The basic strength of these molecules decreases in the order NH\(_3\)> PH\(_3\)> AsH\(_3\)> SbH\(_3\)> BiH\(_3\). Thus, NH\(_3\) is strongly basic and forms salts with weak as well as strong acids:

- NH\(_3\) + HCl → NH\(_4\)Cl
- 2NH\(_3\) + H\(_2\)CO \→ (NH\(_4\))\(_2\)CO

PH\(_3\) is less basic than NH\(_3\), which AsH\(_3\), SbH\(_3\) and BiH\(_3\) have no basic character and are neutral. The above order of basic character of hydrides of Group 15 has been explained on the basis of relative size of the central atom. As
we move down the group, the size of the central. The size of the central atom increases from N to Bi. Since N-atom is the smallest in size, the electron density of lone pair of electrons on it is concentrated over a small region. This electron pair can, therefore, be donated to the Lewis acid quite easily. As the size of the central atom increases down the group, the electron density of lone pair on the central atom gets diffused over a large region and hence the ability of the central atom to donate the lone pair to the Lewis acid decreases. Thus we find that with the increase in the size of the central atom, the electron density of lone pair on the central atom decreases and hence the ability of the central atom to donate the lone pair to the Lewis acid also decreases, i.e., the basic character of AH₃ molecules decreases as we move from NH₃ to BH₃.

7.5 COMPARATIVE ASSESSMENT OF ARRHENIUS, BRONSTED-LOWRY AND LEWIS ACIDS AND BASES

The comparative assessment between Arrhenius, Bronsted-Lowry and Lewis concept of acids and bases can be summarized in following points.

(i) On the Basis of Definition

(a) Arrhenius acid is a compound that gives H⁺ or H₂O⁺ ions in water and Arrhenius base is a compound that provides OH⁻ ions in water.

(b) Bronsted acid is a molecule or an ion that can donate one or more protons (H⁺), i.e., Bronsted acid is a proton-donor. Bronsted base is a molecule or an ion that can accept one or more protons, i.e., Bronsted base is a proton acceptor.

(c) Lewis acid is a molecule or an ion that can accept one or more electron pairs, i.e., a Lewis acid is an electron pair-acceptor. Lewis base is a molecule or an ion that can accept one or more electron pairs, i.e., a Lewis base is an electron pair-donor.

(ii) Arrhenius Acids and Lewis Acids are the same substances, i.e., the substances that act as Arrhenius acids also act as Lewis acids. This fact can be illustrated by considering the behavior of HCl in the following two reactions:

(a) \[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \]

(b) \[ \text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Cl}^- \]

Reaction (a). Since HCl gives H⁺ ion when dissolved in water, this acid acts as an Arrhenius acid in this reaction.

\[
\begin{align*}
\text{HCl} & \quad \rightarrow \quad \text{H}^+ + \text{Cl}^- \\
\text{H}_2\text{O} + \quad \text{H}^+ & \quad \rightarrow \quad \text{H}_3\text{O}^+ \\
\text{HCl (Arrhenius Acid)} + \text{H}_2\text{O} & \quad \rightarrow \quad \text{H}_3\text{O}^+ + \text{Cl}^- 
\end{align*}
\]
Reaction (b). The formation of $\text{NH}_4^+$Cl takes place through the following two steps:

\[
\text{HCl} \quad \rightarrow \quad \text{H}^+ + \text{Cl}^-
\]

\[
\text{H}_2\text{N} : + \text{H}^+ \rightarrow \text{H}_2\text{N} \rightarrow \text{H}^+ \text{ or } \text{NH}_4^+
\]

\[
\text{HCl (Bronsted Acid)} + \text{NH}_4 \quad \rightarrow \quad \text{NH}_4^+ + \text{Cl}^- \text{ or } \text{NH}_4\text{Cl}^-
\]

In reaction (b) HCl undergoes ionization and gives H$^+$ and Cl$^-$ ions. H$^+$ ion thus obtained, has empty 1s orbital and hence accepts an electron pair from NH$_4^-$ and thus forms NH$_4^+$ ion. Now NH$_4^+$ and Cl$^-$ ions combine together to form NH$_4^+$Cl. Thus, we see that since H$^+$ ion obtained by the ionization of HCl accepts an electron pair from NH$_4^-$ molecule, HCl, according to Lewis concept acts as a Lewis acid.

The above discussion clearly shows that HCl, which acts as an Arrhenius acid, also behaves as a Lewis acid. In general, we can say that the substances that act as Arrhenius acids also act as Lewis acids, i.e., Arrhenius acids and Lewis acids are the same substances.

(iii) Bronsted Bases and Lewis Bases are the same substances, i.e., the substances that behave as Bronsted bases also behave as Lewis bases. This can be illustrated by considering the formation of NH$_4^+$ ion by the combination of H$^+$ ion and NH$_4$ molecule, according to Bronsted and Lewis concepts.

According to Bronsted concept, the formation of NH$_4^+$ ion can be shown as follows.

\[
\text{H}^+ + \text{NH}_4 \quad \rightarrow \quad \text{NH}_4^+
\]

In this reaction, since NH$_4^-$ molecule accepts a proton (H$^+$) to form NH$_4^+$ ion, this molecule acts as a Bronsted base.

According to Lewis concept, the combination of H$^+$ and NH$_4^-$ takes place as follows.

\[
\text{H}^+ + \text{NH}_4 \quad \rightarrow \quad [\text{H}^+ \leftarrow \text{NH}_4] \text{ or } \text{NH}_4^+
\]

Here, since NH$_4^-$ molecule loses one electron pair, this molecule acts as a Lewis base.

The above discussion shows that NH$_4^-$ molecule which act as a Bronsted base, also acts as a Lewis base. In general, we can say that the substances that act as Bronsted bases, also act as Lewis bases, i.e., Bronsted bases and Lewis bases are the same substances.
7.6 ADVANTAGES AND LIMITATIONS OF LEWIS CONCEPT

Following are the advantages and limitations of Lewis concept.

Advantages of Lewis Concept

(i) Lewis concept is a broader interpretation of acid-base behaviour.
(ii) This theory is not dependent on the presence of one particular element, upon any given combination of elements, upon the presence of ions, or upon the presence or absence of a solvent.
(iii) The Lewis approach is of great value in case where protons concept is not applicable.
(iv) Lewis theory is frequently employed to interpret reaction mechanism.
(v) It explains the long accepted basic properties of metal oxides and acidic properties of non-metallic oxides.

Limitations of Lewis Concept

(i) In Lewis approach there is a lack of uniform scale of acid and basic strength. The strength of acid and base in term of Lewis approach is variable and dependent on the reaction considered. In this respect it is inferior to Arrhenius concept and the Bronsted-Lowry concept.
(ii) The reactions catalyzed by the Lewis acids are generally not catalyzed by the protonic acids.
(iii) The connectional protonic acids $\text{V}_2\text{O}_5$ and $\text{H}_2\text{SO}_4$ and $\text{HCl}$ are not covered under Lewis concept, as they do not establish a covalent bond by accepting a pair of electrons.

Check Your Progress

1. Define Lewis and Bronsted model of acid and base.
2. State the Lewis theory of acid-base reactions.
3. What is Lewis adduct?
4. Why Lewis defined an acid as a molecule or an ion?
5. What is neutralization reaction according to Lewis concept of acids and bases?
6. Give the Lewis acid character of Boron trihalides.
7. Explain why Lewis approach has a lack of uniform scale of acid and basic strength.
7.7 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

NOTES

1. According in 1923, Gilbert N. Lewis suggested the reaction between H⁺ and OH⁻ ions. In the Bronsted model, the OH⁻ ion is the active species, in this reaction it accepts an H⁺ ion to form a covalent bond. In the Lewis model, the H⁺ ion is the active species, it accepts a pair of electrons from the OH⁻ ion to form a covalent bond.

   \[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}^- \]

2. In the Lewis theory of acid-base reactions, bases donate pairs of electrons and acids accept pairs of electrons. A Lewis acid is therefore any substance, such as the H⁺ ion, that can accept a pair of nonbonding electrons. In other words, a Lewis acid is an electron-pair acceptor. A Lewis base is any substance, such as the OH⁻ ion, that can donate a pair of nonbonding electrons. A Lewis base is therefore an electron-pair donor.

3. In a Lewis adduct, the Lewis acid and base share an electron pair furnished by the Lewis base, forming a dative bond. In the context of a specific chemical reaction between NH₃ and Me₃B, the lone pair from NH₃ will form a dative bond with the empty orbital of Me₃B to form an adduct NH₃·Me₃B⁻.

4. Lewis defined an acid as a molecule or an ion that can accept an electron pair from some other substance and a base as a molecule or an ion which can donate an electron pair (lone pair of electrons) to some other substance. In other words, a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor. Since Lewis acid is an electron pair acceptor, it is an electron-deficient species. Similarly, since Lewis base is an electron pair donor, it is an electron pair rich species. Lewis acid should contain one or more vacant orbitals into which electron pair(s) donated by the Lewis base can be accommodated.

5. According to Lewis concept of acids and bases, the neutralization reaction is that in which a Lewis acid reacts with a Lewis base and forms a compound which is called an adduct or complex compound. This compound contains (Lewis Base → Lewis Acid) co-ordinate bond.

6. The Lewis acid character of Boron tribhalides is found to be in the order BF₃ < BCl₃ < BBBr < BI₃. This means that BBBr⁻ will give more stable adducts than BCl₃ and BCl₃ will yield more stable adducts than BF₃.

7. In Lewis approach there is a lack of uniform scale of acid and basic strength. The strength of acid and base in term of Lewis approach is variable and dependent on the reaction considered. In this respect it is inferior to Arrhenius concept and the Bronsted-Lowry concept.
7.8 SUMMARY

• In 1923, Gilbert N. Lewis suggested another way of looking at the reaction between H⁺ and OH⁻ ions. In the Bronsted model, the OH⁻ ion is the active species, in this reaction it accepts an H⁺ ion to form a covalent bond. In the Lewis model, the H⁺ ion is the active species, it accepts a pair of electrons from the OH⁻ ion to form a covalent bond.

  \[
  \begin{align*}
  \text{H}^+ & \rightarrow \text{H}^- \\
  \text{H}^- & \rightarrow \text{H}^+ \text{H}
  \end{align*}
  \]

• In the Lewis theory of acid-base reactions, bases donate pairs of electrons and acids accept pairs of electrons. A Lewis acid is therefore any substance, such as the H⁺ ion, that can accept a pair of nonbonding electrons. In other words, a Lewis acid is an electron-pair acceptor. A Lewis base is any substance, such as the OH⁻ ion, that can donate a pair of nonbonding electrons. A Lewis base is therefore an electron-pair donor.

• Principally, a Lewis acid is a chemical species that contains an empty orbital which is capable of accepting an electron pair from a Lewis base to form a Lewis adduct. A Lewis base, then, is any species that has a filled orbital containing an electron pair which is not involved in bonding but may form a dative bond with a Lewis acid to form a Lewis adduct.

• In a Lewis adduct, the Lewis acid and base share an electron pair furnished by the Lewis base, forming a dative bond. In the context of a specific chemical reaction between NH₃ and Me₃B, the lone pair from NH₃ will form a dative bond with the empty orbital of Me₃B to form an adduct NH₃•Me₃B⁺.

• An ‘adduct’ (from the Latin adductus, “drawn toward” alternatively, a contraction of “addition product”) is a product of a direct addition of two or more distinct molecules, resulting in a single reaction product containing all atoms of all components. The resultant is considered a distinct molecular species. Examples include the addition of sodium bisulfite to an aldehyde to give a sulfonate.

• Adducts often form between Lewis acids and Lewis bases. A good example is the formation of adducts between the Lewis acid borane and the oxygen atom in the Lewis bases, tetrahydrofuran (THF): BH₃•O(CH₂)₄ or diethyl ether: BH₃•O(CH₂CH₃)₂.

• Lewis defined an acid as a molecule or an ion that can accept an electron pair from some other substance and a base as a molecule or an ion which can donate an electron pair (lone pair of electrons) to some other substance.
• A Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor. Since Lewis acid is an electron pair acceptor, it is an electron-deficient species. Similarly, since Lewis base is an electron pair donor, it is an electron pair rich species. Lewis acid should contain one or more vacant orbitals into which electron pair(s) donated by the Lewis base can be accommodated.

• According to Lewis concept of acids and bases, the neutralization reaction is that in which a Lewis acid reacts with a Lewis base and forms a compound which is called an adduct or complex compound. This compound contains (Lewis Base $\rightarrow$ Lewis Acid) co-ordinate bond.

• Lewis definition of an acid does not attribute acidity to any particular element but rather, to a unique atomic arrangement. Lewis acid is often considered as an acceptor or an electrophile. The property of an acid might be to the availability of an empty orbital for the acceptance of a pair of electrons.

• By accepting the electron pair(s) the central atom of the Lewis acid molecules completes its octet.

• Cations class of Lewis acids is made up of positively charged heavy metal ions with in complete stable orbitals. Theoretically, all cations are potential Lewis acids because they are electron deficient.

• Lewis acid strength is defined as the tendency to accept electron pair(s).

• The Lewis acid character of Boron trihalides is found to be in the order BF$_3$ < BCl$_3$ < BB$_3$ < Br$. This means that BB$_3$ will give more stable adducts than BCl$_3$ and BCl$_3$ will yield more stable adducts than BF$_3$.

• The basic strength an electron releasing power of the substances depend upon the number of lone pairs in them. Greater the number of Lewis pairs, lesser is the tendency of the substance to donate the electron pair and hence lesser in its basic strength.

• Arrhenius acid is a compound that gives $H^+$ or $H_2O^-$ ions in water and Arrhenius base is a compound that provides $OH^-$ ions in water.

• Bronsted acid is a molecule or an ion that can donate one or more protons ($H^+$), i.e., Bronsted acid is a proton-donor. Bronsted base is a molecule or an ion that can accept one or more protons, i.e., Bronsted base is a proton acceptor.

• Lewis acid is a molecule or an ion that can accept one or more electron pairs, i.e., a Lewis acid is an electron pair-acceptor. Lewis base is a molecule or an ion that can accept one or more electron pairs, i.e., a Lewis base is an electron pair-donor.

• In Lewis approach there is a lack of uniform scale of acid and basic strength. The strength of acid and base in term of Lewis approach is variable and dependent on the reaction considered. In this respect it is inferior to Arrhenius concept and the Bronsted-Lowry concept.
7.9 KEY WORDS

- **Neutralization reaction:** According to Lewis concept of acids and bases the neutralization reaction is that in which a Lewis acid reacts with a Lewis base and forms a compound which is called an adduct or complex compound.

- **Lewis acid:** It is a chemical species that contains an empty orbital which is capable of accepting an electron pair from a Lewis base to form a Lewis adduct.

- **Lewis base:** It is any species that has a filled orbital containing an electron pair which is not involved in bonding but may form a dative bond with a Lewis acid to form a Lewis adduct.

- **Cation:** It is an ion with fewer electrons than protons, therefore, it has a positive charge. Theoretically, all cations are potential Lewis acids because they are electron deficient.

7.10 SELF ASSESSMENT QUESTIONS AND EXERCISES

**Short-Answer Questions**

1. Define the concept of Lewis acid and base.
2. Why a Lewis base is an electron-pair donor?
3. What is adduct?
4. Explain cations for Lewis acid.
5. Write advantages and limitations of Lewis concept.

**Long-Answer Questions**

1. Discuss briefly the concept of Lewis acids and bases giving appropriate examples.
2. According to the concept of Lewis, how are acids classified. Explain with the help of examples.
3. Explain the relative order of Lewis acid character of Boron Halides giving appropriate equations.
7.11 FURTHER READINGS


UNIT 8  HSAB: HARD AND SOFT ACIDS AND BASES

Structure
8.0 Introduction
8.1 Objectives
8.2 HSAB: Hard and Soft Acids and Basis
  8.2.1 Applications of HSAB Principle
  8.2.2 Limitations of HSAB Principle
8.3 pH
  8.3.1 Acid-base Indicators
  8.3.2 Solubility Product
  8.3.3 Common Ion Effect
  8.3.4 Applications of Solubility Product and Common Ion Effect
8.4 Buffer Solutions
8.5 Answers to Check Your Progress Questions
8.6 Summary
8.7 Key Words
8.8 Self Assessment Questions and Exercises
8.9 Further Readings

8.0  INTRODUCTION

HSAB: Hard and Soft Acids and Bases concept is an initialism for ‘hard and soft (Lewis) acids and bases’. Also known as the Pearson acid-base concept, HSAB is widely used in chemistry for explaining stability of compounds, reaction mechanisms and pathways. It assigns the terms ‘hard’ or ‘soft’, and ‘acid’ or ‘base’ to chemical species. ‘Hard’ applies to species which are small, have high charge states (the charge criterion applies mainly to acids, to a lesser extent to bases), and are weakly polarizable. ‘Soft’ applies to species which are big, have low charge states and are strongly polarizable. The concept is a way of applying the notion of orbital overlap to specific chemical cases. The theory is used in contexts where a qualitative, rather than quantitative, description would help in understanding the predominant factors which drive chemical properties and reactions.

This is especially so in transition metal chemistry, where numerous experiments have been done to determine the relative ordering of ligands and transition metal ions in terms of their hardness and softness. HSAB theory is also useful in predicting the products of metathesis reactions. In 2005 it was shown that even the sensitivity and performance of explosive materials can be explained on basis of HSAB theory. Ralph Pearson introduced the HSAB principle in the early 1960s as an attempt to unify inorganic and organic reaction chemistry.
In this unit, you will study about HSAB, principles, applications, limitations of HSAB, pH and buffer solutions.

8.1 OBJECTIVES

After going through this unit, you will be able to:

- Discuss about HSAB: Hard and Soft Acid and Bases
- Explain the principles, applications and limitations of HSAB
- Understand pH discussing acid-base indicators
- Discuss buffer solutions and its applications.

8.2 HSAB: HARD AND SOFT ACIDS AND BASIS

Based on preferential bonding Arland, Chatt and Davies (1958) classified the metal ion into two classes:

**Class (a):** The ion included in this category have following characteristics:

- Small size, high polarizing power and high oxidation state.
- The outer electrons or orbital’s are not easily distorted.

This class includes ions of alkali metals, alkaline earth metals, lighter transition metals in high oxidation state like Ti⁷⁺, Cr⁶⁺, Fe⁷⁺, and Co⁷⁺, and the hydrogen ion, H⁺.

**Class (b):** These ions have following characteristics:

- They are large sized.
- Their outer electrons or orbitals are easily distorted.

These includes ion of the heavier transition metals and those in lower oxidation states such as Cu²⁺, Hg²⁺, Ag⁺, Pd²⁺, Pt²⁺ etc.

Based on the behaviour towards the metals of class (a) and (b), the ligands have been classified by Arland, Chatt and Dawies into following class:

**Class (a):** These includes ligands which preferably combines with the metal ions of class (a). For example, the ligands NH₃, R₃N, H₂O and F⁻ ions. The tendency of the complex formation with metals ion of class (a) flows the order:

F > Cl > Br > I
O > S > Se > Te
N > P > As > Sb

**Class (b):** These include ligands which preferably combine with metal ions of class (b). For example, ligands such as R₂P and R₂S. The tendency of the complexation of ligands with class (b) metals ion follows the order:
F < Cl < Br < I
O ≤ P < As < Sb

Pearson's Classification of HSAB

Person in 1963 suggested that the term hard and soft can be used for class (a) and class (b) respectively. Thus in his classification, metal ions of class (a) are called hard acids and ligands of class (a) are called hard bases. On the other hand, metal ions of class (b) are called soft acids and ligands of class (b) are called soft bases.

R.G. Pearson in 1963, classified the Lewis acids and Lewis bases as hard and soft acids and bases. A third category whose characteristics are intermediate between hard and soft acids/bases are called border line acids and border line bases.

HSAB principle states that a hard Lewis acid prefers to combine with an hard Lewis base and similarly as soft Lewis acid prefers to combine with a soft Lewis base, since this type of combination gives a more stable product. Thus we can say that [hard acid + hard base] and [soft acid + soft base] combination gives more stable products than the [hard acid + soft base] or [soft acid + hard base] combinations. The main characteristics of hard and soft acids and bases along with their example are given in Table 8.1.

Table 8.1 Classification of Lewis Acids and Lewis Base into Hard, Soft and Borderline Acids and Bases

<table>
<thead>
<tr>
<th>Lewis Acids (acceptors)</th>
<th>Soft Acids</th>
<th>Borderline (Intermediate) Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard Acids: [Ahlfeld and Chatt (1958) have arbitrarily called hard acids as class (a) metal ions or metal acceptors]</td>
<td>[Those have been called class (b) metal ions or metal acceptors]</td>
<td>The characteristics of borderline acids are intermediate between those of hard acids and soft acids.</td>
</tr>
<tr>
<td>(i) They have acceptor metal atom of small size.</td>
<td>(i) They have acceptor metal atom of large size.</td>
<td>Example: Fe³⁺, Cr⁶⁺, Cd²⁺, Sn⁴⁺, Zn²⁺, Pb²⁺, Sn⁺, Pb⁺, Bi⁺, As⁺, Se⁺, Cl⁻, Br⁻, I⁻, SCN⁻, CH₃⁺, CH₃⁻, NC⁻, NH₂⁻, CH₃CH₂⁻, F⁻, Cl⁻, Br⁻, I⁻, R⁻, R₂⁻, CH₃⁺, CH₃⁻, NC⁻, NH₂⁻, O⁻, OH⁻, CO₂⁻</td>
</tr>
<tr>
<td>(ii) They have acceptor with high positive charge (oxidation state).</td>
<td>(ii) They have acceptor with low or zero positive charge.</td>
<td>Example: Ca²⁺, Ag⁺, Au⁺, Th⁴⁺, Hg⁴⁺, Cu²⁺, Cd²⁺, Pb²⁺, Ga⁺, Ge⁺, Sn⁺, Sb⁺, Fe⁺, Fe⁡⁺, Au⁺, As⁺, Se⁺, Cl⁻, Br⁻, I⁻, SCN⁻, CH₃⁺, CH₃⁻, NC⁻, NH₂⁻, CH₃CH₂⁻, F⁻, Cl⁻, Br⁻, I⁻, R⁻, R₂⁻, CH₃⁺, CH₃⁻, NC⁻, NH₂⁻, O⁻, OH⁻, CO₂⁻</td>
</tr>
<tr>
<td>(iii) The valence-electrons of the acceptor atom of these acids cannot be polarized (or distorted or removed) easily (i.e., they have low polarizability), since they are held strongly and it is for the reason that these Lewis acids have been called hard acids (or hard metal ions) by Pearson (1963).</td>
<td>(iii) The valence-electrons of the acceptor atom of these acids can be polarized easily (i.e., they have high polarizability), since they are held weakly and for this reason these Lewis acids have been called soft acids (or soft metal ions) by Pearson.</td>
<td></td>
</tr>
</tbody>
</table>
8.2.1 Applications of HSAB Principle

The principle of soft and hard acid-base finds application in various domains of chemical reaction common example are discussed below:

**Stability of Complex Compounds having same Ligands**: This can be understood by considering following examples:

- AgF₂ is stable while AgF₃ does not exist. We know that Ag⁺ is a soft acid, F⁻ ion is a hard base and F⁻ ions is a soft base. Thus, since AgF₂ is obtained by the combination of a soft acid (Ag⁺) and soft base (F⁻), AgF₂ results by the interaction of a soft acid (Ag⁺) and a hard base (F⁻), AgF₂⁻, ion is stable but AgF₃ does not exist.

- CoF₆⁻ (hard acid + hard base) is more stable than CoF₅⁻ (hard acid + soft base).

**Stability of Complexes having Different Ligands**: It in a complex compound having different ligands, if all the ligands are of the same nature, i.e., if all the ligands are soft ligands or hard ligands, the complex compound will be stable. On the other hand, if the ligands are of different nature, the complex compound would be unstable. This point may be illustrated by the following examples:

- Since in [Co(NH₃)₂F⁺]⁻ (I) both the ligands viz, NH₃ molecule and F⁻ ion are hard ligands and in [Co(NH₃)₂Cl⁺]⁻ (II) NH₃ is a hard ligand and Cl⁻ ion is an oit ligand, (I) is a stable complex ion while (II) is unstable.

- [Co(CN)₅Cl⁺]⁻ (I) is more stable than [Co(CN)₅F⁺]⁻ (II) because in (I) both the ligands are soft ligands while in (II) CN⁻ ions are soft ligands and F⁻ ion is a hard ligands.

**Symbiosis**: Soft ligands prefer to get attached with a centre which is already linked with soft ligands. Similarly hard ligands prefer to get attached with a centre which is already linked with hard ligands. This tendency of ligands is called symbiosis and can be explained by considering the formation of (F, B ← NH₃) adduct and BH₃⁻ ion. Hard ligand like NH₃ coordinates with B-atom of BF₃.
molecule to form \((F,B \rightarrow NH_3)\) adduct, since \(F^-\) ions which are already attached with B-atom in BF, molecule are also hard ligands. Thus similarly the formation of \(BH^-_4\) ion by the combination of \(BH_4\) (in which H atoms are soft ligands) and \(H^-\) ions (soft ligands) can also be explained (Refer Figure 8.1).

Similarly the formation of \(BH^-_4\) ion by the combination \(BH_4\) (in which H atoms are soft ligands) \(H^-\) ions (soft ligands) can also be explained.

**Fig. 8.1 Symbiosis**

**Stability of Compounds:** Consider the relative stability of HgS and Hg(OH)\(_2\) in acidic aqueous solution. HgS (soft acid + soft base) is more stable than Hg(OH)\(_2\) (soft acid + hard base). More stability of HgS than that of Hg(OH)\(_2\) explains why Hg(OH)\(_2\), readily displace in acidic aqueous solution but HgS does not.

The principle of (hard acid + hard base) and (soft acid + soft base) combination be used in prediction of course of many reactions. For example,

- \(\text{LiI} + \text{CsF} \rightarrow \text{LiF} + \text{CsI}\)
  - (hard acid + soft base) \quad \text{(soft acid + hard base)}
  - (hard acid + hard base) \quad \text{(soft acid + soft base)}

- \(\text{HgF}_2 + \text{BeJ}_2 \rightarrow \text{BeF}_2 + \text{HgJ}_2\)
  - (soft acid + hard base) \quad \text{(hard acid + soft base)}
  - (hard acid + hard base) \quad \text{(soft acid + soft base)}

**8.2.2 Limitations of HSAB Principle**

Although (hard + hard) and (soft + soft) combination is a useful principle, yet many reactions cannot be explained with the help of this principle. For example in the reaction:

\[
\begin{align*}
\text{SO}_3^{2-} + \text{HF} & \rightarrow \text{HSO}_3^- + \text{F}^- \\
\text{or} \quad \text{SO}_3^{2-} + \text{H}^+ + \text{F}^- & \rightarrow [\text{H}]^+ \text{[SO}_3]^2^- + \text{F}^- \\
\text{soft base} & \quad \text{(hard acid + hard base)} \quad \text{(hard acid + soft base)}
\end{align*}
\]
which proceeds towards right, hard acid (H) combines with soft or borderline base \( \text{SO}_4^{2-} \) to form \( [\text{H}^+]\text{SO}_4^{2-} \) or \( \text{HSO}_4^- \) ion which is a stable ion. (Hard acid + soft base) combination is against the HSAB principle.

**Check Your Progress**

1. What does HSAB principle state?
2. What is meant by the symbiosis of ligands?

### 8.3 pH

The acidic or basic character of an aqueous solution can be expressed quantitatively by specifying the [\( \text{H}_2\text{O}^+ \)] concentration. **Sorensen** in 1909 introduced a scale to correlate [\( \text{H}_2\text{O}^+ \)] ion concentration in aqueous solutions of acids and bases and named it as pH scale.

\[ \text{pH} = \log_{10} [\text{H}_2\text{O}^+] \quad \text{or} \quad \text{pH} = -\log \left( \frac{1}{[\text{H}_2\text{O}^+]} \right) \]

It is very easy to convert \( [\text{H}_2\text{O}^+] \) to pH and vice versa. For example, when \( [\text{H}_2\text{O}^+] = 10^{-7} \) in a natural solution at 298 K.

\[ \text{pH} = -\log[\text{H}_2\text{O}^+] = -\log10^{-7} = 7 \]

Like pH, pOH may be expressed as

\[ \text{pOH} = -\log[\text{OH}^-] \]

Substituting different value of \( [\text{H}_2\text{O}^+] \) in pH formula, it is found that

- pH < 7 for acidic solution
- pH > 7 for basic solution
- pH = 7 for natural solution

The pH range which lies between 0 and 14 may be represented on the pH scale as shown below in Figure 8.2

![Fig. 8.2 pH Range Between 0-14 as on pH Scale](image)

**NOTES**

HSAB: Hard and Soft Acids and Bases
Following inference may be drawn from pH scale:

- pH = 0 means $[H_3O^+]$ is 1M.
- If pH lies between 0 and 2, the solution is strongly acidic whereas pH between 2 and 4 is moderately acidic.
- If pH lies in between 4 to 7, it is weakly acidic.
- pH between 7 and 10, 10 and 12 and 12 and 14 represent weakly basic, moderately basic and strongly basic respectively.

### 8.3.1 Acid-Base Indicators

Phenolphthalein is colourless in acidic medium and pink in basic medium. Thus, when phenolphthalein is added to acid solution it shows no colour but during the titration of acid against base, even slight excess of base at the end point turns it to pink. Similarly, methyl arrange indicates the end point from colourless (in base) to red (in acid). The pH range of various common indicators is given in Table 8.2

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Colour change</th>
<th>pH range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>Red – Orange</td>
<td>3.1 – 4.4</td>
</tr>
<tr>
<td>Methyl red</td>
<td>Red – Yellow</td>
<td>4.4 – 6.0</td>
</tr>
<tr>
<td>Lintus</td>
<td>Red – Blue</td>
<td>5.0 – 8.0</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>Yellow – Blue</td>
<td>6.0 – 7.6</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>Colourless – Pink</td>
<td>8.3 – 10.0</td>
</tr>
</tbody>
</table>

1. Calculate the pH value of (i) $\frac{N}{100} \text{H}_2\text{SO}_4$ and (ii) $\frac{n}{10} \text{NaOH}$ assuming complete ionization.

**Solution:** $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O}^+ + \text{SO}_4^{2-}$

- $[H^+]$ for $\text{H}_2\text{SO}_4 = 2\text{H}_2\text{O} = 1 \times 10^{-2}$ mole/lit.
  
  - (i) $[H^+] = 1 \times 10^{-2}$ mole/lit.
  - pH = $-\log[10^{-2}] = 2$

  - (ii) $[OH^-] = 10^2$ mole/lit.

- $\left[\frac{[H^+]}{10^{-14}}\right] = 10^{13}$

  - pH = $-\log[10^{-13}] = 13$

2. Calculate the pH of a solution obtained by mixing 50 ml of 0.01 m $\text{Ba(OH)}_2$ with 50 ml $\text{H}_2\text{O}$. 

---

**NOTES**

**HSAB: Hard and Soft Acids and Bases**

---

**Self-Instructional Material**
Solution: Total volume of solution = 100 ml
Molarity of final solution
\[ M_{V_1} = M_{V_2} \]
\[ 0.01 \text{ M} \times 50 = M_2 \times 100 \]
\[ M_2 = \frac{0.01 \text{ M} \times 50}{100} = 0.005 \text{ M} \]
\[ [\text{OH}^-] = 2 \times [\text{Ba(OH)}_2] = 2 \times 0.005 \text{ M} = 0.01 \text{ M} \]
\[ [\text{H}^+] = \frac{K_{10}}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-7}} = 10^{-7} \]
Hence, pH = -log 10^{-7} = 7

3. At what molar concentration the pH of nitrous acid would be 2.0? [K_1 of nitrous acid = 4.5 \times 10^{-4}].
Solution: pH = -log [H^+] = 2
• [H^+] = 10^{-2}

We know, [H^+] = \sqrt{K_1 \times c}
\[ 10^{-2} = \sqrt{4.5 \times 10^{-4} \times c} \]
squaring on both sides,
\[ 10^{-4} = 4.5 \times 10^{-4} \times c \]
\[ c = \frac{1}{4.5} = 0.222 \text{ mole/lit} \]

4. Find the pH of the following solutions.
(i) 3.2 g of HCl dissolved in 1 - 0 L of water.
(ii) 0.28 g of KOH dissolved in 1.0 L of water.
Solution: [H^+] = \frac{3.2}{36.5} = 0.0877 mile/lit  \quad [? \text{ Mol. wt. of HCl = 36.5}]
\[ \text{pH} = \text{-log}[0.0877] = 1.06 \]
(ii) [OH^-] = \frac{0.28}{56} = 0.005 \text{ mil/lit.}  \quad [? \text{ Mol. wt. of KOH = 56}]
\[ \text{pOH} = \text{-log}[0.005] = 2.3 \]
\[ \text{pH} = 14 - \text{pOH} = 14 - 2.3 = 11.7 \]

5. A sample of H$_2$SO$_4$ was prepared by dissolving 0.0049 g H$_2$SO$_4$ per 100 ml solution. Calculate the pH of the solution.
Solution: Concentration of \( \text{H}_2\text{SO}_4 \) = 0.0049 g per 100 ml = \( \frac{0.0049 \times 1000}{100} \) = 0.049 g/litre

\[ [\text{H}^+] = \frac{0.049}{49} = 10^{-2} \text{ g equivalent/litre.} \]

\[ \text{pH} = -\log[10^{-2}] = 3 \]

[\text{Mol. wt. of H}_2\text{SO}_4 = \frac{98}{2} = 49 ]

6. How many moles of calcium hydroxide must be dissolved to produce 250 ml of an aqueous solution of pH 10.65?

Solution: pH + pOH = 14

\[ \text{pOH} = 14 - 10.65 = 3.35 \]

\[ \log [\text{OH}^-] = 03.35 = 4.47 \times 10^{-4} \text{ mole/litre} \]

Number of [OH\(^-\)] in 250 ml = \( \frac{4.47 \times 10^{-4} \times 250}{1000} \) = 1.12 \times 10^{-4}

Since 1 molecule of Ca(OH)_2 has 2OH\(^-\) ions

Therefore, number of moles of Ca(OH)_2 in 250 ml solution = \( \frac{1.12 \times 10^{-4}}{2} \) = 0.56 \times 10^{-4}

7. The pH of 0.05 M solution of diethyl amine is 12. Calculate its \( K_c \).

\( \text{(C}_2\text{H}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons \text{(C}_2\text{H}_3)_2\text{NH}^+ + \text{OH}^- \)

Solution: pH = 12

\[ [\text{H}^+] = 10^{-12} \]

[OH\(^-\)] = 10^{-2} \text{ mole/litre} \]

We know, [OH\(^-\)] = \( \sqrt{K_c} \times c \]

\[ 10^{-2} = \sqrt{K_c} \times 0.05 \]

Squaring on both sides

\[ 10^{-4} = K_c \times 0.05 \]

\[ K_c = \frac{10^{-4}}{0.05} = 2.0 \times 10^{-3} \]

8. What is the pH of a 1.0 M solution of acetic acid? \( K_c \) of CH\(_3\)COOH is 1.8 \times 10^{-5}.
Solution: 

\[
[H^+] = \sqrt{K_a \times c}
\]

\[
= \sqrt{1.8 \times 10^{-5} \times 1} = 4.24 \times 10^{-3}
\]

\[
pH = -\log[H^+] = -\log[4.24 \times 10^{-3}]
\]

\[
= 3 - \log 4.24 = 3 - 0.628 = 2.372
\]

9. Calculate the pH of a solution made by diluting 10 ml of \( \frac{N}{100} \) to one litre.

Solution: 

\[N_1 V_1 = N_2 V_2\]

\[N_1 \times 1000 = \frac{N}{100} \times 10\]

\[N_1 = \frac{N}{100} \times 1000 = 10^4\]

\[\text{[H}^+] = 10^{-4}\]

\[pH = -\log[\text{[H}^+]] = -\log[10^{-4}] = 4\]

8.3.2 Solubility Product

There are many compounds which appear to be practically insoluble in water. In fact, such compounds are very slightly soluble in water. These are known as sparingly soluble salts. For example, \( \text{BaSO}_4 \), \( \text{AgCl} \), \( \text{PbCl}_2 \), \( \text{ZnS} \), etc. When these sparingly soluble salts are dissolved in water, at a particular temperature, an equilibrium is established between the ions and the solid salt. Such solution is known as saturated solution of the salt. For example, a saturated solution of \( \text{AgCl} \) has the following equilibrium between the solid \( \text{AgCl} \) and the ions of \( \text{AgCl} \) in solution.

\[
\begin{align*}
\text{AgCl(s)} & \rightleftharpoons \text{Ag}^+ \text{(aq)} + \text{Cl}^- \text{(aq)} \\
\text{Undissolved salt} & \text{Ions in solution}
\end{align*}
\]

Applying the concept of equilibrium

\[
K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]} \quad \text{at constant temperature.}
\]

Since the concentration of solid \( \text{AgCl} \) is fixed, irrespective of the amount of solid in contact with the solution, we can write

\[
K \times \text{AgCl(s)} = [\text{Ag}^+][\text{Cl}^-]
\]

\[
K \times \text{AgCl(s)} \text{ is replaced by another constant known as solubility product (} K_{sp} \text{)}
\]

\[
K_{sp} = [\text{Ag}^+][\text{Cl}^-]
\]

For a sparingly soluble salt with the general formula

\[
A_{x}B_{y} \text{(s)} \rightleftharpoons xA^+ + yB^-
\]
the solubility product expression is

\[ K_p = [A^+][B^{3-}] \]

Example of some sparingly soluble salts with their \( K_p \) expressions are given below:

- \( \text{BaSO}_4 \Rightarrow \text{Ba}^{2+} + \text{SO}_4^{2-} \) \( K_p = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \)
- \( \text{Ag}_2\text{CrO}_4 \Rightarrow 2\text{Ag}^+ + \text{CrO}_4^{2-} \) \( K_p = [\text{Ag}^+][\text{CrO}_4^{2-}] \)
- \( \text{Al(OH)}_3 \Rightarrow \text{Al}^{3+} + 3\text{OH}^- \) \( K_p = [\text{Al}^{3+}][\text{OH}^-]^3 \)
- \( \text{Mg}_3(\text{PO}_4)_2 \Rightarrow 3\text{Mg}^{2+} + 2\text{PO}_4^{3-} \) \( K_p = [\text{Mg}^{2+}]^3[\text{PO}_4^{3-}]^2 \)

Thus the solubility product of a salt at a specific temperature may be defined as the product of molar concentration of its ions in solution each raised to the power equal to their coefficients in balanced chemical equation.

Following are some inferences derived from the expression of solubility product:

- When ionic product is equal to solubility product, it is called saturated solution.
- When ionic product is less than solubility product, the solution is unsaturated i.e., more salt can be dissolved in it.
- When ionic product is greater than solubility product the solution is termed supersaturated. In such solutions, the ions will recombine to form solid so that ionic product becomes equal to that of solubility product and thus precipitation takes place, thus the \( K_p \) value represents the upper limit of ionic product in any saturated solution. This property is applied to precipitate the weak electrolyte from its solution by addition a common ion, this is known as common ion effect.

8.3.3 Common Ion Effect

It states that a solution of strong electrolyte capable of furnishing an ion common to that furnished by weak electrolyte when added to a solution of that weak electrolyte, the ionization of weak electrolyte is further suppressed. For example, \( \text{NH}_4\text{OH} \) is a weak electrolyte and ionizes to a small extent as,

\[ \text{NH}_4\text{OH} \Rightarrow \text{NH}_4^+ + \text{OH}^- \]

\[ K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \]

When a strong electrolyte like \( \text{NH}_4\text{Cl} \) or \( \text{NaOH} \) is added to \( \text{NH}_4\text{OH} \) solution then the equilibrium will shift to the left because of the high concentration of either...
NH₄⁺ ions or of OH⁻ ions. In order to maintain the value of K, the ionization of 
NH₄OH will be suppressed.

Similarly, the ionization of CH₃COOH is suppressed by the addition of 
CH₃COONa⁺ or HCl. Thus in short, the ionization of a weak acid or weak base 
is suppressed by the addition of one of its own ion; this is known as common ion 
effect.

Solutions of weak electrolytes are said to be isohydric solutions, if the 
concentration of the common ion present in them is same and on mixing such 
solutions there occurs no change in the degree of dissociation of either of the 
electrolyte.

8.3.4 Applications of Solubility Product and Common Ion Effect

Some of the applications of solubility product and common ion effect in industries 
are discussed below.

**Purification of Sodium Chloride:** To a saturated solution of sodium chloride 
dissolved in minimum quantity of water, when HCl gas is bubbled, then due to 
common ion (Cl⁻), the solubility of NaCl decreases and NaCl is precipitated out 
leaving other impurities in solution.

\[
\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-
\]

\[
\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-
\]

Due to common ion (Cl⁻), concentration of Cl⁻ is increased resulting in the 
precipitation of NaCl.

**Salting Out of Soap:** Soap is sodium slat of higher fatty acids (CₙH₂₃COO⁻ 
Na⁺) obtained in the form of paste as a result of saponification of oil or fat. Addition 
of a saturated common salt solution to it increases the Na⁺ ion concentration and 
herefore the ionic product exceeds the solubility product. Thus, soap is precipitated 
out.

**Solvay’s Ammonia Soda Process:** When saturated NaCl solution is added to 
NH₄HCO₃ solution, four ions Na⁺, Cl⁻, NH₄⁺ and HCO₃⁻ are present in solution.

Due to lower Kₛₚ value of NaCHO₂, it separates out from solution in the form of 
precipitate.

**In qualitative inorganic analysis:** The separation of basic radicals (cations) 
into different groups of qualitative analysis is based on the theory of solubility 
product and common ion effect. For example.

- **Precipitation of group first radicals (Pb⁺, Ag⁺, Hg⁺):** The group reagent 
is dilute HCl. When excess dilute HCl is added to a solution containing a 
mixture of these cations, these radicals are precipitated out because the 
ionic product of the chlorides of these radicals exceeds their corresponding 
solubility product i.e.,
[Ag⁺][Cl⁻] > K_p for AgCl
However, the K_p value of other chlorides is high; and therefore, these are not precipitated.

- **Use of HCl for group second sulphides**: H₂S is a weak electrolyte and is used for the precipitation of sulphides of group II radicals (i.e. Hg²⁺, Cd²⁺, Bi³⁺, Cu²⁺, Sn⁴⁺, Pb⁴⁺, Sb⁴⁺, As³⁺)

\[ H_2S \rightarrow 2H^+ + S^{2-} \]

Applying law of mass action, \[ K = \frac{[H^+]^2 + [S^{2-}]}{[H_2S]} \]

In presence of H⁺ ions, the ionization of H₂S is further suppressed (due to common ion effect) with the result that only those radicals whose ionic product exceeds their solubility product are precipitated.

Metal sulphides | HgS | CdS | Bi₂S₃ | CuS | PbS | Sb₂S₃ |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility product</td>
<td>$4 \times 10^{-48}$</td>
<td>$1.4 \times 10^{-39}$</td>
<td>$1.6 \times 10^{-32}$</td>
<td>$8.5 \times 10^{-46}$</td>
<td>$5 \times 10^{-39}$</td>
<td>$1.6 \times 10^{-39}$</td>
</tr>
</tbody>
</table>

- **Use of NH₄Cl in analysis of third group radicals (Al³⁺, Cr⁶⁺, Fe⁸⁺)**: Ammonium hydroxide is a precipitating reagent for the third group radicals. It is a weak electrolyte and ionizes in water as follows.

\[ NH_4OH = NH_4^+ + OH^- \]

Addition of NH₄Cl in group III further suppresses the ionization of NH₄OH so that the ionic products of only III group radicals exceeds their solubility products. Hence the III group radicals are precipitated out as their hydroxides while radicals of group IV, V and Mg²⁺ remain in solution.

Metal hydroxides | Fe(OH)₃ | Al(OH)₃ | Cr(OH)₃ |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility products</td>
<td>$11 \times 10^{-36}$</td>
<td>$8.5 \times 10^{-33}$</td>
</tr>
</tbody>
</table>

- **Precipitation of fourth group radical as sulphides (Co³⁺, Ni²⁺, Zn²⁺, Mn⁵⁺)**: The group reagent is H₂S in presence of NH₄OH.

\[ H_2S \rightarrow 2H^+ + S^{2-} \]

\[ NH_4OH = NH_4^+ + OH^- \]

H⁺OH⁻ → H₂O (non-ionised)

The OH⁻ ions from NH₄OH combines with H⁺ ions from H₂S to form un-ionisable H₂O with the result that more H₂S is ionized to give greater concentration of S²⁻ ions. This increases the ionic product of group IV radicals and S²⁻ ions which becomes greater than the K_p value for the sulphide of Mn²⁺, Zn²⁺, Ni²⁺, Co²⁺ cations.
Metal sulphides  CoS  ZnS  NiS  MnS
Solubility product  $5 \times 10^{-22}$  $2.5 \times 10^{-22}$  $3 \times 10^{-21}$  $2.3 \times 10^{-19}$
Thus ZnS, CoS, NiS and MnS are precipitated out.

### 8.4 BUFFER SOLUTIONS

Generally, pH of an aqueous solution decreases an addition of small amount of HCl due increases in concentration of H$^+$ ions. On the other hand, if a small amount of NaOH is added, the pH of the solution increases. However, there are some solutions which resist the change in pH on addition of small amount of strong acid or alkali. Such solutions are called buffer solutions. Thus, buffer solution is defined as that solution which resists the change in hydrogen ion concentration on addition of small amount of acid or base.

Buffer solutions are of two types:

**Acidic Buffer:** It is obtained by mixing equimolar quantities of a weak acid and its salt with strong base, for example,
- CH$_3$COOH + CH$_3$COONa
- HCOOH + HCOOK

The pH value of acidic buffers is usually less than 7.

**Basic Buffer:** it contains equimolar quantities of weak base and its salt with strong acid. For example
- NH$_3$OH + NH$_4$Cl
- C$_2$H$_5$NH$_2$ + C$_2$H$_5$N$^+$HCl

The pH value of basic buffers is usually more than 7.

Some example of the common buffer solution with their pH values are listed below.

<table>
<thead>
<tr>
<th>Buffer solution Range of pH value</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$COOH + CH$_3$COONa</td>
<td>4.74</td>
</tr>
<tr>
<td>HCOOH + HCOOK</td>
<td>3.70 + 5.6</td>
</tr>
<tr>
<td>Citric acid + Sod. Citrate</td>
<td>1.0 – 5.0</td>
</tr>
<tr>
<td>Phthalic acid + Pot. hydrogen phthalate</td>
<td>2.2 – 3.8</td>
</tr>
<tr>
<td>KH$_2$PO$_4$ + K$_2$HPO$_4$</td>
<td>5.8 + 8.0</td>
</tr>
<tr>
<td>NH$_3$OH + NH$_4$Cl</td>
<td>9.25</td>
</tr>
</tbody>
</table>
Buffer Action: The ability of buffer solution to resist the change in its pH value on addition of small amount of strong acid or strong base is called buffer action.

Let us consider an acidic buffer containing equimolar amount of CH₃COOH and CH₃COONa to understand the buffer action. Buffer solution has large concentration of species namely CH₃COO⁻, Na⁺ and unionized CH₃COOH.

\[ \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+ \]

\[ \text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+ \]

When few drops of HCl are added to this buffer solution, the H⁺ ions of HCl immediately combine with CH₃COO⁻ ions to form undissociated acetic acid molecules.

\[ \text{CH}_3\text{COO}^- + \text{H}^+ (\text{aq}) \rightarrow \text{CH}_3\text{COOH} \]

Thus, there will be no appreciable change in its pH value.

Likewise, if few drops of NaOH are added to buffer solution, the OH⁻ ions (provided by NaOH) will combine with H⁺ ions present in buffer solution to form unionized water molecules. Thus, additional OH⁻ ions are neutralized by acetic acid and the pH of the solution remains almost constant.

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \]

Similarly, a basic buffer solution consisting of equimolar amounts of NH₃ OH and NH Cl has large concentration of NH₄⁺ ions, Cl⁻ ions and unionized NH₃ OH.

\[ \text{NH}_\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^- \]

\[ \text{NH}_\text{OH} \rightarrow \text{NH}_4^+ + \text{OH}^- \]

When few drops of HCl are added to it, the H⁺ ions of HCl are neutralized by OH⁻ ions of weakly ionized NH₃ OH, i.e., the pH of the solution is almost restored.

\[ \text{NH}_\text{OH}(\text{aq}) \rightarrow \text{NH}_4^+ (\text{aq}) + \text{OH}^- (\text{aq}) \]

\[ \text{OH}^- (\text{aq}) + \text{H}^+ (\text{aq}) \rightarrow \text{H}_2\text{O} \]

On the other hand, if few drops of NaOH are added to the buffer solution, the OH⁻ ions provided by NaOH combine with NH₄⁺ to form weakly ionized NH₃ OH, thus the pH of the cation is almost constant.

Buffer Capacity: It is defined as the number of moles of acid (or base) required by one litre of buffer solution for changing its pH by 1 unit.
Buffer capacity = \frac{\text{Number of Moles of acid or base added per litre}}{\text{Change in pH}}

Thus higher the amount of acid or base used to produce a definite change of pH in a buffer solution, higher will be its buffer capacity. In general, the buffer capacity of a solution is maximum when both the components of buffer solution are present in equivalent amounts (i.e., when the molar ratio of salt to acid is 1).

**Calculation of pH of buffer solutions**

The pH of buffer solutions can be calculated applying Henderson’s equation:

For pH of an acidic buffer solution

\[
pH = pK_a + \log\left(\frac{\text{Salt}}{\text{Acid}}\right)
\]

where \( pK_a = -\log K_a \)

For pH of a basic buffer solution

\[
pOH = pK_b + \log\left(\frac{\text{Salt}}{\text{Acid}}\right)
\]

where \( pK_b = -\log K_b \)

\[
pH = 14 - pK_b - \log\left(\frac{\text{Salt}}{\text{Acid}}\right)
\]

\( ? \) pH + pOH = 14

10. Calculate the pH of a buffer solution containing 0.3 mole/litre CH₃COONa and 0.15 mole/litre CH₃COOH. \( K_a \) for acetic acid is \( 1.8 \times 10^{-5} \) [log 1.8 = 0.2552]

**Solution:**

\[
pK_a = -\log K_a = -\log 1.8 \times 10^{-5}
= 5 - \log 1.8 = 5 - 0.2552 = 4.7448
\]

\[
pH = pK_a + \log\left(\frac{\text{Salt}}{\text{Acid}}\right) = 4.7448 + \log\left(\frac{0.3}{0.15}\right)
= 4.7448 + 0.3010 = 5.0458
\]

11. A buffer solution contains 0.75 M NH₃ and 0.25 M NH₄Cl. Calculate the pH of solution, \( pK_b \) for ammonia = 4.7448.

**Solution:**

\[
pOH = pK_b + \log\left(\frac{\text{Salt}}{\text{Acid}}\right) = 4.7448 + \log\left(\frac{0.25}{0.75}\right)
= 4.7448 - \log 3 = 4.7448 - 0.4771 = 4.2677
\]

12. How much CH₃COOH should be added to 1 litre of 0.01 M CH₃COONa to make buffer solution of pH = 5? \( K_a \) = \( 1.8 \times 10^{-5} \)

**Solution:**

\[
pK_a = -\log 1.8 \times 10^{-5} = 4.7448
\]
\[ 5 = 4.7448 + \log \left( \frac{10^{-2}}{[\text{Acid}]} \right) \]

\[ \log \left( \frac{10^{-2}}{[\text{Acid}]} \right) = 5.0 - 47448 = 0.2552 \]

\[ \log 10^2 - \log [\text{Acid}] = 0.2552 \]
\[ -2 - \log [\text{Acid}] = 0.2552 \]
\[ \log [\text{Acid}] = -2.0 - 0.2552 = -2.2552 \]
\[ [\text{Acid}] = \text{Antilog} (-2.2552) = \text{Antilog} 3.7448 \]
\[ = 5.56 \times 10^{-3} \text{ mole/lit.} \]

13. 630.50 ml of 0.2 M CH₃COOH are mixed with 150 ml of 0.4 M CH₃COONa solution. Calculate the pH of the mixture, pKₐ CH₃COOH = 4.73

**Solution:** Total volume of the mixture = 50 + 150 = 200 ml

Let molarity of acid in mixture is M₁, then

\[ 50 \times 0.2 = 200 \times M₁ \]
\[ M₁ = 0.05 \text{ M} \]

Similarly molarity, M₂, of CH₃COONa = 0.3 M

Applying Henderson equation

\[ \text{pH} = \text{pK}_a + \frac{[\text{Salt}]}{[\text{Acid}]} \log \left( \frac{0.3}{0.05} \right) \]
\[ = 4.73 + 0.778 = 5.508 \]

**Important Applications of Buffer Solution**

Many important industrial processes as well as biological processes make use of buffer solution, for example,

- Electroplating
- Dyeing, manufacturing of leather and photographic materials.
- Calibration of pH meter
- Analytical chemistry
- Bacteriological culture medium
- pH of human blood is 7.4 which is not altered inspite of various acid and base producing reactions going on in our body due to consumption of different variety of foods and species.
Check Your Progress

5. What is a buffer solution?
6. How is acidic buffer obtained?
7. What does basic buffer contain?

8.5 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. HSAB principle states that a hard Lewis acid prefers to combine with a hard Lewis base and similarly as soft Lewis acid prefers to combine with a soft Lewis base, since this type of combination gives a more stable product.

2. Soft ligands prefer to get attached with a centre which is already linked with soft ligands. Similarly hard ligands prefer to get attached with a centre which is already linked with hard ligands. This tendency of ligands is called symbiosis.

3. pH is defined as the negative logarithm of \([H_3O^+]\) ion concentration in moles per litre. Mathematically, it is expressed as:

   \[\text{pH} = \log_{10}[H_3O^+]\text{ or } \text{pH} = \log\frac{1}{[H_3O^+]}\]

4. Phenolphthalein is colourless in acidic medium and pink in basic medium. Thus, when phenolphthalein is added to acid solution it shows no colour but during the titration of acid against base, even slight excess of base at the end point turns it to pink.

5. Buffer solution is defined as that solution which resists the change in hydrogen ion concentration on addition of small amount of acid or base.

6. Acidic Buffer is obtained by mixing equimolar quantities of a weak acid and its salt with strong base, for example,
   - \(\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}\)
   - \(\text{HCOOH} + \text{HCOOK}\)

7. Basic buffer contains equimolar quantities of weak base and its salt with strong acid. For example
   - \(\text{NH}_3\text{OH} + \text{NH}_4\text{Cl}\)
   - \(\text{C}_2\text{H}_5\text{NH}_2 + \text{C}_2\text{H}_5\text{N}^+\text{H}_3\text{Cl}^-\)
8.6 SUMMARY

- HSAB principle states that a hard Lewis acid prefers to combine with a hard Lewis base and similarly as soft Lewis acid prefers to combine with a soft Lewis base, since this type of combination gives a more stable product.

- Person in 1963 suggested that the term hard and soft can be used for class (a) and class (b) respectively. Thus in his classification, metal ions of class (a) are called hard acids and ligands of class (a) are called hard bases. On the other hand, metal ions of class (b) are called soft acids and ligands of class (b) are called soft bases.

- R.G. Pearson in 1963, classified the Lewis acids and Lewis bases as hard and soft acids and bases. A third category whose characteristics are intermediate between hard and soft acids/bases are called borderline acids and borderline bases.

- Consider the relative stability of HgS and Hg(OH)₂ in acidic aqueous solution. HgS (soft acid + soft base) is more stable than Hg(OH)₂ (soft acid + hard base). More stability of HgS than that of Hg(OH)₂ explains why Hg(OH)₂ readily dissolves in acidic aqueous solution but HgS does not.

- The acidic or basic character of an aqueous solution can be expressed quantitatively by specifying the [H₂O⁻] concentration. Sorensen in 1909 introduced a scale to correlate [H₂O⁻] ion concentration in aqueous solutions of acids and bases and named it as pH scale.

- pH is defined as the negative logarithm of [H₂O⁻] ion concentration in moles per litre. Mathematically, it is expressed as:

$$\text{pH} = \log_{10}\left(\frac{1}{[\text{H}_2\text{O}^-]}\right)$$

- There are many compounds which appear to be practically insoluble in water. In fact, such compounds are very slightly soluble in water. These are known as sparingly soluble salts.

- A solution of strong electrolyte capable of furnishing an ion common to that furnished by weak electrolyte when added to a solution of that weak electrolyte, the ionization of weak electrolyte is further suppressed.

- Buffer solution is defined as that solution which resists the change in hydrogen ion concentration on addition of small amount of acid or base.

8.7 KEY WORDS

- **Sparingly soluble salts**: There are many compounds which appear to be practically insoluble in water. In fact, such compounds are very slightly soluble in water. These are known as sparingly soluble salts.
• **Buffer solution:** It is defined as that solution which resists the change in hydrogen ion concentration on addition of small amount of acid or base.

• **Buffer action:** the ability of buffer solution to resist the change in its pH value on addition of small amount of strong acid or strong base is called buffer action.

• **Buffer capacity:** It is defined as the number of moles of acid (or base) required by one litre of buffer solution for changing its pH by 1 unit.

### 8.8 SELF ASSESSMENT QUESTIONS AND EXERCISES

#### Short Answer Questions

1. Write a short note on HSAB.
2. What is stability of complex compounds that have same ligands?
3. Brief a note on stability of compounds.
4. What are the limitations of HSAB?
5. What is acid base indicator?

#### Long Answer Questions

1. Write a detailed note on HSAB, also mention its classification.
2. What are the applications and limitations of HSAB?
3. Elaborate a note on solubility product and its applications and common ion effects.
4. Write a detailed note on buffer solutions.

### 8.9 FURTHER READINGS


9.0 INTRODUCTION

The polymerization of simple monomeric oxide anions of Cr, Mo, W, V, Nb and Ta occurs when their alkaline solutions are gradually acidified. If from any oxyacid, the O atoms are replaced by radicals of the same acid (for example, introduction of one or more CrO₆ radicals in H₂CrO₇) the resulting compounds are termed as poly acids. They can also be defined as compounds derived from a simple acid by the elimination of water between two or more molecules of the acid.

The acids which are obtained as a result of the apparent condensation of number of simple O containing acid molecules to give compounds containing more than a single molecule of acid anhydride is called polyacid. The ions of the polyacids are similarly derived from those of the simple acids by the elimination of O₂⁻ ions are known as poly anions. A familiar example is, the reaction of chromate solution (CrO₄²⁻) which is yellow, with excess acid to form dichromate (Cr₂O₇²⁻) which is orange in colour.

The polyacids can be divided into two groups – Isopolyacids (where the acids/ anions which condense together are all of the same type, i.e., all Mo O₆ groups or all WO₆ groups) and Heteropolyacids (where two or more different types of anions condense together i.e., molybdate or tungstate groups with phosphate (PO₄)³⁻, silicate (SiO₄)⁴⁻ or borate groups).
In this unit, you will study about isopolyacids and heteropolyacids, the formation and structure of polyacids in detail.

## 9.1 Objectives

After going through this unit, you will be able to:

- Know about polyacids
- Understand the formation and structure of polyacids
- Know about heteropolyacids
- Understand the formation and structure of heteropolyacids

## 9.2 Polyacids

The oxides of metals of Group Va and VIA, particularly vanadium, molybdenum, chromium and tungsten, are weakly acidic. When dissolved in strong basic solution of NaOH, they furnish anions like vanadates, molybdates, chromates and tungstates respectively. These anions have interesting property of condensing reversibly as the pH of their solutions is lowered to give a series of larger anions. These anions contain more than one metal atom.

If the larger anions are derived by the condensation of same metal oxide, then they are called as isopolyacids.

If this condensation process takes place in presence of other anions like phosphate, borate etc., then the resulting anions are said to be derived from heteropolyacids.

Balts of both types of polyanion are well known. In principle, the condensation process is same in both the case it involves the formation of an oxo bridge by elimination of water from two molecules of the weak acid.

\[
[XO_4]^n^- + H^+ \rightleftharpoons [XO_4(OH)]^{n+1} \quad (9.1)
\]

\[
2[XO_4(OH)]^{n+1} \rightleftharpoons [O_{x}XOX_{3}]^{2n-2} + H_2O \quad (9.2)
\]

These condensation reactions take place reversibly in dilute aqueous solutions. This shows that there is an appropriate balance between the acidity constants equation 9.1) and the true condensation equilibrium (Equation 9.2).

### 9.2.1 Isopolyacids of Group VIA Metals

The oxides CrO, MoO and WO are strongly acidic and dissolve in aqueous NaOH forming discrete tetrahedral chromate CrO, molybdate MoO and tungstate WO. These anions exist both in solution and as solids chromates are strong oxidizing agents but other two have only weak oxidizing powers.
**Polychromes**

On acidifying, chromates \( \text{CrO}_4^{2-} \) and orange - red dichromates \( \text{Cr}_2\text{O}_7^{2-} \), 
HcrO_4^- and Cr_2O_7^{2-} exist in equilibrium over a wide range of pH from 2 to 6.

\[
\text{CrO}_4^{2-} \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}, \quad \text{yellow} \rightarrow \text{orange}
\]

In \( \text{Cr}_2\text{O}_7^{2-} \), two tetrahedral units join together by sharing the oxygen atom at one corner (Refer Figure 9.1).

![Fig. 9.1 Chromate and Dichromate Ions](image)

There is some evidence for further polymerization giving a limited polychromate series. Trichromates, \( \text{Cr}_3\text{O}_{13}^{4-} \) and tetrachromates \( \text{Cr}_4\text{O}_{17}^{6-} \) have been found.

**Isopolyborates and Isopolymolybdates**

The formation of polycarboxylates is a prominent feature of the chemistry of Mo and W. When molybdate and tungstate solutions are acidified, they condense and give an extensive range of polyborates and polyanioniates.

The polyanions of Mo and W are divided into two main types:

1. **Isopolyborates**, where the anions, which condense together are all of the same type - for example, the structure contains only MoO_4 Octahedra or only WO_4 tetrahedra.
2. **Heteropolyborates**, where two or more different types of anion condense together - for example, molybdate or tungstate combines with borate or phosphate.

**Formation of Isopolyborates**

The only ion present in molybdate solution at pH > 10 is [MoO_4]^{3-}. If the pH is lowered about 6-8, polyanion formation commences;

\[
7\text{[MoO_4]^{3-} + 8H^+ \rightleftharpoons [Mo_7O_{24}]^{2-} + 4H_2O}
\]
The existence of this ion in crystalline salts is proved by structural studies. Such an ion is likely to be protonated or associated with water molecules in aqueous solution.

When the solution containing \([\text{Mo}_7\text{O}_{23}]^{10-}\) is acidified further to about pH 1.5 – 2.9, octamolybdate ion \([\text{Mo}_8\text{O}_{26}]^{10-}\) is formed. But when pH > 1, trioxide is precipitated.

\[
\begin{align*}
\text{[MoO}_4]^{4-} & \quad \text{pH = 6} \\
\text{[Mo}_7\text{O}_{23}]^{10-} & \quad \text{pH = 1.5 – 2.9} \\
\text{MoO}_3 & \quad \text{pH > 1} \\
\text{[Mo}_8\text{O}_{26}]^{10-} & \quad \text{hydrate oxide}
\end{align*}
\]

**Formation of Iso Polytungstates**

The formation of isopolytungstates may be summarized as follows:

\[
\begin{align*}
\text{[WO}_4]^{2-} & \quad \text{pH = 6 – 7} \\
\text{[HHW}_3\text{O}_{12}]^{2-} & \quad \text{fast boil OH}^- \\
\text{[HW}_2\text{O}_7]^{2-} & \quad \text{para-tungstic A} \\
\text{[H}_2\text{W}_6\text{O}_{19}]^{2-} & \quad \text{slow} \\
\text{[H}_2\text{W}_2\text{O}_8]^{2-} & \quad \text{meta-tungstic} \\
\text{[H}_2\text{W}_3\text{O}_9]^{2-} & \quad \text{hydrated tungsten trioxide}
\end{align*}
\]

When alkaline solution containing \([\text{WO}_4]^{2-}\) is acidified to pH = 6 – 7, there is a fast reaction which results in the formation of para-tungstic-A, \([\text{HW}_3\text{O}_{12}]^{2-}\). This ages in solution hours or days to form another ion \([\text{W}_6\text{O}_{19}]^{10-}\), known as para-tungstic-B. This is a stable ion. At pH = 3 – 4, the \(\gamma\)-meta-tungstic ion, \([\text{H}_2\text{W}_3\text{O}_9]^{2-}\) is formed. This condenses to form meta-tungstic, \([\text{H}_2\text{W}_3\text{O}_9]^{2-}\). Tungsten trioxide is precipitated at pH = 1.

**9.2.2 Isopolyacids of Group VA: Polyvanadates**

**Formation of Isopolyvanadates**

\(\text{V}_2\text{O}_5\) is amphoteric in nature, but mainly acidic. It dissolves in a very strong solution of \(\text{NaOH}\) to form ortho-vanadate ion, \(\text{VO}_3^\text{2-}\) or possibly, \([\text{VO}_2\text{(OH)}]^{2-}\). As the
pH is reduced from 13 to about 8, $[\text{VO}_3^-]$ condenses to $[\text{V}_2\text{O}_7]^{2-}$. As the pH is reduced still further, deca-vandate, $[\text{V}_{10}\text{O}_{28}]^{3-}$ is produced at about pH 6. This ion is protonated in turn, to $[\text{H}V_{10}\text{O}_{28}]^{4-}$ and $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$ at pH = 3.5. In acidic pH (pH = 2), $[\text{VO}_2]^+$, dioxovanadium \( \text{V} \) is formed. Finally, hydrated $\text{V}_2\text{O}_5$ gets precipitated.

9.2.3 Structure of Isopolyacids

Structure of Isopoly Molybdates and Tungstates

These isopoly-molybdates and tungstates are made up of MoO\(_4\) or WO\(_4\) octahedra (Mo/W ions lie at the centre of octahedra and six corners are occupied by oxygen). (Refer Figure 9.2)
The structures are built up of these octahedra by sharing of corners or edges, but not faces.

![Diagram of octahedra]

**NOTES**

**Fig. 9.3** [Mo₆O₃]³⁻  
**Fig. 9.4** (NH₄)₆Mo₆O₃·5H₂O

In ammonium para-molybdate, (NH₄)₆Mo₆O₃·5H₂O, the anion, [Mo₆O₃]³⁻ has the actahedra arranged as shown in Figure 9.3. The way in which the octahedra are assembled can be understood as follows: those labelled 1 and 2 and 3 and 4 share edges, while 1 and 3 and 2 and 4 share corners, so that the centres of 1, 2, 3 and 4 form a rectangle. The remaining three octahedra are then placed so that they share edges with their nearest neighbours. The octamolybdate ion, (NH₄)₆Mo₆O₃·5H₂O, has a similar, though somewhat more complicated structure, as shown in Figure 9.4.

The x-ray structure of sodium salt of para-tungstate-B, Na₆[W₁₀O₃₉]·28H₂O, showed an interesting feature. The unit cell contains the [W₁₀O₃₉]³⁻ anion but rather than [W₁₀O₃₉]³⁻ its proton-nmr spectrum showed a broad line indicating the presence of hydroxyl groups, in addition to water molecules.

Based on these observations, the formula of sodium para-tungstate B can be resolved as Na₆[W₁₀O₃₉(OH)₉]·23H₂O.

As the medium becomes more acidic, the smaller ions are built into larger ions. Attack of free -OH groups by H⁺ (from the medium) and simple condensation between different WO₆ octahedra (to remove H₂O) are involved in the process.

\[
6[WO₆(OH)]^{2⁻} + H⁺ \rightleftharpoons [HW₂O₅]^{³⁻} + 3H₂O \\
\text{Tungstate - para-tungstate-A}
\]

\[
2[HW₂O₅]^{³⁻} + 2H⁺ \rightleftharpoons [W₂O₃]^{⁵⁻} + H₂O \\
\text{para-tungstate-B}
\]

\[
[HW₆O₃]^{³⁻} + 2H⁺ \rightleftharpoons [H₂W₆O₁₆]^{⁹⁻} \\
\text{β-Meta-tungstate}
\]
para-tungstate ion and meta-tungstate ion are isostructural with 12-tungsto- and 12-Molybdo hetero anions (Refer Figure 9.5).

![Structure of [W₆O₁₉]⁴⁻](image)

**Fig. 9.5 Structure of [W₆O₁₉]⁴⁻ Unit in Para-tungstate Ion**

**Structure of Isopoly Vanadates**

The structure of meta-vanadate consists of chains of VO₄ tetrahedra linked by sharing corner. The species in solution is almost a trimer, 

\[ [V₂O₆]^{3-} \text{ or tetramer } [V₃O₉]^{4-} \text{ unit} \]

\[ \text{study of } Ca₃[V₃O₉]₂.16H₂O \text{ and } K₂[Zn₃(V₃O₉)₂.16H₂O (occurs as minerals) showed that they contain } [V₃O₉]^{3-} \text{ anion. This anion is made up of ten VO₆ octahedra joined by sharing edges.} \]

**Check Your Progress**

1. What does Cr₂O₇²⁻ form when dissolved in aqueous NaOH?
2. Write the molecular formula of tetrachromate.
3. Name the polyacids in which anions two or more different types of anions condense together.

**9.3 HETEROPOLYACIDS AND THEIR SALTS**

**Formation of Heteropolyacids**

They are formed when molybdate and tungstate solutions are acidified in presence of other oxo anions (like SO₄²⁻, PO₄³⁻) or metal ions. The free acids and most of their salts are soluble in water and in various oxygenated organic solvents such as ethers, alcohols and ketones. In contrast to isopolyacids, many of the heteropolyacids are stable in acidic solution and do not undergo depolymerization. More than 25 elements are known to be capable of functioning as the hetero atoms. They include:
(i) Elements capable of oxy-acid formation (e.g. B, Al, Si, Ge, Sn, P, As, Sb, Se, Te and I).

(ii) Metals of transition series (e.g. Ti, Zr, Ce, Th, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, Rh, Os, Ir, and Pt).

- Solubility: Heteropoly Molybdates and tungstates of small cations including those of some heavy metals, are water soluble; with larger cations, insolubility is frequently found.
  - Cs+, Pb+ and Ba+ salts: usually insoluble
  - NH4+, K+, and Rb+ salts: sometimes insoluble
  - [h(C6H6)2], Fe+, R,N+, R,P+: invariably insoluble

- The anions are usually classified in terms of the ratio of the number of central atoms to the number of metal atoms associated with the surrounding octahedra - mostly Mo, W or V.

**Table 9.1 Principle Types of Heteropoly Molybdates**

<table>
<thead>
<tr>
<th>Ratio of heteroatoms (%) to Mo atoms</th>
<th>Principle heteroatoms (%) occurring</th>
<th>Anion formula (M = M')</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:12</td>
<td>P(IV), As(V)</td>
<td>( [X^{n+} M_{12} O_{40}]^{(12-4n)} )</td>
</tr>
<tr>
<td>1:11</td>
<td>P(IV), As(V), Ge(IV)</td>
<td>( [X^{n+} M_{11} O_{30}]^{(12-4n)} )</td>
</tr>
<tr>
<td>1:10</td>
<td>P(IV), As(V), Ge(IV)</td>
<td>( [X^{n+} M_{10} O_{20}]^{(12-4n)} )</td>
</tr>
<tr>
<td>1:9</td>
<td>M(IV) Na(IV)</td>
<td>( [X^{n+} M_{10} O_{20}]^{(10-4n)} )</td>
</tr>
<tr>
<td>1:6</td>
<td>Ta(VI), Ir(VII), Cr(III), Fe(III), Rb(II)</td>
<td>( [X^{n+} M_{10} O_{12}]^{(12-4n)} )</td>
</tr>
<tr>
<td>2:18</td>
<td>P(IV), As(V)</td>
<td>( [X_{2}^{n+} M_{12} O_{40}]^{(16-2n)} )</td>
</tr>
<tr>
<td>2:17</td>
<td>P(IV), As(V)</td>
<td>( [X_{2}^{n+} M_{15} O_{20}]^{(12-30-2n)} )</td>
</tr>
</tbody>
</table>

- Out of these, 1:12, 1:9 and 1:6 types occur frequently. They form three main series and have structural evidence.
- Other ratios, 1:11, 1:10, 2:18 and 2:17 are based on the analysis of solid phases deposited from solutions; some may be mixtures.
9.3.1 Structure of Heteropolyacids

- The discrete heteropoly anions exist in definite pH ranges.
- For example, on progressive acidification of sodium silicate solution to ammonium molybdate solution, 1-, 2-, 6- and 12-silico molybdate ions are formed.
- The 12-heteropolyanions are stable over the pH range of 1–4.
- All the 12-molybdo anions with P(V), As(V), Ti(IV) and Zr(IV) are isomorphous with 12-tungsto species with hetero atoms B(III), Ge(VI), P(V), As(V) and Si(IV). The structure is shown in Figure 9.6.

![Fig. 9.6 Structure of 12-Molybdoheteropolyanionic Species](image-url)

- This structural study was first made by Keggin on the crystalline hydrate of 12-phosphotungstic acid.
- The structure consists of central P₀ tetrahedra surrounded by MoO₆/W₀ octahedra.
- There are four groups of three MoO₆/W₀ octahedra.
- In each group, there is one oxygen atom common to all three octahedra, referred to as triply shared oxygen.
• In the complete structure, these groups are so oriented that the four triply shared oxygen atoms are placed at the corners of a central tetrahedron. The hetero atom is placed at the corners of a central tetrahedron. The hetero atom is placed in the center of this tetrahedron in heteropolyanions. (Refer Figure 9.7)

![Fig. 9.7 Arrangement of W Ions in [SiW<sub>12</sub>O<sub>41</sub>]<sup>3+</sup> Ion](image)

• The same structure is found in a number of 12-heteropoly acids of other elements also, for example silicotungstates, borotungstates, silicomolybdates etc.

• All the heterospecies occurring in series A of 12-heteropoly anions are small enough to make a coordination number of four towards oxygen atoms. (Refer Figure 9.8)

• In the 12-hetero acids of series B, the hetero atoms are in the central octahedra of oxygen atoms.

![Fig. 9.8 The Structure of Series A 12-molybdo and 12-tungsto Heteropolyanions of General Formula (X<sup>n-</sup>M<sub>y</sub>O<sub>z</sub>OH<sup>z</sup>·<sup>2</sup>n<sup>–</sup>)](image)
- In the heteropolyacids, the central atom like I or Te is larger and capable of coordinating with six atoms of oxygen. A geometrical arrangement of octahedra which fulfills this condition for the \([\text{XM}_4\text{O}_{12}]^3\) group was first proposed by Anderson. (Refer Figure 9.9)

![Figure 9.9 Structure of \([\text{Mo}_7\text{O}_{24}]^{12-}\) with Large Central Cavity](image)

- Six Mo octahedra are arranged in a hexagonal fashion, so as to share two corners with two neighbouring octahedra. The central cavity of the resulting \([\text{Mo}_7\text{O}_{24}]^{12-}\) structure is found to be large enough to accommodate an octahedron, corresponding with that of the hetero atom. Similar structure is identified in potassium and ammonium molybdo tellurates, \([\text{Te Mo}_7\text{O}_{24}]^{3-}\) ion.

- In the 6-molybdo heteropoly species, \([\text{MMO}_4\text{O}_{24}\text{H}_4]^{3+}\) series, where M = Cr, Al, Fe, Co, Rh or Ga, all are iso structural and the Cr salts are studied in detail. The structure of the anion \([\text{CrMO}_4\text{O}_{24}\text{H}_4]^{3+}\) is shown in Figure 9.10.

![Figure 9.10 Structure of \([\text{CrMo}_4\text{O}_{24}\text{H}_4]^{3+}\) Ion](image)
- The most likely sites for the six hydrogen atoms are the oxygen atoms of the central octahedron.
- The various dimeric 9-molybdo and 9-tungsto heteropoly anions with general formula \([X_nM_nO_{x-}]^n\) ion (the empirical formula is \(K_2P_2W_{12}O_{40}\cdot14H_2O\)) as shown in Figure 9.11.

![Figure 9.11 Structure of the Dimeric Anion \([P,W_{12}O_{40}]^n\)\]

The structure consists of two half-units each of which is derived from the series-A 12-molybdo heteropolyanions; it has two P0₆ tetrahedra enclosed within Mo₆ octahedra bonded together by sharing oxygen atoms.

- The 11- and 10-molybdo heteropoly anions may also be dimeric and consist of appropriate fragments of 12-molybdo structure, but the exact structures are unknown.

### 9.3.2 Redox Chemistry of Heteropolyanions

- The 12-tungstocobaltate (II) and (III) are inter convertible, which involves the novel feature of tetrahedrally co-ordinated Co(III).
- An interesting feature of the heteropolyanions with a central atom such as P is that it does not account for the redox properties, but can be reduced by addition of 1 to 6 electrons per anion to give, the so-called heteropolyblues.
- The redox reactions occur reversibly, without major structural change.
- Spectroscopic studies indicate that the added electrons reside on individual Mo(V) or W(V) species, with only slow ‘hopping’ from one metal atom to another. The colour is due to the intervalence charge transfer bands.
- Example of redox series are:
4. Name two elements which are capable of oxy-acid formation.
5. What is the IUPAC name of Na₂[PMo₁₀O₄₀]?
6. What does the spectroscopic study of heteropolyanions indicate?

**9.4 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS**

1. It forms discreet tetrahedral chromate CrO₄²⁻.
2. Cr₂O₇²⁻.
3. Heteropolyacids.
4. Silicon and Germanium.
5. Sodium 12-molybdophosphate; Sodium dodecamolybdophosphate.
6. Spectroscopic studies indicate that the added electrons reside on individual Mo(V) or W(V) species, with only slow 'hopping' from one metal atom to another. The colour is due to the intervalence charge transfer bands.

**9.5 SUMMARY**

- If the larger anions are derived by the condensation of same metal oxides, then they are called as isopolyacids.
- If this condensation process takes place in presence of other anions like phosphate, borate etc., then the resulting anions are said to be derived from heteropoly acids.
The oxides Cr₂O₃, MoO₃, and WO₃ are strongly acidic and dissolve in aqueous NaOH forming discrete tetrahedral chromate CrO₄²⁻, molybdate MoO₄²⁻ and tungstate WO₄²⁻ ions. These anions exist both in solution and as solids. Chromates are strong oxidizing agents but other two have only weak oxidizing powers.

- The polyacids of Mo and W are divided into two main types:
  1. Isopolyacids, where the anions, which condense together are all of same type - for example, the structure contains only MoO₃ octahedra or only WO₄ tetrahedra.
  2. Heteropolyacids, where two or more different types of anion condense together - for example, molybdate or tungstate combines with borate or phosphate.

- They are formed when molybdate and tungstate solutions are acidified in presence of other oxo anions (like SO₄²⁻, PO₄³⁻) or metal ions. The free acids and most of their salts are soluble in water and in various oxygenated organic solvents such as ethers, alcohols and ketones. In contrast to isopolyacids, many of the heteropoly acids are stable in acidic solution and do not undergo depolymerization.

- An interesting feature of the heteropolyanions with a central atom such as P is that it does not account for the redox properties, but can be reduced by addition of 1 to 6 electrons per anion to give, the so called heteropoly blues.

### 9.6 KEY WORDS

- **Polyacids**: A compound which has more than one acidic group, especially an acid containing polymeric anions.
- **Anion**: A negatively charged ion, i.e. one that would be attracted to the anode in electrolysis.
- **Cation**: A positively charged ion, i.e. one that would be attracted to the cathode in electrolysis.
- **Ion**: An atom or molecule with a net electric charge due to the loss or gain of one or more electrons.

### 9.7 SELF ASSESSMENT QUESTIONS AND EXERCISES

**Short Answer Questions**

1. Write a short note on polyacids.
2. What are chromate and dichromate ions?
3. How are isopolymolybdates formed?
4. Discuss the formation of isopolytungstates.
5. What are principle types of heteropoly molybdates?

Long Answer Questions
1. Describe the structure of isopolymolybdates and isopolytungstates.
2. How are heteropolyacids formed? Explain.
3. Describe the structure of heteropolyacids given by Anderson.
4. Describe the structure of heteropolyacids given by Keggin.
5. What do you understand by redox chemistry of heteropolyanions? Discuss.

9.8 FURTHER READINGS
UNIT 10 SILICATES

10.0 INTRODUCTION

The silicates, owing to their abundance on the Earth, constitute the most important mineral class. Approximately 25 percent of all known minerals and 40 percent of the most common ones are silicates; the igneous rocks that make up more than 90 percent of the Earth’s crust are composed of virtually all silicates.

The fundamental unit in all silicate structures is the silicon-oxygen (SiO4)4-tetrahedron. It is composed of a central silicon cation (Si4+) bonded to four oxygen atoms that are located at the corners of a regular tetrahedron. The terrestrial crust is held together by the strong silicon-oxygen bonds of these tetrahedrons. Approximately 50 percent ionic and 50 percent covalent, the bonds develop from the attraction of oppositely charged ions as well as the sharing of their electrons.

In this unit, you will study about silicates and its different types, i.e., ortho and meta silicates, pyrosilicates, ring silicates, chain silicates, double chain silicates, sheet silicates and three dimensional silicates.

10.1 OBJECTIVES

After going through this unit, you will be able to:

- Explain what silicates are
- Discuss about different types of silicates
- Describe about ortho and meta silicates
• Understand about pyrosilicates, ring, chain, double chain silicates
• Learn about sheet and three dimensional silicates

10.2 SILICATES

A silicate is any member of a family of anions consisting of silicon and oxygen, usually with the general formula \([\text{SiO}_2(4-2x) - 4x\mathbb{N}]\), where \(0 \leq x < 2\). The family includes orthosilicate \(\text{SiO}_2 - 4 (x = 0)\), metasilicate \(\text{SiO}_2 - 3 (x = 1)\), and pyrosilicate \(\text{SiO}_6 - 7 (x = 0.5, n = 2)\). The name is also used for any salt of such anions, such as sodium metasilicate; or any ester containing the corresponding chemical group, such as tetramethyl orthosilicate.

Silicate anions are often large polymeric molecules with an extensive variety of structures, including chains and rings (as in polymeric metasilicate[\(\text{SiO}_2 - 3\)]\(n\)), double chains (as in [\(\text{Si}_2\text{O}_5\)]\(n\)), and sheets (as in [\(\text{Si}_2\text{O}_5\)]\(2n\)).

Earth’s crust is mainly made up of silicate minerals or aluminosilicate clays which form bulk of all rocks and of soils and sands. The average composition of earth’s crust consist of following (elemental composition calculated in grams/tonne).

<table>
<thead>
<tr>
<th>Element</th>
<th>Pct</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>46.6%</td>
</tr>
<tr>
<td>Silicon</td>
<td>27.7%</td>
</tr>
<tr>
<td>Aluminum</td>
<td>8.1%</td>
</tr>
<tr>
<td>Iron</td>
<td>5.0%</td>
</tr>
<tr>
<td>Calcium</td>
<td>3.6%</td>
</tr>
<tr>
<td>Sodium</td>
<td>2.8%</td>
</tr>
<tr>
<td>Potassium</td>
<td>2.6%</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2.1%</td>
</tr>
</tbody>
</table>

This means that the majority of the minerals must be made up of a combination of oxygen and silicon with other elements forming bonding cations.

Silicates in most simple way may be defined as a compound containing \([\text{SiO}_2]^n\) anions. However, there are numerous branches of silicates that include oxygen atoms replaced by fluorine atoms to make hexafluorosilicates or other exceptions. Silicates itself include over 500 different minerals.

Formation of Silicates (Bowen’s Reaction Series)

During the cooling of the earth, the higher silicate materials crystallized and floated to the surface, resulting in the concentration of silicates in the earth’s crust. Bowen’s reaction series given by N.L. Bowen has the sequence in which crystalline minerals appeared when the magma cooled. The various steps in this series are:

• The simpler silicate units crystallized first.
• Hydroxyl groups appear in the later minerals and F may be substituted instead of OH.
• Isomorphous replacement, i.e., changing one metal for another without changing the structure, occurs particularly in later minerals.
Silicates

- The orthoclase feldspars, muscovite mica and quartz are the major minerals of granite.
- As the silicates cooled further, they shrank and cracked. The hydro thermal (hot water) solution moved through the cracks near the surface to regions of lower temperature and pressure where the elements precipitated and then combined with S, forming veins of sulphides (Refer Figure 10.1).

<table>
<thead>
<tr>
<th>First</th>
<th>Olivine</th>
<th>$M_2^+\text{SiO}_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyroxenes</td>
<td></td>
<td>$M_2^+\text{SiO}_3$</td>
</tr>
<tr>
<td>Amphiboles</td>
<td></td>
<td>$M^+\text{(Al}_2\text{Si}_3\text{O}_8)\cdot\text{(OH)}_2$</td>
</tr>
<tr>
<td>Biotite micas</td>
<td></td>
<td>$(K,\text{H})z\text{(Mg,Fe}^{2+}z\text{Al,Fe}^{3+})(\text{Si,Al})_z\text{SiO}_4$</td>
</tr>
<tr>
<td>Orthocase feldspars</td>
<td></td>
<td>$\text{KA}_2\text{Si}<em>3\text{O}</em>{10}$</td>
</tr>
<tr>
<td>Muscovite micas</td>
<td>$\text{KA}_2\text{(Al}_2\text{Si}_3\text{O}_10)\cdot\text{(OH)}_2$</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td></td>
<td>$\text{SiO}_2$</td>
</tr>
<tr>
<td>Zeolites</td>
<td></td>
<td>$\text{Na}_2\text{(Al}_2\text{Si}_3\text{O}_10)\cdot2\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

**Fig. 10.1 Sequence in which Minerals are thought to have Crystallized**

Leaving a small amount of water, $\text{SO}_2$, $\text{S}$, $\text{Pb}$, $\text{Cu}$, $\text{Ag}$, $\text{Sn}$, $\text{As}$, $\text{Sb}$, $\text{Bi}$ and other transition metals in solution under a very high temperature and pressure.

**Types of Silicates**

Broadly silicates may be divided into two types:

- Soluble Silicates
- Insoluble Silicates

**Soluble Silicates**: These are derived mainly from alkali metals and have usually metal oxide, silica and water in their composition. These are generally obtained by fusion of silica with sodium carbonate at about 1000°C. These contain a variety of crystalline compounds like $\text{Na}_2\text{SiO}_3$, $\text{Na}_2\text{Si}_2\text{O}_5$, $\text{Na}_4\text{SiO}_4$, $\text{Na}_2\text{Si}_3\text{O}_8$, etc.

**Insoluble Silicates**: These are naturally occurring mineral materials together with certain synthetic zeolite like compounds. Structurally the soluble and insoluble salts are similar.

**Structure of Silicates**

**Pauling Rules**: Pauling proposed certain rules to study the structure of silicates. These rules are summarized as:

**Rule 1**: A coordinated polyhedron of anions is formed about each cation. The cation-anion distances are determined by sum of the radii and the coordination number by radius ratio.

**Rule 2**: The charge on each anion (with charged sign) is exactly equal to the sum of the strengths of bonds linked to it from the adjacent cations.
The strength of an electrostatic bond is defined as the charge on the cation [z divided by the number of coordinated atoms (z/n)]. This bond can be broken only on treatment with reagents like hydrofluoric acid. For example, the strength of each bond in SiO$_2$ group is 4/4 or 1/1, in AlO$_2$ is 3/6 or 1/2. Hence each oxygen is surrounded by four aluminium ions (½ x 4 = 2).

**Rule 3:** The presence of shared edges and especially of shared faces of coordinated polyhedra decreases the stability of structure. This effect has been found to be very large for cations having high charge and small coordination number. However, silicon always shares corners but does not share edges in silicates.

**Rule 4:** In a crystal containing different cations those with large charge and small coordination number tend not to share polyhedron elements with each other. As the charge on the cations increases, and coordination number decreases, the cation-cation repulsion increases. Shared edges are usually necessary to satisfy rule (b) for cations with low charge, particularly if the coordination number is high.

**X-Ray Diffraction Method**

W.L. Braggs and coworker have successfully devised x-ray crystallographic method for elucidating the structure of silicates. The main points about the structure of silicates are summarized below:

- The electronegativity of oxygen is 3.5 and that of silicon is 1.8. The electronegativity difference (3.5 – 1.8) or 1.7 suggests that Si – O bond though covalent, has an appreciable degree of ionic character. The structure of all silicates is based on the formation of coordinate lattices of anions about cations. Generally, the cation is Si$^4+$ and anion is generally O$^-$ ion. The anion (O$^-$), being of much large size than any of the cation present, mainly determines the dimensions and generally lays out the structure of silicates.

- The radius ratio Si$^4+$: O$^-$ is 0.29 which suggests that the structures of silicates are based on four coordinate silicon, i.e., on the [SiO$_4$]$^+$ tetrahedron in which four oxygen atoms are arranged at the four corners of the tetrahedron with the silicon atom at the center. Thus, in all silicates the basic structural unit is [SiO$_4$]$^+$ tetrahedron in which Si – O bond distance is 1.62 Å and O – O bond distance is 2.70 Å. These SiO$_4^+$ tetrahedra condense together by sharing one or more oxygen atoms thus giving rise to different types of silicates. The SiO$_4^+$ units are formed by sp$^3$hybridisation.

The silicon atom, in the excited state, has four unpaired electrons, i.e., it is hybridized. These four sp$^3$ hybridised orbitals are used to link with four oxygen atoms forming SiO$_4$ which has a tetrahedral structure.

- In SiO$_4$ species, silicon gets its octet complete but each of four oxygen atoms is short of one electron each. The oxygen atoms try to get electrons from some other atoms and acquire negative charges giving rise to discrete
Silicates

The Si – O and O – O bond distances are 1.62 Å and 2.7 Å respectively. These SiO₄⁺ tetrahedra condense together by sharing one or more oxygen atoms thus giving rise to different type of anions.

In ZrSiO₄, SiO₄ species (not SiO₂⁺) gains four electrons from zirconium to give SiO₄⁺ and Zr⁴⁺ which are held together by electrostatic forces of attraction.

In silicates, bond angles in tetraheda are ~ 109°, i.e., nearly tetrahedral.

Check Your Progress

1. What are silicates?
2. How many types of silicates are there? Name them.
3. What are insoluble silicates?

10.3 CLASSIFICATION OF SILICATES

All silicates contain tetrahedral SiO₄⁺ units in their structures. There units may be linked together by sharing corners and never by sharing edges or faces.

Tetrahedral shape of SiO₄⁺ ion is due to sp³ hybridisation of Si-atom, in its excited state. Valence-shell configuration of Si-atom is 3s² 3p², while this configuration, in the excited state is 3s² 3p³. These four orbitals undergo sp³ hybridisation and give rise to the formation of four singly-filled sp³ hybrid orbitals. Each of the four Si – O bonds in SiO₄⁺ ion is [sp³ (Si) – 2p (O)] σ-bond. Note that the valence-shell configuration of O has one singly-filled 2p orbital [O = 2s² 2p³ 2p², O = 2s² 2p³ 2p²]. Tetrahedral shape of SiO₄⁺ ion can be represented by any of the three figures shown in Figure 10.3.
The above figure shows the various ways of representing tetrahedral shape of SiO$_4^+$ ion (a, b) and in c white circles represents O-atoms and black circle represents Si-atom.

Depending upon the linking of SiO$_4^+$ units, silicates have been broadly classified into following groups:

**10.3.1 Orthosilicates**

This type of silicates are obtained when SiO$_4^+$ tetrahedra are discrete, i.e., no oxygen atoms belonging to one SiO$_4^+$ tetrahedra is shared with that of the neighboring SiO$_4^+$ tetrahedra. Some of the important orthosilicates are discussed below:

**Phenacite** ($Be_2SiO_4$) and **Willemite** ($Zn_2SiO_4$): In the structure of $Be_2SiO_4$ the metal ions are tetrahedrally coordinated and each oxygen atom is common to one SiO$_4$ tetrahedron and two BeO$_4$ tetrahedra. The bond distance $Be – O$ is $1.65 \text{ Å}$. Similar the structure of $Zn_2SiO_4$, in this, $Zn – O$ bond distance is $1.92 \text{ Å}$. A number of salts including Li$_2$MoO$_4$, Li$_2$WO$_4$ and Li$_2$BeF$_4$ are isostructural with phenacite and willemite (Refer Figure 10.4).

![Fig. 10.4 Structure of Phenacite ($Be_2SiO_4$) and Willemite ($Zn_2SiO_4$)](image)

**Olivine** ($9Mg_2SiO_4$, $Fe_2SiO_4$): The olivine can be represented by the general formula $M_2SiO_4$ where $M$ is a divalent metal like Mg, Fe, Mn or a mixture of such metals.

![Fig. 10.3 Various ways of Representing Tetrahedral Shape of SiO$_4^+$ Ion.](image)
In the structure of this, one in every ten Mg\(^{2+}\) ions in Mg\(_2\)SiO\(_4\) is replaced by Fe\(^{3+}\) ion. Each magnesium or ferrous ion (Mg\(^{2+}\) or Fe\(^{2+}\)) is surrounded octahedrally by six oxygen atoms. Each oxygen is then linked directly to one silicon atom and coordinated to three magnesium atoms.

The positively charged Mg\(^{2+}\) or Fe\(^{3+}\) ions are uniformly distributed throughout the structure and bind the negative SiO\(^{4-}\) radicals together. The oxygen atoms lie in approximately hexagonal close packed structure.

Zircon (ZrSiO\(_4\)): In zircon, the Zr\(^{4+}\) ion is eight coordinated, i.e., each zirconium atom is surrounded by eight oxygen atoms. The distances of these oxygen atoms are not same, i.e., four at 2.05 Å, four at 2.41 Å.

Garnet Minerals: This group of orthosilicates is represented by the general formula:

\[
M_{12}^{III}[SiO_4]_4
\]

Where M\(^{III}\) = Ca\(^{2+}\), Mg\(^{2+}\) or Fe\(^{3+}\) and these are six coordinate and M\(^{II}\) = Al\(^{3+}\), Cr\(^{3+}\) or Fe\(^{2+}\) and these are eight coordinate.

The garnets are an important group of minerals with discrete tetrahedral. Large crystals of garnet are cut and polished and used as a red gemstone. Much larger amounts are used to make ‘sandpaper’.

Examples of garnet minerals include crossular Ca\(_2\)Al\(_2\)(SiO\(_4\))\(_4\), uvarovite, Ca\(_2\)Cr\(_2\)(SiO\(_4\))\(_4\) and andradite Ca\(_3\)Fe\(_3\)(SiO\(_4\))\(_4\).

In the structures of these silicates SiO\(^{4-}\) ions are packed together with M\(^{II}\) ions in positions of six co-ordination and M\(^{III}\) in positions of eight.

10.3.2 Pyrosilicates

A pyrosilicate is a type of chemical compound; either an ionic compound that contains the pyrosilicate anion SiO\(_6\)\(^-\), or an organic compound with the hexavalent \(\equiv Si-O-Si-O\equiv\) group. The anion is also called disilicate or diorthosilicate.

 Ionic pyrosilicates can be considered salts of the unstable pyrosilicic acid, H\(_2\)SiO. Unlike the acid, the salts can be stable. Indeed, pyrosilicates occur widely in nature as a class of silicate minerals, specifically the sorosilicates.

The basic unit in these silicates is pyrosilicate ion, SiO\(_4\)\(^{4-}\). This ion is formed when two SiO\(_4\)\(^{4-}\) tetrahedrons share one O-atom (bridging O-atom), i.e., in this ion one O-atom acts as a bridge between two Si-atoms. The structure of this ion is shown in Figure 10.5.

![Fig. 10.5 Structure of Pyrosilicate Ion, SiO\(_4\)\(^{4-}\)](image)
This structure shows that each Si-atom is surrounded by $3 + \frac{1}{2} = 3.5$ oxygen atoms. Thus the basic unit found in these silicates can be represented as $[\text{SiO}_4]^{4-}$ or $\text{Si}_4\text{O}_{10}^{4-}$ ion.

It may be noted from the structure of $\text{Si}_4\text{O}_{10}^{4-}$ ion that O-atom, which is shared by two $\text{SiO}_4^{4-}$ units, does not carry any charge on it. O-atoms, forming no bridges between $\text{SiO}_4^{4-}$ tetrahedrons, have negative charge. This negative charge is produced because each of these O-atoms picks up an electron from some metal.

Examples of pyrosilicates are:

- **Thortveitite**: It is Scandium pyrosilicate $[\text{Sc}(\text{SiO}_4)]$ in which scandium is trivalent and, therefore, six positive charges are present on two scandium atoms which are balanced by six negative charges present on the six oxygen atoms. The seventh oxygen atom forms the bridge between two $\text{SiO}_4^{4-}$ tetrahedra.

- **Hemimorphite** $[\text{OH}, \text{Zn}_2\text{Si}_2\text{O}_7] \cdot \text{H}_2\text{O}$: In this structure the crystal contains $\text{OH}$ ions as well as $\text{Si}_2\text{O}_5^{5-}$ ions. The $\text{Si}_2\text{O}_5^{5-}$ groups are joined through $\text{ZnO}_2$-$\text{OH}$ tetrahedra. The water molecule exists as isolated water molecule in the structure.

- **Thalenite**: Thalenite, $\text{Y}_2\text{Si}_2\text{O}_7$ in which each ytterium ion is surrounded octahedrally by oxide ions.

- **The minerals vesuvianite**: The minerals vesuvianite, $\text{Ca}_2\text{Al}_5(\text{Mg, Fe})_2\text{Si}_4\text{O}_{12}(\text{OH})_2$, and epidote $\text{Ca}_2(\text{Al, Fe})_2\text{A}_2\text{O}_5(\text{Si}_4\text{O}_{12})\cdot \text{OH}$ contain separate $\text{Si}_4\text{O}_{12}^{4+}$ group as well as $\text{Si}_2\text{O}_5^{5-}$ groups and are both ortho and disilicates.

### 10.3.3 Ring Silicates

Ring silicates have cyclic structure and contain $[\text{SiO}_4]^{4-}$ ion as the primary unit. These silicates are formed when each $\text{SiO}_4^{4-}$ tetrahedron shows two O-atoms (bridging O-atoms). The structures of cyclic ions, i.e., $[\text{SiO}_4]^{4-}$ or $\text{Si}_4\text{O}_{10}^{4-}$ and $[\text{SiO}_4]^{4-}$ or $\text{Si}_4\text{O}_{10}^{4-}$ ions is shown in Figure 10.6.

![Fig. 10.6 Structure of $\text{Si}_4\text{O}_{10}^{4-}$ and $\text{Si}_4\text{O}_{10}^{4-}$ ions.](image-url)
In the above figure, i.e., a shows the structure of \([\text{SiO}_4]^{4-}\) or \(\text{SiO}_4^{4-}\) ion and b shows the structure of \([\text{SiO}_4]^{2-}\) or \(\text{SiO}_4^{2-}\) ion.

Rings of these tetrahedra give rise to six-membered rings constraining the anion \([\text{SiO}_4]^{2-}\) are encountered in benitoite Ba\text{Si}_2\text{O}_5\text{Al} and wollastonite Ca\text{Si}_2\text{O}_5\).

The anion \([\text{SiO}_4]^{2-}\), consisting of a ring of six tetrahedra is found in beryl, Ba\text{Al}_2\text{Si}_4\text{O}_{10}\.

Some of the common examples include:

- **Benitoite**: In this silicate, the rings are arranged in sheets and the \(\text{SiO}_4^+\) tetrahedral are cemented by \(\text{Ba}^{2+}\) and \(\text{Ti}^{4+}\) ions. Both \(\text{Ti}^{4+}\) and \(\text{Ba}^{2+}\) are 6 coordinate. The Ba-O bond distance is greater than the Ti-O bond distance.

- **Beryl**: The anion of this silicate contains a ring of tetrahedral, in which an oxygen is shared by one silicon, one aluminium (co-ordination number six) and one Be (co-ordination number four). In beryl, the \(\text{Si}_4\text{O}_{16}\) groups in different layers are so arranged that wide channel, roughly large enough to accommodate an oxygen atom are formed down the centre of superimposed \(\text{Si}_4\text{O}_{16}\) hexagons and it becomes permeable to gases with small molecules (for example, helium).

### 10.3.4 Chain Silicates

Chain silicates are further classified into two types:

#### Single Chain Silicate

These silicates contain \([\text{SiO}_4]^{2-}\) as the primary unit. \([\text{SiO}_4]^{2-}\) ion is obtained when each tetrahedron shares two O-atoms (bridging O-atoms) as shown in Figure 10.7.

![Fig. 10.7 Structure of \([\text{SiO}_4]^{2-}\) Ion](image_url)

Silicates of this are called pyroxenes or metasilicates. These include enstatite Mg\text{Si}_2\text{O}_4\, \text{diopside}, Ca\text{Mg(Si}_2\text{O}_4)_2, jadeite NaAl(Si}_2\text{O}_6, and spodumene, LiAl(Si}_2\text{O}_6. In the crystals of pyroxene minerals, the single chain anions are packed together and the cations occupy the sides left between these chains. In enstatite, non-bridging oxygen atoms are shared with oxygen so as to give the co-ordination number of six to magnesium whereas in diopside calcium has a coordination number of eight and magnesium has coordination number of six. Both Li and Al are six coordinated in spodumene.
Double Chain Silicates

These silicates contain \([\text{Si}_4\text{O}_{10}\text{O}_6]\)^{4+} ion as the primary unit. \([\text{Si}_4\text{O}_{10}\text{O}_6]\)^{8+} ion is formed by further sharing of O-atom by half the Si-atom as shown in Figure 10.8.

![Fig. 10.8 Structure of \([\text{Si}_4\text{O}_{10}\text{O}_6]\)^{8+} Ion](image)

These minerals are also called amphiboles. These minerals contain silicates such as:
- Tremolite, \(\text{Ca}_2\text{Mg}_3(\text{Si}_4\text{O}_{10}\text{O}_6)(\text{OH})_2\). In tremolite the OH- ions are not linked to Si atoms but are coordinated round the cations. Tremolite is monoclinic with a unit cell and the atomic arrangement is very closely related to that of diopside. The only difference is that its b-axis is twice the length of the diopside. The binding force between the chains is ionic and not as strong as Si–O bonds along the chains.
- Asbestos
- Crou dolite, \(\text{Na}_2(\text{Fe}_3\text{Mg})_2(\text{Si}_4\text{O}_{10}\text{O}_6)(\text{OH})_2\)

10.3.5 Sheet Silicates or Silicates with Layer Structure

These silicates are formed when three O-atoms (bridging O-atoms) of each SiO₄ unit are shared. This type of sharing gives an infinite two-dimensional layered structure to the silicates (Refer Figure 10.10). \([\text{Si}_4\text{O}_{10}\text{O}_6]\)^{2+} ion is the basic unit of sheet silicates. In Figure 10.8, O-atom, shown round Si-atom of each SiO₄ tetrahedron carries a negative charge, while the remaining three O-atoms, which act as bridging O-atoms, do not carry this charge. Negative charge on non-bridging O-atom is neutralized by the positive charge on the cations, which lie in between the sheets.
Examples of sheet silicates are given below:

**The Clay Minerals:** These are produced by weathering and decomposition of igneous rocks. They are composed of very fine particles. For example, Kaoline (china clay) having the formula \( \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \) has a sheet structure, in which sheets are held together by OH bridges.

When clay is mixed with water, it becomes plastic-soft and moldable. Water of plasticity can be removed by heating at 100°C. Clay becomes rigid and brittle when water of plasticity has been eliminated. On heating beyond 100°C, structural water of crystallization is removed and carbonaceous matter of the clay gets oxidized. At about 900°C, mullite (\( \text{Al}_2\text{Si}_3\text{O}_9 \)) begins to be formed. This new substance has glassy appearance. Clay is widely used in making chinaware, fire bricks and many other useful materials.

- Bentonites contains montmorilinite (\( \text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O} \)) and beidellite (\( \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O} \)). Al can be replaced wholly or partially by \( \text{Fe}^{3+} \) and it becomes \( 3\text{SiO}_2 \cdot \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O} \) (nontronite).
- The formula of montmorillonite is \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O} \). X-ray studies have shown that montmorillonite has the same structure as pyrophyllite. It adsorbs considerable amount of water which must be packed between these layers and so the whole structure shrinks on the dehydration or swells on adsorbing water. The unidimensional swelling and shrinkage are also found in nontronite.
- Halloysite contains alternating layers of hydrated silica \( \text{Si}_4\text{O}_{10} \cdot (\text{OH})_2 \), and of gibbsite \( \text{Al} \cdot (\text{OH})_3 \), and the formula is \( \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O} \).

**Talc:** It is formulated as \( \text{Mg}_2 \cdot (\text{OH})_2 \cdot (\text{SiO}_2)_n \), which consists of electrically neutral sheets and has no cations in between them. It is soft and smooth. It is chemically inert. It is used as a dry lubricant, in ceramics, paper manufacture and cosmetics.

**Caps:** Muscovite, \( \text{KAl}_3 \cdot (\text{OH})_2 \cdot (\text{Si}_{3} \cdot \text{AlO}_{10})_n \). Muscovite is an example of mica. It is obtained when one Si-atom in \( \text{Si}_4\text{O}_{10} \cdot (\text{OH})_2 \) ion is replaced by Al-atom. Thus we see, that in muscovite, the sheet composition is \( (\text{Si}_{3} \cdot \text{AlO}_{10})_n \). Two \( (\text{Si}_{3} \cdot \text{AlO}_{10})_n \) sheets, which have tetrahedral vertices inward, are linked by binding Al\(^{3+} \) cations, whose
octahedral coordination is completed by OH ions. The double sheets, which have
the composition, [Si₄Al₂O₁₀(OH)₂], are stacked one upon another with sufficient
number of K⁺ cations. These cations are located in between two such double
sheets and maintain electrical neutrality. The cleavage of mica is due to the weakening
of these layers of K⁺ ions. The binding Al³⁺ ions and the sandwiched K⁺ ions can
be replaced by Mg²⁺ and Na⁺ ions respectively.

Micas are often tough, elastic and transparent. These are chemically inert, stable
towards heat and have high dielectric constant. They are used in furnace
windows and electrical appliances. The powdered mica is used as a filler for
rubbers, plastics and in insulation boards.

10.3.6 Silicates with Three Dimensional Network

In these silicates, all the four O-atoms act as bridging atoms, i.e., in these silicates,
each SiO₄ tetrahedron shares all its four O-atoms with other SiO₄ tetrahedron.
This type of sharing gives three-dimensional silicates, corresponding to the
composition (SiO₂)n RO shown in Figure 10.10 as all the four oxygen atoms
serve as bridge atoms and there is no oxygen atom having negative charge i.e.
these silicates are neutral and are commonly known as silica.

Silica is a high-melting solid. It exists in three forms: quartz, tridymite and
cristobalite. Each of these forms has a different structure at high and low
temperatures.

<table>
<thead>
<tr>
<th>Low Temp.</th>
<th>α-quartz</th>
<th>α-tridymite</th>
<th>α-cristobalite</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑ 573°C</td>
<td>↑ 120 — 160°C</td>
<td>↑ 200 — 275°C</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>High Temp.</th>
<th>β-quartz</th>
<th>β-tridymite</th>
<th>β-cristobalite</th>
<th>β-cristobalite</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑ 1710°C</td>
<td>↓ 1350°C</td>
<td>↓ 1550°C</td>
<td>1710°C, liquid SiO₂</td>
<td></td>
</tr>
</tbody>
</table>

The difference between these structures is the arrangement of the tetrahedral
SiO₄ units. The relation between tridymite and cristobalite is the same as between
wurtzite and zinc blende. Quartz has a helical arrangement and since the screw
may be left or right handed, it has optical isomers too.

Replacement of Si⁴⁺ by Al³⁺ in tetrahedral positions in SiO₂ lattice requires
the presence of additional metal ion in the lattice, to preserve electrical neutrality.
Such isomorphism results in groups of important minerals called feldspars, zeolites
& ultramarines, which (excepting ultramarines) are among the most widespread,
diverse and useful silicate minerals in nature.
10.4 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. A silicate is any member of a family of anions consisting of silicon and oxygen, usually with the general formula \([SiO_{4-2x}) - 4-x])\), where \(0 \leq x < 2\).
2. There are two types of silicates, i.e., soluble and insoluble silicates.
3. Insoluble Silicates are naturally occurring mineral materials together with certain synthetic zeolite like compounds.
4. Ortho Silicates are obtained when \(SiO_4^{-}\) tetrahedra are discrete, i.e., no oxygen atoms belonging to one \(SiO_4^{-}\) tetrahedra is shared with that of the neighboring \(SiO_4^{-}\) tetrahedra.
5. Thortveitile is Scandium pyrosilicate \([Sc_2(Si, O_4)])\) in which scandium is trivalent and, therefore, six positive charges are present on two scandium atoms which are balanced by six negative charges present on the six oxygen atoms. The seventh oxygen atom forms the bridge between two \(SiO_4^{-}\) tetrahedra.
6. Sheet silicates are formed when three O-atoms (bridging O-atoms) of each \(SiO_4^{-}\) unit are shared.

10.5 SUMMARY

- A silicate is any member of a family of anions consisting of silicon and oxygen, usually with the general formula \([SiO_{4-2x}) - 4-x])\), where \(0 \leq x < 2\). The family includes orthosilicate \(SiO_4^{-}\) \((x = 0)\), metasilicate \(SiO_2-3\) \((x = 1)\), and pyrosilicate \(SiO_6-7\) \((x = 0.5, n = 2)\).
- The name is also used for any salt of such anions, such as sodium metasilicate; or any ester containing the corresponding chemical group, such as tetramethyl orthosilicate.
- Silicate anions are often large polymeric molecules with an extreme variety of structures, including chains and rings (as in polymeric metasilicate \([SiO_2-3])\), double chains (as in \([SiO_2-5])\) n, and sheets (as in \([Si 2O_2-5])\) n.
- Soluble silicates are derived mainly from alkali metals and have usually metal oxide, silica and water in their composition. These are generally obtained by fusion of silica with sodium carbonate at around 1000°C. These contain a variety of crystalline compounds like Na$_2$SiO$_3$, Na$_2$Si$_2$O$_5$, Na$_2$SiO$_4$, Na$_2$SiO$_5$, etc.
- Insoluble silicates are naturally occurring mineral materials together with certain synthetic zeolite like compounds.
- The electronegativity of oxygen is 3.5 and that of silicon is 1.8. The electronegativity difference (3.5 – 1.8) or 1.7 suggests that Si – O bond though covalent, has an appreciable degree of ionic character.
- The structure of all silicates is based on the formation of coordinate lattices of anions about cations. Generally, the cation is Si$^4^+$ and anion is generally O$^2^-$ ion. The anion (O$^2^-$), being of much large size than any of the cation present, mainly determines the dimensions and generally lays out the structure of silicates.
- The radius ratio Si$^4^+$: O$^2^-$ is 0.29 which suggests that the structures of silicates are based on four coordinate silicon, i.e., on the [SiO$_4$]$^4^-$ tetrahedron in which four oxygen atoms are arranged at the four corners of the tetrahedron with the silicon atom at the center.
- Thus, in all silicates the basic structural unit is [SiO$_4$]$^4^-$ tetrahedron in which Si – O bond distance is 1.62 Å and O – O bond distance is 2.70 Å. These SiO$_4^4^-$ tetrahedra condense together by sharing one or more oxygen atoms thus giving rise to different types of silicates. The SiO$_4^4^-$ units are formed by sp$^3$ hybridisation.
- Ortho silicates are obtained when SiO$_4^4^-$ tetrahedra are discrete, i.e., no oxygen atoms belonging to one SiO$_4^4^-$ tetrahedra is shared with that of the neighboring SiO$_4^4^-$ tetrahedra.
- A pyrosilicate is a type of chemical compound; either an ionic compound that contains the pyrosilicate anion SiO$_6^6^-$, or an organic compound with the hexavalent "OSi-O-SiO$_2^2^-$" group. The anion is also called disilicate or diorthosilicate.
- Thortveitite is Scandium pyrosilicate [Sc$_6$(SiO$_4$)$_3$] in which scandium is trivalent and, therefore, six positive charges are present on two scandium atoms which are balanced by six negative charges present on the six oxygen atoms. The seventh oxygen atom forms the bridge between two SiO$_4^4^-$ tetrahedra.
- Ring silicates have cyclic structure and contain [SiO$_4^4^-$]$^{20^+}$ ion as the primary unit. These silicates are formed when each SiO$_4^4^-$ tetrahedron shows two O-atoms (bridging O-atoms). The structures of cyclic ions viz., [SiO$_4^4^-$]$^{16^+}$ or Si$_2$O$_4^4^-$ and [SiO$_4^4^-$]$^{12^+}$ or Si$_4$O$_{14}^{12^-}$ ions.

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SILICATES

• Rings of these tetrahedra to give rise six-membered rings constraining the anion [Si\textsubscript{4}O\textsubscript{10}\textsuperscript{4-}]. They are encountered in benitoite BaTiSi\textsubscript{3}O\textsubscript{8} and wollastonite Ca\textsubscript{2}[Si\textsubscript{2}O\textsubscript{5}]\textsuperscript{3-}. The anion [Si\textsubscript{8}O\textsubscript{22}\textsuperscript{7-}], consisting of a ring of six tetrahedra is found in beryl, Be\textsubscript{3}Al\textsubscript{2}Si\textsubscript{3}O\textsubscript{18}.

• Talc is formulated as Mg\textsubscript{3}(OH)\textsubscript{2}(Si\textsubscript{2}O\textsubscript{5})\textsubscript{3}, which consists of electrically neutral sheets and has no cations in between them. It is soft and smooth. It is chemically inert. It is used as a dry lubricant, in ceramics, paper manufacture and cosmetics.

10.6 KEY WORDS

• Soluble silicates: Soluble silicates are derived mainly from alkali metals and have usually metal oxide, silica and water in their composition.

• Insoluble Silicates: Insoluble Silicates are naturally occurring mineral materials together with certain synthetic zeolite like compounds.

• Orthosilicate: Orthosilicate is the anion SiO\textsubscript{4}– 4, or any of its salts and esters. It is one of the silicate anions. It is occasionally called the silicon tetroxide anion or group.

• Pyrosilicate: A pyrosilicate is a type of chemical compound, either an ionic compound that contains the pyrosilicate anion SiO\textsubscript{6}– 6, or an organic compound with the hexavalent a"OSi-O-SiOa” group.

10.7 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions

1. Write a short note on silicates.
2. How are silicates formed?
3. How many types of silicates are there?
4. Write short note on structure of silicates.
5. What are orthosilicates?
6. Write a brief note on pyrosilicates.

Long Answer Questions

1. Give a detailed note on silicates writing about its formation, types and structure,
2. Give a detailed note on orthosilicates and its different types.
3. What are pyrosilicates? Explain with the help of examples.
4. Distinguish between chain and double chain silicates.
5. Give a descriptive note on sheet silicates and silicates with 3D network.

10.8 FURTHER READINGS

UNIT 11 SILICATES WITH FRAMEWORK STRUCTURES

11.0 INTRODUCTION

Silicates are compounds where Si and O are abundant and are major mineral components of the earth’s crust and mantle. The basic unit for all silicates is the (SiO4)4- tetrahedron. The variety of silicate minerals is produced by the (SiO4)4-tetrahedra linking to self-similar units sharing one, two, three, or all four corner oxygen of the tetrahedron. Since Si invariably occurs in tetrahedral coordination the fundamental unit of the silicate structure is the Si-O tetrahedra. The different types of silicate structure arise from the ways in which these tetrahedra are arranged: they may exist as separate unlinked entities, as linked finite arrays, as infinite 1-dimensional chains, as infinite 2-dimensional sheets or as infinite 3-dimensional frameworks. These possibilities give rise to the six primary structural types of silicates, each with a characteristic Si : O ratio.

Silicate minerals are salt-like crystalline materials with metal cations and various types of silicate anions. Each silicon atom in a silicate is tetrahedrally coordinated by oxygen atoms. The structure of feldspar is similar to that of the SiO2 polymorphs, consisting of an infinite network of tetrahedra inter-connected via bridging oxygen atoms.

In this unit, you will study about silicates with frame work structures, feldspar, zeolites, molecular sieves and clay minerals in detail.
11.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand about feldspar
- Discuss what zeolites are
- Explain molecular sieves
- Describe what clay minerals are

11.2 FELDSPARS

Feldspar is by far the most abundant group of minerals in the earth’s crust, forming about 60% of terrestrial rocks. Most deposits offer sodium feldspar as well as potassium feldspar and mixed feldspars. Feldspars are primarily used in industrial applications for their alumina and alkali content. The term feldspar encompasses a whole range of materials. Most of the products we use on a daily basis are made with feldspar; glass for drinking, glass for protection, fiberglass for insulation, the floor tiles and shower basins in our bathrooms, and the tableware from which we eat. Feldspar is part of our daily life (Refer Figure 11.1).

![Fig. 11.1 Feldspar](image)

Feldspar minerals are essential components in igneous, metamorphic and sedimentary rocks, to such an extent that the classification of a number of rocks is based upon feldspar content. The mineralogical composition of most feldspars can be expressed in terms of the ternary system Orthoclase (KA\textsubscript{Si3}O\textsubscript{8}), Albite (NaAl\textsubscript{Si3}O\textsubscript{8}) and Anorthite (CaAl\textsubscript{2}Si\textsubscript{2}O\textsubscript{8}). Chemically, the feldspars are silicates of aluminium, containing sodium, potassium, iron, calcium, or barium or combinations of these elements.

Feldspars are a group of rock-forming tectosilicate minerals that make up about 41% of the Earth’s continental crust by weight. These are also known as aluminosilicates almost 67% of igneous rocks are composed of feldspar minerals. Based on symmetry of structures, these are further classified into two groups, i.e.,

**Orthoclase Feldspars:** These possess monoclinic symmetry common examples include:
Silicates with Framework Structures

- Orthoclase $\text{KAlSi}_3\text{O}_8$
- Celsian $\text{BaAl}_2\text{Si}_2\text{O}_8$

**Plagioclase Feldspars**: These possess triclinic symmetry common examples include:

- Albite $\text{NaAlSi}_3\text{O}_8$
- Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$

Both ortho and palgios class feldspars possess different symmetries due to the difference of ionic radii of $\text{K}^+$, $\text{Ba}^+$, and $\text{Na}^+$ and $\text{Ca}^+$. In ortho-class feldspar, the ionic radii of barium and potassium cations are 1.35 Å and 1.33 Å respectively. These have just the right size to fit into the lattice. In palgio-class feldspars, the sizes of $\text{Na}^+$ and $\text{Ca}^+$ are 0.99 and 0.95 Å respectively. Their sizes are small and the frame work of silicate lattice contracts slightly around the $\text{Na}^{2+}$ and $\text{Ca}^+$ ions and thus permit distortion.

**Structure**: In the structures of the feldspars, there is a three-dimensional linked frame work (having negative charge) of $\text{SiO}_4$ and $\text{AlO}_4$ terahedra in which the cations $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$ or $\text{Ba}^{2+}$ are situated in the interstices of this framework the $(\text{Si}, \text{Al})\text{O}_4$ framework is built from the layers of tetrahedral which are placed at the points of the plane 4:8. The fourth apex of each tetra hedron is pointing either upward or downswords out of the plane of the paper. These layers are then joined through the projecting apices so that the adjacent layers are related by planes of symmetry.

**Applications of Feldspars**

- **Glass**: Feldspar is an important ingredient in the manufacture of glass and an important raw material as well, because it acts as a fluxing agent, reducing the melting temperature of quartz and helping to control the viscosity of glass. The alkali content in feldspar acts as flux, lowering the glass batch melting temperature and thus reducing production costs.

- **Ceramics**: In the manufacture of ceramics, feldspar is the second most important ingredient after clay. Feldspar does not have a strict melting point, since it melts gradually over a range of temperatures. This greatly facilitates the melting of quartz and clays and, through appropriate mixing, allows modulations of this important step of ceramic making. Feldspars are used as fluxing agents to form a glassy phase at low temperatures and as a source of alkalis and alumina in glazes. They improve the strength, toughness, and durability of the ceramic body, and cement the crystalline phase of other ingredients, softening, melting and wetting other batch constituents.

- **Fillers**: Feldspars also are used as fillers and extenders in applications such as paints, plastics and rubber. Beneficial properties of feldspars include good dispersability, high chemical inertness, stable pH, high resistance to abrasion, low viscosity at high filler loading, interesting refractive index and...
resistance to frosting. The products used in such applications are generally fine-milled grades.

- **Enamel Frits and Glazes**: Feldspar assists the enamel composition, assuring the absence of defects and the neatness of the end product: for example, enamel frits, ceramic glazes, ceramic tile glazes, sanitaryware, tableware, electrical porcelain and giftware.
- It is also used in other areas like paint, mild abrasives, urethane, welding electrodes (production of steel), latex foam, the welding of rod coating, and road aggregate.

### Check Your Progress
1. What is feldspar?
2. How is feldspar used in glasses?
3. What does Plagioclase Feldspars includes?

### 11.3 MOLECULAR SIEVES

Molecular sieves is a material with very small pores of uniform size. These pores diameters are similar in size to small molecules, and thus large molecules cannot enter or be adsorbed, while smaller molecules can. As a mixture of molecules migrate through the stationary bed of porous, semi-solid substance referred to as a sieve (or matrix), the components of highest molecular weight (which are unable to pass into the molecular pores) leave the bed first, followed by successively smaller molecules. Some molecular sieves are used in chromatography, a separation technique that sorts molecules based on their size. Other molecular sieves are used as desiccants (some examples include activated charcoal and silica gel). Figure 11.2 shows different types of molecular sieves.

![Fig. 11.2 Different Types of Molecular Sieves](image)
These materials are further classified as:

**Microporous Materials**: These materials have pore diameters of less than 20 Å or 2 nm. These include zeolites, porous glass, active carbon, clays, etc.

**Mesoporous Materials**: These materials have pore size 2-50 nm. Common example is silicon dioxide (SiO₂) used to make silicone gel having pore size of 2-4nm.

**Macroporous Materials**: These materials have pore size more than 50 nm. For example, meroporous silica of pose size 20-100 nm.

Applications of Molecular Sieves

- Molecular sieves are utilized in petroleum industry for drying gas streams. For example in LNG industry, the water content of the gas needs to be reduced to less than 1ppmv to prevent blockages caused by ice.
- In labs, these are used to dry solvents.
- Under the name zeolites, these are used for a wide range of catalytic applications. They catalyze isomerization, alkylation and epoxidation. These are used in large scale industrial processes like hydrocracking and fluid catalytic cracking.
- They are also used in the filtration of air supplies for breathing apparatus.
- Porous glass is ideal for material separation, because of their small pore size distribution. These are also used for dental implants.
- Meroporous silica nanoparticles have many applications in medicine, biosensors, thermal energy storage, etc.

**Check Your Progress**

4. What is molecular sieve?
5. What does microporous materials includes?
6. What are mesoporous materials?
7. What are macroporous materials?

### 11.4 Zeolites

These are the most important three dimensional aluminosilicates, made up of [(Si, Al)]O₉ networks. They possess much more open structure than feldspars and contain the cavities into which gases like CO₂, NH₃, etc. and liquids like water ethyl alcohol can enter and adsorb there. Thus, they act as molecular sieves. In zeolites, the cations move freely through the open pore structure and can be exchanged reversibly with other cations. Sodium ions in zeolites, for instance, can be exchanged for calcium ions in hard waters. This explains the use of these materials in water softening operations. Similarly, sodium zeolite like analcrite on
treatment with a solution of silver nitrate, the sodium is replaced by silver (Refer Figure 11.3).

\[ \text{Na[AlSi}_2\text{O}_5\cdot \text{H}_2\text{O} + \text{AgNO}_3 \leftrightarrow \text{Ag[AlSi}_2\text{O}_5\cdot \text{H}_2\text{O} + \text{NaNO}_3} \]

Fig. 11.3 Zeolite

There are three types of Zeolites:

First Type: This type consists of (Si Al)O₄ tetrahedra linked into four and six-membered rings which are joined together into a three-dimensional network as in analcime, NaAl₅Si₇O₂₂(OH)₂. In analcime, there is a complex arrangement of linked SiO₄ and AlO₄ tetrahedra, resulting in a comparatively large channels through the structure in which Na⁺ ions and water molecules could be accommodated.

Second Type: This type involves lamellar zeolites which consist of closely knit sheets of tetrahedral and cleaving into plates as in heulandites Ca₃[Al₂Si₄O₁₂]·12H₂O.

Third Type: This type is made up of fibrous zeolites in which chains of characteristic type can be distinguished. However, these chains are cross-linked to each other by comparatively few bonds, resulting in the crystal having a fibrous structure. Examples are Natrolite, Na₇Al₂Si₅O₁₆·2H₂O and Thomsonite NaCa₂Al₂Si₅O₁₆·6H₂O.

Application of Zeolites

- Softening of Water: The softening of water is done by permuit water softener which is sodium zeolite and produced artificially by heating a mixture of varying amounts of soda, alumina and silica. This permuit possesses the property of base exchange, i.e., by the replacement of sodium ions by other cations like Ca²⁺, Mg²⁺, etc. The base exchange reactions are reversible and attain a state of equilibrium when hard water is percolated through permuit, the calcium and magnesium ions causing hardness are taken up by the permuit in place of sodium ions which pass into solution. The resulting water thus contains sodium ions but is free from calcium and magnesium...
ions and is, therefore, soft water. The permutit is regenerated by treatment with sodium chloride when the reverse process takes place.

\[ \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot n\text{H}_2\text{O} + \text{CaSO}_4 \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot n\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 \]

\[ \text{Ca}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot n\text{H}_2\text{O} + 2\text{NaCl} \rightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot n\text{H}_2\text{O} + \text{CaCl}_2 \]

- **Separation of Gaseous Mixture**: Gases are also able to pass through the channels in zeolite crystal by a process which is a combination of diffusion and adsorption. For example, in modernite with sodium cations, the channels are of cross section 4.0 – 4.9Å. This substance occludes nitrogen (molecular diameter 3Å) and oxygen (molecular diameter 2.8 Å) rapidly, and methane and ethane only slowly, but it does not occlude hydrocarbons with greater cross sections. If, however, the sodium cations in modernite are replaced by calcium cations, the cross section of the channel is reduced to 3.8Å, and methane and ethane are no longer adsorbed. By choice of appropriate zeolites and appropriate conditions it is possible to bring about a complex separation of gases which would otherwise be separable only by rigorous fraction. For example, butane may be separated by isobutene.

- **Catalysis**: Zeolites are extremely useful as catalysts for several important reactions involving organic molecules. The most important are cracking, isomerisation and hydrocarbon synthesis. Zeolites can promote a diverse range of catalytic reactions including acid-base and metal induced reactions. Zeolites can also be acid catalysts and can be used as supports for active metals or reagents.

Zeolites can be shape-selective catalysts either by transition state selectivity or by exclusion of competing reactants on the basis of molecular diameter. They have also been used as oxidation catalysts. The reactions can take place within the pores of the zeolite, which allows a greater degree of product control.

The main industrial application areas are: petroleum refining, synfuels production, and petrochemical production. Synthetic zeolites are the most important catalysts in petrochemical refineries.

- **Adsorption**: Zeolites are used to adsorb a variety of materials. This includes applications in drying, purification, and separation. They can remove water to very low partial pressures and are very effective desiccants, with a capacity of up to more than 25% of their weight in water. They can remove volatile organic chemicals from air streams, separate isomers and mixtures of gases. A widely used property of zeolites is that of gas separation. The porous structure of zeolites can be used to ‘sieve’ molecules having certain dimensions and allow them to enter the pores. This property can be fine tuned by varying the structure by changing the size and number of cations around the pores. Other applications that can take place within the pore include polymerisation of semi conducting materials and conducting polymers to produce materials having unusual physical and electrical attributes.
• **Ion Exchange**: Hydrated cations within the zeolite pores are bound loosely to the zeolite framework, and can readily exchange with other cations when in aqueous media. Applications of this can be seen in water softening devices, and the use of zeolites in detergents and soaps. The largest volume use for zeolites is in detergent formulations where they have replaced phosphates as water-softening agents. They do this by exchanging the sodium in the zeolite for the calcium and magnesium present in the water. It is even possible to remove radioactive ions from contaminated water.

**Check Your Progress**

8. What are zeolites?
9. How is softening of water done?

### 11.5 CLAY MINERALS

Clay minerals are the characteristic minerals of the earths near surface environments. They form in soils and sediments, and by diagenetic and hydrothermal alteration of rocks. Water is essential for clay mineral formation and most clay minerals are described as hydrous alumino silicates. Structurally, the clay minerals are composed of planes of cations, arranged in sheets, which may be tetrahedrally or octahedrally coordinated (with oxygen), which in turn are arranged into layers often described as 2:1 if they involve units composed of two tetrahedral and one octahedral sheet or 1:1 if they involve units of alternating tetrahedral and octahedral sheets. Additionally some 2:1 clay minerals have interlayers sites between successive 2:1 units which may be occupied by interlayer cations, which are often hydrated. The planar structure of clay minerals give rise to characteristic platy habit of many and to perfect cleavage, as seen for example in larger hand specimens of micas (Refer Figure 11.4).

![Fig. 11.4 Clay Mineral](image-url)

The classification of the phyllosilicate clay minerals is based collectively, on the features of layer type (1:1 or 2:1), the dioctahedral or trioctahedral character...
of the octahedral sheets (i.e., 2 out of 3 or 3 out of 3 sites occupied), the magnitude of any net negative layer charge due to atomic substitutions, and the nature of the interlayer material.

**NOTES**

Clay minerals are produced by weathering and decomposition of igneous rocks. They are composed of very fine particles. For example, Kaoline (china clay) having the formula \( \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \) has a sheet structure, in which sheets are held together by OH bridges.

When clay is mixed with water, it becomes plastic—soft and mouldable. Water of plasticity can be removed by heating at 100°C. Clay becomes rigid and brittle when water of plasticity has been eliminated. On heating beyond 100°C, structural water of crystallization is removed and carbonaceous matter of the clay gets oxidized. At about 900°C, mullite (\( \text{Al}_2\text{SiO}_5 \)) begins to be formed. This new substance has glassy appearance. Clay is widely used in making chinaware, fire bricks and many other useful materials.

There are three main groups of clay minerals:

**Kaolinite:** It also includes dickite and nacrite; formed by the decomposition of orthoclase feldspar (for example, in granite); kaolinite is the principal constituent in china clay (Refer Figure 11.5).

![Fig. 11.5 Kaolinite](image)

**Illite:** It also includes glauconite (a green clay sand) and are the commonest clay minerals; formed by the decomposition of some micas and feldspars; predominant in marine clays and shales (Refer Figure 11.6).

![Fig. 11.6 Illite](image)
**Smectites or Montmorillonites:** It also includes bentonite and vermiculite; formed by the alteration of mafic igneous rocks rich in Ca and Mg; weak linkage by cations (for example, Na\(^+\), Ca\(^{2+}\)) results in high swelling/shrinking potential.

**Applications of Clay Minerals**

- **Filtering:** Clays are used to decolorize, filter, and purify animal, mineral, and vegetable oils and greases due to their high absorbing properties.
- **Environmental Sealants:** Bentonite is used to establish low permeability liners in landfills, sewage lagoons, water retention ponds, golf course ponds, and hazardous waste sites.
- **Pharmaceuticals/ Cosmetics:** Bentonite is used as a binder in tablet manufacturing and in diarrhea medications. Clays are used as thickeners in a wide variety of cosmetics including facial creams, lipsticks, shampoos and calamine lotion.
- **Pelletizing:** Bentonite is used to bind tiny particles of iron ore, which are then formed into pellets for use as feed material for blast furnaces.
- **Paints:** Finely ground clays are used in the paint industry to disperse pigment evenly throughout the paint. Without clays, it would be extremely difficult to evenly mix the paint base and color pigment.

<table>
<thead>
<tr>
<th>Check Your Progress</th>
</tr>
</thead>
<tbody>
<tr>
<td>10. What are clay minerals?</td>
</tr>
<tr>
<td>11. What does kaolinite include?</td>
</tr>
<tr>
<td>12. What does smectites include?</td>
</tr>
</tbody>
</table>

### 11.6 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. **Feldspars** are a group of rock-forming tectosilicate minerals that make up about 41% of the Earth’s continental crust by weight. These are also known as aluminosilicates almost 67% of igneous rocks are composed of feldspar minerals.

2. **Feldspar** is an important ingredient in the manufacture of glass and an important raw material as well, because it acts as a fluxing agent, reducing the melting temperature of quartz and helping to control the viscosity of glass. The alkali content in feldspar acts as flux, lowering the glass batch melting temperature and thus reducing production costs.

3. **Plagioclase** Feldspars possess triclinic symmetry common examples include:
   - Albite NaAlSi\(_3\)O\(_8\)
   - Anorthite CaAl\(_2\)Si\(_2\)O\(_8\)
4. Molecular sieves is a material with very small pores of uniform size. These pore diameters are similar in size to small molecules, and thus large molecules cannot enter or be adsorbed, while smaller molecules can.

5. Microporous materials are the materials that have pore diameters of less than 20 Å or 2 nm. These include zeolites, porous glass, active carbon, clays, etc.

6. Meso porous materials are the materials having pore size 2-50 nm. Common example is silicon dioxide (SiO₂) used to make silicone gel having pore size of 2-4 nm.

7. Meso porous materials are the materials having pore size more than 50 nm. For example, mesoporous silica of pore size 20-100 nm.

8. Zeolites are the most important three dimensional aluminosilicates, made up of ([Si, Al]₆O₁₈)₆ networks. They possess much more open structure them feldspars and contain the cavities into which gases like CO₂, NH₃, etc. and liquids like water ethyl alcohol can enter and adsorbed there.

9. The softening of water is done by permutit water softener which is sodium zeolite and produced artificially by heating a mixture of varying amounts of soda, alumina and silica. This permutit possesses the property of base exchange, i.e., by the replacement of its sodium ions by other cations like Ca²⁺, Mg²⁺, etc.

10. Clay minerals are the characteristic minerals of the earths near surface environments. They form in soils and sediments, and by diagenetic and hydrothermal alteration of rocks.

11. Kaolinite includes dickite and nacrite; formed by the decomposition of orthoclase feldspar (for example, in granite); kaolinite is the principal constituent in china clay.

12. Smectites or montmorillonites includes bentonite and vermiculite; formed by the alteration of mafic igneous rocks rich in Ca and Mg; weak linkage by cations (for example, Na⁺, Ca++) results in high swelling or shrinking potential.

11.7 SUMMARY

- Feldspar is by far the most abundant group of minerals in the earth’s crust, forming about 60% of terrestrial rocks. Most deposits offer sodium feldspar as well as potassium feldspar and mixed feldspars.

- Feldspars are primarily used in industrial applications for their alumina and alkali content. The term feldspar encompasses a whole range of materials.

- Most of the products we use on a daily basis are made with feldspar: glass for drinking, glass for protection, fiberglass for insulation, the floor tiles and shower basins in our bathrooms, and the tableware from which we eat.
• Feldspar minerals are essential components in igneous, metamorphic and sedimentary rocks, to such an extent that the classification of a number of rocks is based upon feldspar content.

• The mineralogical composition of most feldspars can be expressed in terms of the ternary system Orthoclase (KAlSi3O8), Albite (NaAlSi3O8) and Anorthite (CaAl2Si2O8). Chemically, the feldspars are silicates of aluminium, containing sodium, potassium, iron, calcium, or barium or combinations of these elements.

• Feldspar is an important ingredient in the manufacture of glass and an important raw material as well, because it acts as a fluxing agent, reducing the melting temperature of quartz and helping to control the viscosity of glass.

• The alkali content in feldspar acts as flux, lowering the glass batch melting temperature and thus reducing production costs.

• Feldspars also are used as fillers and extenders in applications such as paints, plastics and rubber. Beneficial properties of feldspars include good dispersability, high chemical inertness, stable pH, high resistance to abrasion, low viscosity at high filler loading, interesting refractive index and resistance to frosting.

• Molecular sieves is a material with very small pores of uniform size. These pores are similar in size to small molecules, and thus large molecules cannot enter or be adsorbed, while smaller molecules can.

• As a mixture of molecules migrate through the stationary bed of porous, semi-solid substance referred to as a sieve (or matrix), the components of highest molecular weight (which are unable to pass into the molecular pores) leave the bed first, followed by successively smaller molecules.

• Some molecular sieves are used in chromatography, a separation technique that sorts molecules based on their size. Other molecular sieves are used as desiccants (some examples include activated charcoal and silica gel).

• Clay minerals are the characteristic minerals of the earths near surface environments. They form in soils and sediments, and by diagenetic and hydrothermal alteration of rocks. Water is essential for clay mineral formation and many clay minerals are described as hydrous aluminosilicates.

• Structurally, the clay minerals are composed of planes of cations, arranged in sheets, which may be tetrahedrally or octahedrally coordinated (with oxygen), which in turn are arranged into layers often described as 2:1 if they involve units composed of two tetrahedral and one octahedral sheet or 1:1 if they involve units of alternating tetrahedral and octahedral sheets.

Silicates with Framework Structures

NOTES
11.8 KEY WORDS

- **Zeolites**: Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents and catalysts.
- **Molecular sieve**: A molecular sieve is a material with pores of uniform size. These pore diameters are similar in size to small molecules, and thus large molecules cannot enter or be adsorbed, while smaller molecules can.
- **Feldspars**: Feldspars are a group of rock-forming tectosilicate minerals that make up about 41% of the Earth’s continental crust by weight.
- **Orthoclase**: Orthoclase, or orthoclase feldspar, is an important tectosilicate mineral which forms igneous rock.
- **Celsian**: Celsian is an uncommon feldspar mineral, barium aluminosilicate, BaAl, Si, O−. The mineral occurs in contact metamorphic rocks with significant barium content.
- **Albite**: Albite is a plagioclase feldspar mineral. It is the sodium endmember of the plagioclase solid solution series.
- **Microporous material**: A microporous material is a material containing pores with diameters less than 2 nm. Examples of microporous materials include zeolites and metal-organic frameworks.

11.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

**Short Answer Questions**

1. Write a short note on feldspar.
2. What is the structure of feldspar?
3. Write a short note on applications of molecular sieves.
4. Write short note on types of zeolites.
5. How does adsorption occur in zeolites?
6. Write the applications of clay minerals.

**Long Answer Questions**

1. Explain about feldspar in detail mentioning its structure and applications.
2. Give a detailed note on molecular sieve writing about its different types and applications.
3. What are zeolites? Explain about its different types and applications.
4. Elaborate a note on clay minerals mentioning about its different groups and applications.
11.10 FURTHER READINGS


UNIT 12 CRYSTAL STRUCTURE OF SOLIDS

12.0 Introduction
12.1 Objectives
12.2 Crystal Structure of Solids
  12.2.1 Elements of Crystal Symmetry
12.3 The Space Lattice and Unit Cell
  12.3.1 Lattice Point
12.4 Packing of Ions in Ionic Crystals
12.5 Interstitial Sites or Voids in Ionic Crystals
  12.5.1 Types of Interstitial Sites
  12.5.2 Size of the Interstitial Sites
  12.5.3 Range of Radius Ratio Values of a Coordination Number
  12.5.4 Effect of Radius Ratio on the Structure of Ionic Crystals
12.6 Structure of Ionic Crystals
  12.6.1 Structure of Ionic Compounds of the Type Ax
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12.0 INTRODUCTION

A crystalline structure is any structure of ions, molecules, or atoms that are held together in an ordered, three-dimensional arrangement. Crystalline structure is one of two types of structural ordering of atoms, the other being the amorphous structure. The key difference in the crystalline and amorphous structure is the ordering of the structure. Crystalline structure can be thought of as the highest level of order that can exist in a material, while an amorphous structure is irregular and lacks the repeating pattern of a crystal lattice.

Simply, the crystal structure can be thought of as a small box with atoms, molecules, or ions located in specific areas of the box. The atoms within this box represent the smallest group of repeating atoms in the entire molecule. That means each atom found in the small box continues to repeat on and on in the same
connectivity throughout the entire compound. The general arrangement and order of the atoms in the structure are directly related to the natural properties of the crystal. The crystalline structure is unique and specific for each material. That is to say, there will be no other compound organized in exactly the same way as any other. Essentially, the crystalline structure is the ‘identification marker’ for the compound.

In this unit, you will study about the crystal structure of solids, close packing of atoms and ions, HCP, FCC and BCC types of solids, calculation of packing voids, radius ratio rule, classification of ionic structures, etc. in detail.

12.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the close packing of atoms and molecules - HCP, FCC and BCC
- Calculate the packing voids
- Explain the classification of ionic structures
- Discuss about layer structures

12.2 CRYSTAL STRUCTURE OF SOLIDS

Solids have both definite shape and volume. There are characterized by rigidity, in compressibility, slow diffusion and chemical strength. These characteristics are because the constituent particles (atoms, molecules or ions) are closely packed and held together by strong attractive forces.

Classification of Solids

Solids may be classified in following ways:

- **True Solids and Pseudo Solids**: True solids have definite shape and volume and do not lose their shape and volume on standing. There are rigid and have sharp melting point. Common examples include solids like NaCl, KCl, Fe, Cu sugar, etc.

- **Pseudo Solids**: They do not have definite shape and volume and are less rigid. These melt over a range of temperature and common examples are glass and pitch.

- **Crystalline Solids or Amorphous Solids**: In crystalline solids, the constituent particles (atom, molecules or ions) are arranged in three dimensional space in a definite and regular manner. For example, NaCl Diamond, Sugar, Sulphur etc., whereas, in Amorphous Pseudo Solids, the constituent particles (atom, molecules or ions) are not arranged in a regular manner, for examples, rubbers, glass, fused silica, etc.
Crystal Structure of Solids

- **Polycrystalline Solids**: There are the solids which occur as powder and resemble amorphous solids, but their individual particles have all the characteristics of crystalline solids.

**NOTES**

### 12.2.1 Elements of Crystal Symmetry

All the crystals of the same substance possess the same elements of symmetry. Three elements of symmetry are discussed below:

- **Plane of Symmetry**: It is an imaginary plane which can divide the crystal into two halves such that one is the image of the other. A cubic crystal for example, has two types of plane of symmetry.

- **Rectangular Plane of Symmetry**: There are the planes situated midway and parallel to the opposite faces. Since a cubic crystal has six faces, i.e., three pairs of opposite faces, so it has three rectangular plane of symmetry as shown in Figure 12.1.

- **Diagonal Plane of Symmetry**: There are the planes touching the opposite edges. Since there are 12 edges or six pairs of opposite edges in a cubic crystal, so six diagonal planes of symmetry in a cubic crystal. One plane passing diagonally through the cubic crystal in shown in Figure 12.1.

![Figure 12.1 Plane of Symmetry](image)

(a) Rectangular Plane of Symmetry (three)  (b) Diagonal Plane of Symmetry (six)

**Centre of Symmetry**

In a such an imaginary point within the crystal that if a straight line is drawn through it, it will meet the surfaces of the crystal at equal distances on each side of point. The centre of symmetry in cubical crystal like NaCl has been shown by A in Figure 12.2

![Figure 12.2 Centre and Axis of Symmetry in a Crystal](image)

(a) Centre of symmetry in a cubical crystal  (b) Axis of two-fold symmetry (six)  (c) Axis of three-fold symmetry (Plane)
Axis of Symmetry

It is such an imaginary line within the crystal that if the crystal is rotated about this line, the crystal will have the same appearance more than once during the course of a complete rotation. A cubical crystal like NaCl can have in all 13 axes of symmetry. These are:

- **Six Axes Of Two-Fold Symmetry**: Each of these six axes is called *diad axis*. When the crystal is rotated about any of these axes, it presents the same appearance two times in a complete rotation. Each of these three axes intersects at the middle points of the two opposite edges of the cube.

- **Four Axes Of Three-Fold Symmetry**: Each of these axes is called *triax axis*. When the crystal is rotated about any of these axes, it presents the same appearance three times in a complete rotation. Each of these four axes intersects at the two opposite solid angles (i.e., corners) of the cube.

- **Three Axes Of Four-Fold Symmetry**: Each of these three axes is called *tetraed axis*. When the crystal is rotated about any of these axes, it presents the same appearance four times in a complete rotation. Each of these three axes intersects at the middle points of the two opposite faces of a cube. All the three axes are at right angles to one another.

### Check Your Progress

1. What are true solids and pseudo solids?
2. What is plane of symmetry?

### 12.3 THE SPACE LATTICE AND UNIT CELL

The regular arrangement of an infinite set of points (atoms, molecules or ions) in space is called a lattice or space lattice. The space lattice may be one, two or three dimensional depending upon the number of parameters required to define it. (Refer Table 12.1 and Fig. 12.3)

<table>
<thead>
<tr>
<th>Type of lattice</th>
<th>Repeat distances</th>
<th>Interfacial angles</th>
<th>No. of parameters required for defining the lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Dimensional</td>
<td>$a, b$</td>
<td>$\gamma$</td>
<td>One repeat distance two repeat distances and an interfacial angle</td>
</tr>
<tr>
<td>2. Dimensional</td>
<td>$a, b, c$</td>
<td>$\alpha, \beta, \gamma$</td>
<td>Three repeat distances and three interfacial angles</td>
</tr>
<tr>
<td>3. Dimensional</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
NOTES

Fig. 12.3 Three Types of Lattices
It is important to note that in a lattice it is the arrangement of points and not the
lines joining them; lines are used simply to present the complete shape. Thus a
space lattice with reference to crystal may be defined as an array of points showing
the arrangement of constituents in three dimensional space.

- **Unit cell**: The smallest repeating pattern (unit) from which the lattice is built
is known as a **unit cell**. The unit cells are repeated over and over again in
three dimensions and result into the whole of the space lattice of the crystal.
Thus the unit cell, in fact, is the smallest sample that represents the picture of
the entire crystal. The crystal may, therefore, be considered to consist of
infinite number of unit cells.

- The space lattice (an array of points in a three dimensional space) and the
unit cell (marked by bold lines) are shown in Figure 12.4.

Fig. 12.4 Space Lattice and Unit Cell
Always remember that it is points and not lines which represent the space lattice.
The lines drawn represent three area which describe the relative positions of the
points.

For describing a unit cell, we must know

- The distances a, b and c, i.e., the lengths of the edges of unit cell
- The angle, α, β and γ between the three imaginary axes.
Broadly speaking, the shape of a unit cell may be of following types.

- **Simple or Primitive**: In this type, points (i.e., atoms, ions or molecules) are present only at the corners of the unit cell.
- **Face Centered**: In this type, points are present at the corners as well as at the centre of each of the six faces.
- **Body Centered**: In this type, points are present at the corners and an additional point is present at the centre of the unit cell.
- **End Face Centered**: In this type, points are present at the corners and at the centre of the two ends (Refer Figure 12.5)

![Figure 11.5 Four Types of Unit Cells](image)

The 14 Bravais lattices may belong to either of the above mentioned four types of unit cells.

### 12.3.1 Lattice Point

The points represents the atoms, molecules or ions in a unit cell are known as lattice points. In the various unit cells, there are three kinds of lattice points.

- Points located at the corners of a unit cell. Since such point lies at the corner of a unit cell, it is shared between eight such unit cells. Thus only $1/8$th part of each such point contributes to any one cell.
- Points located at the centre of a face of a unit cell. Since such point is shared between two such cells, only $1/2$ of each such point contributes to any cell.
- Points located at the centre of the unit cell. This point, being present entirely within a unit cell, wholly belongs to this unit cell.

Thus the total number of lattice points (or number of atoms) per unit cell in the four types of unit cells may be calculated as below:

- Simple or primitive: $8 \times \frac{1}{8} = 1$
- Face-centered: $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$
- Body-centered: $8 \times \frac{1}{8} + 1 = 2$
- End centered: In addition to 8 points present on the corners, such unit cell also has points only on the end (two faces). Since each point of the latter type is
shared between two unit cells, it contributes to $\frac{1}{2}$ to each unit cell. Such points are present only in end face-centered unit cells. Thus the number of atoms per unit cell

$$\text{NOTES} \quad 8\times\frac{1}{8}+2\times\frac{1}{2} = 2.$$  

The number of atoms belonging to unit cell is also termed lattice sites and is denoted by $Z$. The number of particles immediately adjacent to each particle in the crystal lattice is known as the coordination number for that lattice. It is characteristic of a given lattice. In a simple cubic lattice, each particles is adjoined by 6 other particles and so the coordination number of a simple cubic lattice is 6. Similarly, the coordination number for body centered and face centered cubic lattices are 8 and 12 respectively.

**Check Your Progress**

3. What is unit cell?
4. What is primitive unit cell?
5. What happens in face centered unit cell?

### 12.4 PACKING OF IONS IN IONIC CRYSTALS

Most of the metal ions crystallize in one of the three common structures:

- Hexagonal Close Packed (HCP)
- Cubic Close Packed (CCP)
- Body Centered Cubic Packed (BCP)

**Hexagonal Close Packed (HCP) Structure**: In this arrangement, atoms are located at the corners and centre of two hexagons placed parallel to each other, three move atoms are placed in a parallel plane midway between these two planes. The hexagonal close-packed arrangement has following salient features:

![Fig. 12.6 AB. AB, System of Close Packing of Spheres or Hexagonal Close Packing (HCP) of Shapes](image)
Here each atom is surrounded by 12 others and is said to have co-ordination number of 12.

It has a 6-fold of symmetry.

This type of packing gives the arrangement of the layers as AB AB AB ... which indicates that odd numbered layers as well as even numbered layers are alike.

The HCP arrangement of atoms occupy 74% of the available space and thus has 26% vacant space.

It has only one set of parallel close-packed layers. Hence the chances for slipping of one layer over the other are less in the HCP structure that in the CCP structure having four equivalent sets of parallel planes, known as diagonal planes.

**Cubic Close Packed (CCP) or Face Centered Cubic (FCC):** In this structure atoms are arranged at the corners and at the centers of all the six faces of a cube.

![Fig. 12.7 Cubic Close-Packing Arrangement](image)

The cubic close packed structure has following salient features.

- As in HCP, each atom in CCP arrangements has 12 nearest neighbours. In other words, the co-ordination number of the atom is 12 as the central atom of a layer is surrounded by six atoms in its own layer and by three atoms each form the layers at the top and at the bottom. It touches all these atoms hence the co-ordination number of the central atom is $6 + 3 + 3$, i.e., 12.
- It has cubic symmetry, i.e., the whole structure has four 3-fold axis of symmetry.
- This type of packing gives the arrangement of the layers as ABC ABC ABC, i.e., the first three layers do not resemble each other but the fourth, fifth and sixth layers resemble first, second and third respectively and the sequence is repeated with the addition of more layers.
- The CCP arrangement of atoms occupy 74% of the available space and thus has 26% vacant space.
- It has hour sets of parallel close packed layers. Hence the chances for slipping of one layer over the other are more in the CCP arrangement that in
the HCP arrangement. Hence metals having CCP structure (for example, Cu, Ag, Au and Pt) are highly malleable and ductile.

Cubic Close Packed structure is found in Al, Cr, Co, Cu, Au, Ag, Fe, Pb, Mn, Ni, Ca and Sr. Nearly 60 percent of the metals have been found to possess either HCP or CCP structure.

**Body Centered Cubic (BCC):** This arrangement of spheres (or atoms) is not exactly close packed. This structure can be obtained if spheres in the first layer (A) of close packing are slightly opened up. As a result none of these spheres are in contact with each other. The second layer of spheres (B) may be placed on top of the first layer so that each sphere of the second layer is in contact with four spheres of the layer below it. Successive building of the third layer will be exactly like the first layer. If the pattern of building layers is repeated infinitely we get an arrangement as shown in Figure 12.8 (a)

![Figure 12.8 (a) Body-centered Cubic Packing of Spheres.](image)

**Figure 12.8 (a) Body-centered Cubic Packing of Spheres.**

**Figure 12.8 (b) Body-centered Cubic Arrangement**

Body Centered Cubic arrangement has following salient features

- In a Body Centered Cubic arrangement, the atoms occupy corners of a cube with an atom at its centre. Thus each atom is in contact with eight other atoms (four atoms in the layer just above and four atoms in the layer just below) and hence the coordination number in this type of arrangement is six.
- This arrangement of atoms is not exactly close packed, and only 68% of the total volume is actually occupied.
- This type of arrangement is found in Na, K, Cs, Rb, W, V, Mo and Ba.
- Nearly 60% of the metals have been found to possess either hexagonal close-packed or cubic close-packed structure; while 20% of the metallic elements possess BCC arrangement. It is important to note that several metals can exist in more than one form, for example, Cr, Fe, Li and Mn can possess BCC or FCC arrangement; Ca can form HCP as well as BCC and FCC packing.
### Table 12.2 Summary of Structure of Metals

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Property</th>
<th>Hexagonal Close Packed (HCP)</th>
<th>Cubic Close Packed (CCP)</th>
<th>Body Centered Cubic (BCC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Arrangement of packing</td>
<td>Close packed</td>
<td>Close packed</td>
<td>Not close packed</td>
</tr>
<tr>
<td>2.</td>
<td>Type of packing</td>
<td>AB AB AB A…</td>
<td>ABC ABC A…</td>
<td>AB AB AB A…</td>
</tr>
<tr>
<td>3.</td>
<td>Available space occupied</td>
<td>74%</td>
<td>75%</td>
<td>68%</td>
</tr>
<tr>
<td>4.</td>
<td>Coordination number</td>
<td>12</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>5.</td>
<td>Malleability and ductility</td>
<td>Less malleable, hard and brittle</td>
<td>Malleable and ductile</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Examples</td>
<td>Be, Mg, Ca, Cr, Mo, V, Zn</td>
<td>Cu, Au, Al, Pt</td>
<td>Alkali metals, Fe</td>
</tr>
</tbody>
</table>

### 12.5 INTERSTITIAL SITES OR VOIDS IN IONIC CRYSTALS

An ionic crystal consists of cations and anions. Generally, the cation is smaller in size than the anion. The bigger ions (ions) have closed packed structures which may be hexagonal closest packed (HCP) or cubical closest packed (CCP). In close-packed structure some vacant space is left between the anions. This vacant space is called interstitial site or interstitial void or interstitial hole.

#### 12.5.1 Types of Interstitial Sites

Depending on the number of the anions and the way in which they surround a cation in a given ionic crystal, we have the following four types of interstitial sites: trigonal or triangular site (coordination number of cation = 3), tetrahedral site (C.N. of cation = 4), octahedral site (C.N. of cation = 6) and cubic site (C.N. of cation = 8).

#### Number of Tetrahedral Voids for each Sphere in a FCC Unit Cell (CCP Arrangement)

In close packing arrangement each sphere in the second layer rests on the hollow (triangular void) in the three touching spheres in the first layer. The centre of these four spheres are at the corners of a regular tetrahedron. The vacant space between these four touching spheres is called tetrahedral void.
Let us consider a face-centered cubic unit cell shown in Figure 12.9. Obviously, in this unit cell, one sphere is placed at each of the 8 corners and one sphere is present at the centre of each of the six faces of the cube. We have already said that the total number of spheres present in the face-centered cubic unit cell.

\[
\begin{align*}
= \text{No. of spheres contributed by 8 spheres placed at the eight corners.} \\
+ \text{No. of sphere contributed by 6 spheres placed at the centre of the six faces.}
\end{align*}
\]

\[
8 \times 1 + 6 \times \frac{1}{2} = 1 + 3 = 4
\]

The face-centered cubic unit cell, shown in Figure 12.9, can be divided into eight small cubes. One of the eight small cubes has been shown as ABCDEFGH (cube shown by dark lines). Four spheres, namely A, C, G and F, which are situated at the alternate corners of the small cube, form a tetrahedron. Fifth sphere (J) placed at the centre of the cube or tetrahedron, occupies the tetrahedral site, created by the four spheres (A, C, G and F). Thus, we see that the small cube (ABCDEFGH) has one tetrahedral site. Now, since the entire face-centered cubic unit cell is divided into 8 small cubes, the total number of tetrahedral holes present in the entire unit cell is equal to \(8 \times 1 = 8\). Now:

- No. of tetrahedral holes for a sphere present in the unit cell = 8
- No. of tetrahedral holes for one sphere present in the unit cell = \(\frac{8}{4} = 2\)

or No. of tetrahedral holes for \(N\) spheres present in the unit cell = \(2N\)

\[\text{Fig. 12.9 Determination of Number of Tetrahedral Sites (holes) for each Sphere present in a Face-Centered Cubic Unit Cell}\]

Thus, we see that every sphere present in a face-centered cubic unit cell (also called cubic close-packed (CCP) structure- has two tetrahedral sites. For example, since in the structure of zinc blend (ZnS) crystal, \(S^2^-\) ions are present at each of the 8 corners and at the centre of each of the 6 faces (i.e., \(S^2^-\) ions have FCC or CCP arrangement), there are two tetrahedral sites for every \(S^2^-\) ion.

Number of octahedral voids for each sphere in a FCC unit cell
The interstitial void formed by combination of two triangular voids of first and second layer is called octahedral void because this is enclosed between six spheres, centers of which occupy corners of a regular octahedron.

Let us consider a face-centered cubic unit cell (cubic close packed) shown in Figure 12.10. In this figure M denotes an intersection point at which the lines joining six spheres (A, B, C, D, E and F) situated at the centre of the six faces of the cubic unit cell intersect. This point is not occupied by any sphere and is surrounded octahedral by six spheres, since the six spheres are placed at the six corners of an octahedron, this point, therefore, becomes the octahedral hole, when all the six spheres touch each other. Thus we see that the unit cell has one octahedral hole (intersection point, M) at its centre. In addition to the intersection point M (octahedral hole), the centre of each of the 12 edges of the unit cell also has an intersection point. Now since each edge is shared by 4 adjacent unit cell, the actual number of intersection (or octahedral holes) contributed by each edge = \( \frac{1}{4} \) and hence the total number or intersections (octahedral holes) contributed by 12 edges in equal to \( 12 \times \frac{1}{4} = 3 \). Thus:

Total number of octahedral holes present in the entire face-centered cubic unit cell = No of octahedral holes situated at the centre of the unit cell + No. of octahedral holes contribute by 12 edges of the unit cell = 1 + 3 = 4.

Now, we know that the total number of spheres present in the face-centered cubic unit cell = 4. Hence:

- No. of octahedral holes for 4 spheres present in the unit cell = 4
- No. of octahedral holes for 1 spheres present in the unit cell = \( \frac{4}{4} = 1 \)
- No. of octahedral holes for N spheres present in the unit cell = 1N

![Figure 12.10 Determination of Number of Octahedral Holes for each Sphere present in a Face-Centered Cubic Unit Cell](image-url)
example, since, in the structure of NaCl crystal, Cl⁻ ions are situated at the 8 corners and at the centre of each of the six faces (i.e., Cl⁻ ions have FCC as CCP arrangement), there is only one octahedral site for every Cl⁻ ion, i.e., there is only one Na⁺ ion for every Cl⁻ ion. The above discussion shows that the number of octahedral sites (or holes) present in the face-centered cubic unit cell (=4). The above study shows that the total number of octahedral holes created by the cubic close packed arrangement of anions is equal to the number of anions. For example, since the number of Cl⁻ ions in the unit cell of NaCl crystal is 4 and all these anions have close-packed arrangement, the number of octahedral holes in this closed-packed arrangement of Cl⁻ ions is also equal to 4.

### 12.5.2 Size of the Interstitial Sites

As described earlier, the interstitial site left in between the closely packed anions is an ionic crystal is occupied by a cation. The radius of the cation occupying the interstitial site is considered as the size of site under consideration.

**Radius Ratio Value (r<sub>c</sub> / r<sub>a</sub>)**

We know that size of a given site created by the anions (in an ionic crystal) is the radius of the cation (r<sub>c</sub>) occupying the given site. The value of r<sub>c</sub> is calculated in terms of radius ratio value and is given by ratio of the radius of the cation (r<sub>c</sub>) to that of the anions (r<sub>a</sub>) which create the interstitial site. We shall now calculate r<sub>c</sub>/r<sub>a</sub> value for each of the four sites mentioned above.

**Trigonal Site (CN of cation = 3):** A vacant space formed when three spheres representing anions are placed at the corners of an equilateral triangle is known as trigonal site. This site is occupied by a cation is an ionic crystal and the radius of the cation is the size (radius) of the trigonal site.

In order to calculate the size of trigonal site, let us consider the unit cell of an ionic crystal having triangular (trigonal) structure. In this crystal the coordination number of the cation is three, i.e., each cation is surrounded by three anions (trigonal arrangement of three anions round the central cation). Although the three anions are closely packed with each other (i.e., these ions touch each other), some empty space is left between them. The empty space, as we have already mentioned, is called trigonal or triangular site. This space (or site) is occupied by the central cation. The radius of this cation is called the size (radius) of the trigonal site. How this trigonal site is formed has been shown in Figure 12.11 which shows that the anions (represented by bigger spheres having negative sign) lie at the vertices of the equilateral triangle EBC and the cation (represented by a smaller sphere with a positive sign) is situated at the centre of AEB. Under this condition we say that the cation is occupying the trigonal site. In Figure 12.11, for the sake of simplicity, the cations and anions have been shown not touching each other. Actually the cations and anions are touching one another, i.e., cation anion and anion-anion contacts are present in the ionic crystal.
Now let \( r_a \) and \( r_b \) be the radii of the cation and anion respectively. It is obvious from the figure that:

- In equilateral \( \Delta EBC \), \( bE = BC = CE = r_a + r_b = 2r_b \). Also \( AF = r_a \), \( BF = r_a \) and \( BD = r_a \).
- Since \( A \) is the centre of \( \Delta EBC \) (or \( A \) is the centre of the cation) and the cation is touching all the three anions, \( AB = AF + BF = r_a + r_a \).

Now in right angled \( \Delta ABD \), \( \angle BDA = 90^\circ \) and \( \angle ABD = 30^\circ \) and hence

\[
\cos 30^\circ = \frac{BD}{AB} = \frac{r_a}{r_a + r_b} \quad \text{or} \quad \frac{\sqrt{3}}{2} = \frac{r_b}{r_a + r_b}
\]

or,

\[
\frac{2}{\sqrt{3}} = \frac{r_b}{r_a + r_b} = \frac{r_b}{r_a} \quad \text{or} \quad \frac{2}{\sqrt{3}} = 0.155
\]

This value indicates that the radius ratio value for a cation to fit into a trigonal site should not be less than 0.155, i.e., the lowest value of radius ratio for a cation having CN 3 (trigonal site) is 0.155.

**Tetrahedral (CN of cation = 4):** Consider three spheres, \( A \), \( B \) and \( C \) touching each other and placed in the source plane (Refer Figure 12.12). Now let us place another sphere, \( D \) (shown by dotted) on the centre of the triangle obtained by joining the centers of three sphere. A small empty space is left at one point only where the four spheres touch each other. This small space is denoted by \( E \) and is called tetrahedral site.

---

**Fig. 12.12** A tetrahedral Site (E). All the Four Spheres (A, B C and D) Touch each other and are of the Same Size
In the unit cell of an ionic crystal having CN 4 (ZnS type structure), a tetrahedral site can be created within the tetrahedron obtained by placing the four anions (i.e., four spheres A, B, C and D) at the alternate corners of a cube in such a way that they touch each other. A tetrahedral site is created at the centre of tetrahedron (ABCD) as shown is Figure 12.13. The cation (E) shown by the smaller sphere with positive charge is placed at the centre of the tetrahedron.

Fig. 11.13: Tetrahedral arrangement (ABCD) is the tetrahedron) of four anions (represented by bigger spheres having negative sign) around a cation, E (shown by smaller sphere with a positive sign) in an ionic crystal having zinc blende (Zns) type structure. All the anions namely A, B, C and D touch each other and have the same size (radius).

Since the center of the tetrahedron, center of the cube and the center of the body diagonal (BF) lies at the same point, the cation (E) is said to be placed at the center of the body diagonal or at the center of the tetrahedron. Under the condition we say that the cation is occupying the tetrahedral site. Thus we see that the name ‘tetrahedral site’ is used to indicate that the arrangement of the four anions (A, B, C and D) around the cation (E) is tetrahedral. Tetrahedral site, therefore, does not mean that the shape of the site is tetrahedral. The most stable arrangement of the ions present in the ionic crystal is that in which all the four anions placed at the corners of the cube touch each other as well as the cation put at the centre of the cube.

Now if \( a \) is the length of each side of the cube, then, as we know,

- Face diagonal, \( AB = \sqrt{3}a \)
- and Body diagonal, \( BF = \sqrt{5}a \)

Now, since the anions namely A and B touch each other,
\[ r + r_c = \text{Face diagonal} = \sqrt{3}a \]

or \[ 2r = \sqrt{3}a \]

or \[ r_c = \frac{\sqrt{3}}{2}a = \frac{a}{\sqrt{2}} \] \( \ldots(\text{i}) \)

Now, since the cation (E) lies at the center of body diagonal \((BF')\) and touches the anion (B),

\[ r_e + r_c = \frac{1}{2} \times BF \quad \text{or} \quad r_e + r_c = \frac{1}{2} \times \sqrt{3}a = \frac{\sqrt{3}}{2}a \]

\( \ldots(\text{ii}) \)

On dividing equation (ii) by (i), we get:

\[ \frac{r_e + r_c}{r_c} = \frac{\sqrt{3}}{2} \times \frac{\sqrt{3}}{\sqrt{2}} = 1.255 \]

or \[ 1 + \frac{r_e}{r_c} = 1.255 \]

or \[ \frac{r_e}{r_c} = 1.255 - 1 = 0.255 \]

This value indicates that the radius ratio value for a cation to fit into a tetrahedral site should not be less than 0.255.

**Octahedral Site (CN of cation = 6):** Consider three spheres A, B and C lying in one plane and the dotted three spheres D, E and F placed on them in the second layer as shown in Fig. 11.14. When the centers of A, B and C are joined together, we get a triangle. Similarly, another triangle shown by dotted lines is obtained in the other layer, when the centers of dotted spheres are joined. When these two triangles which lie in different layer are superimposed one above the other, we get an octahedron, shown by a cross (\( \ast \)) in Figure 12.14 The apices of these two triangles point in opposite direction, so an octahedral site is created between the six spheres placed at the six vertices of a regular octahedron.

![Figure 12.14 Formation of an Octahedral Hole (site) Between Six Spheres. All the Six Spheres are of the Same Size (radius)](image)
Fig. 12.15 Octahedral Arrangement of Six Anions (represented by Bigger Spheres with Negative Signs) Around a Cation, G (shown by smaller sphere with a positive sign) in an Ionic Crystal Having NaCl Type Structure. All the Six Anions have the Same Size (radius)

A similar octahedral site is created in NaCl by placing the six anions shown as the bigger spheres with negative sign at the centre of the six faces of a cube, as shown in Figure 12.15. The four anions namely A, B, C and D lie at the four corners of the square plane, one anion (E) lies above the one anion (F) lies below the square plane. Octahedral site is created at the center of the square plane containing the four anions.

The cation (shown by a smaller sphere with a positive sign) is placed at the centre of the square. Under this condition, we say that the cation (G) is occupying the octahedral site created by the six anions placed at the six vertices of an octahedron. Here the cation is surrounded octahedral by six anions. For the sake of simplicity, the cation and the six anions have been shown not touching each other. Actually they touch one another so that the most stable structure may be given to the ionic crystal.

In order to calculate the value of $r_A/r_G$ for an octahedral site, let us consider only the square plane of the octahedron, which contains four anions (A, B, C and D) at its four corners and one cation (G) at its center (octahedral site) (Fig. 11.16). Let $r_A$ and $r_G$ be the radii of the cation and each of the anions respectively. All the four anions touch each other and the cation simultaneously; the value of $r_A/r_G$ (radius ratio) can be calculated by simple geometry as shown below. Let X and Z be the centers of the cation (G) and the anion (D) respectively. Let Y be the point at which the two anions viz. C and D touch each other. Now join the points X, Y and Z to get the right angled XYZ, in which XYZ = 90° and XZY = 45°.

Now since the central cation (G) is touching all the four anions, XZ = XP + PZ = $r_A + r_G$.

Fig. 12.16 A Cross Section through an Octahedral Site
Only four anions (A, B, C, D) and the central cation (G) lying in the square of the octahedron have been shown. Here, \(XP = r_1\), \(PZ = YZ = r_1\), \(XZ = r_1 + r_e\), \(\angle XZY = 45^\circ\) and \(\angle XYZ = 90^\circ\).

Now, \(\cos 45^\circ = \frac{YZ}{AX} = \frac{r_e}{r_1 + r_e}\)

or \(\frac{1}{\sqrt{2}} = \frac{r_e}{r_1 + r_e}\)

or \(\sqrt{2} \cdot \frac{r_e + r_1}{r_e} = \frac{r_e}{r_e} + 1\)

or \(\frac{r_e}{r_e} = \sqrt{2} - 1 = 1.414 - 1 = 0.414\)

Thus the radius ratio value for a cation to fit into octahedral site should not be less than 0.414.

Cubic Site (CN of Cation = 8): Consider an ionic crystal having CN of cation eight such as CsCl. Since the CN of cation and anion is eight, i.e., each ion is surrounded by 8 ions of opposite change. The cubic arrangement of 8 anions is obtained by placing the 8 anions at the eight corners of a cube in such way that they touch each other and the cation is put at the body centre of the cube (Refer Figure 12.17). In this condition, the cation is said to occupy the cubic interstitial site left is between the eight anions.

\[\text{Fig. 12.17 Cubic Arrangement of Eight Anions}\]

The above figure represents cubic arrangement of eight anions (represented by bigger spheres having negative sign) round a cation (shown by smaller sphere with a positive sign) in an ionic crystal having caesium chloride (CsCl) type structure. All the eight anions have the same size (radius.).

Suppose the length of each side of the cube is \(a\) and \(r_e\) and \(r_1\) are the radii of the cation and anion respectively. Since the anions A and B touch each other,

\[AB = a = r_e + r_1 = 2r_e \text{ or } r_e = \frac{a}{2}\]  \(\ldots (i)\)

We know that:

Body diagonal, \(AC = \sqrt{3a}\)
Crystal Structure of Solids

Now, since the cation lies at the centre of the body diagonal AC and touches both the anions viz, A and C,

\[ AC = r_i + 2r_j = 2r_i + 2r_j \]

or \( \sqrt{3}a = 2r_i + 2r_j \) or \( r_i + r_j \)

\[ = \frac{\sqrt{3}a}{2} \]...

(ii)

On dividing equation (ii) by (i), we get:

\[ \frac{\sqrt{3}a}{2} \frac{2}{a} \frac{r_i}{r_j} + 1 = \sqrt{3} \text{ or } \frac{r_i}{r_j} - 1 = 0.732 \]

This value indicates that the radius ratio value for a cation to fit into a cubic site should not be less 0.732, i.e., the lowest value of radius ratio for a cation having CN = 8 (cubic site) is 0.732.

12.5.3 Range of Radius Ratio Values of a Coordination Number

From the discussions in the above section it is clear that the lowest value of radius ratio \( (r_i/r_j) \) for an ionic crystal having trigonal (CN = 3), tetrahedral (CN = 4), Octahedral (CN = 6) and cubic (CN = 8) geometry is 0.155, -0.255, 0.414 and 0.732 respectively; the range of radius ratio values for different geometries of ionic crystals is shown in Table 12.3.

<table>
<thead>
<tr>
<th>Range of Radius Ratio ((r_i/r_j))</th>
<th>C.N. of the Cation in Ionic Crystal</th>
<th>Arrangement of Anions Round the Cation (Geometry of IOnic Crystal)</th>
<th>Examples of Ionic Crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.155 – 0.225</td>
<td>3</td>
<td>Planar trigonal</td>
<td>Boron oxide, BO(_3^+), BN</td>
</tr>
<tr>
<td>0.225 – 0.414</td>
<td>4</td>
<td>Tetrahedral</td>
<td>Ionic crystals having zinc blende (ZnS) type structure (e.g. ZnO, CuCl, CuBr, CuS) SiO(_2^+)</td>
</tr>
<tr>
<td>-0.414 – 0.732</td>
<td>6</td>
<td>Octahedral</td>
<td>Ionic crystals having rock salt (NaCl) type structure (e.g. AgF, AgCl, AgBr).</td>
</tr>
<tr>
<td>0.732 – 1.000</td>
<td>8</td>
<td>Cubic</td>
<td>Ionic crystals having cesium chloride (CsCl) type structure (e.g. CsBr, CsI, TICl, TiBr).</td>
</tr>
</tbody>
</table>

12.5.4 Effect of Radius Ratio on the Structure of Ionic Crystals

Consider an ionic crystal in which a cation occupies the octahedral site created by six closely packed anions as shown in Figure 12.18. In figure, only four anions placed at the four corners of the square base of the octahedron are shown for the sake of simplicity. The anions lying above and below the square base have not been shown in the figure. The cation is situated at the centre of the square base and hence occupies the octahedral site.
Since the anions are closely packed, the anions touch one another and the cation simultaneously and hence $r_+/r_-$ value lies in the range 0.414 – 0.732. Now let us consider the following two cases:

![Diagram showing the effect of the change in the value of $r_+/r_-$ on the coordination number or the structure of the ionic crystal.]

**Fig 12.18 Effect of the Change in the Value of $r_+/r_-$ on the Coordination Number or the Structure of the Ionic Crystal**

If we decrease the radius of the cation, the value of $r_+/r_-$ ratio also decreases and the four anions touch one another but are not able to touch the cation as they do in structure (a). In order to make the anions to touch the cation, the anions will have to come closer and closer to each other and, therefore, the repulsion between them will increase. The increase in the repulsion between the anions will make structure (a) unstable. In order to get a stable structure, we will have to push away one or more anions so that the remaining anions touch the cation and a more stable structure is obtained. In other words, we can say that in order to get a stable structure, we will have to decrease the coordination number of the cation from 6 to 4. With the change of coordination number of the cation, the geometry of the ionic crystal will also change from octahedral to tetrahedral.

If we increase the radius of the cation, the value of $r_+/r_-$ ratio also increases and the four anions touch the cation but are not able to touch one another as they do in structure (a), since they go away from each other. If the value of $r_+/r_-$ ratio is further increased, the anions go farther and farther apart and structure (a) becomes unstable. In order to make the anions to touch one another, more anions have to be accommodated between the four anions. So the coordination number of the central cation may increase from 6 to 8.

So, we may conclude that the decrease or increase in the value of $r_+/r_-$ ratio changes the coordination number of the cation and hence changes the structure of ionic crystals.
12.6 STRUCTURE OF IONIC CRYSTALS

Ions in a crystal should be arranged in such a way that forces of attraction are maximum and the forces of repulsion are minimum. Hence, for maximum stability the oppositely charged ions should be as close as possible and similarly changed ions as far away as possible from one another.

Depending upon the relative number of positive and negative ions present in ionic compounds, it is convenient to divide them into groups like AX, AX₂, AX₃, etc.

11.6.1 Structure of Ionic Compounds of the Type AX

Ionic compounds of the type AX have three types of crystalline structures:

**Sodium Chloride (Rock Salt) Type Structure:** The sodium chloride structure consists of Na⁺ and Cl⁻ ions. The number of sodium and chloride are equal and ratio of their ions is:

\[
\frac{r_{Na^+}}{r_{Cl^-}} = \frac{95 \text{ pm}}{181 \text{ pm}} = 0.524
\]

The radius ratio of 0.524 for NaCl suggests an octahedral void. Thus the salient features of this structure are as follows:

- Chloride ions (being larger in size) are arranged in cubic close packing (CCP) manner. In this arrangement, Cl⁻ ions are present at the corners and at the centre of each face of the cube. Recall that this arrangement is also regarded as face centered cubic arrangement.
- The sodium ions are present in all the octahedral holes.
- Since the number of octahedral holes in ccp structure is equal to the number of anions, every octahedral hole is occupied by Na⁺ ion so that the formula of sodium chloride is NaCl, i.e., the stoichiometry of NaCl is 1 : 1.
- Since there are six octahedral holes around each chloride ion, each Cl⁻ ion is surrounded by 6 Na⁺ ions. Similarly, each Na⁺ ion is surrounded by 6 Cl⁻ ions. Therefore the coordination number of Cl⁻ as well as of Na⁺ ion is six. This is called 6 : 6 coordination.
- It should be noted that for Na⁺ ions to exactly fit the octahedral holes, the radius ratio \( \frac{r_{Na^+}}{r_{Cl^-}} \) should be equal to 0.414. However, the actual radius
ratio \( \frac{r_{Na^+}}{r_{Cl^-}} = 0.524 \) exceeds this value. Therefore, to accommodate larger Na\(^+\) ions, the Cl\(^-\) ions move apart (opens up) slightly, i.e., they do not touch each other and form an expanded face centered lattice.

**Fig. 11.19 Unit cell Representation of NaCl Structure**

The unit cell of sodium chloride has 4 sodium ions and 4 chloride ions as calculated below:

Calculation of number of Na\(^+\) ions. It is clear from Figure 12.19 that there are 12 Na\(^+\) ions on the edges and one in the centre of the cell. Further, each Na\(^+\) ion on the edge is shared by four unit cells and thus its contribution per unit cell is \( \frac{1}{4} \), while each ion at the body centre contributes only to one unit cell and thus its contribution to unit cell is 1.

Total number of Na\(^+\) ions per unit cell = \( \left( \frac{1}{4} \times 12 \right) + 1 \times 1 = 3 + 1 = 4 \)

Calculation of Number of Cl\(^-\) ions. From Figure 12.19 it is obvious that there are 8 chloride ions at the corners and 6 at the faces of the unit cell. Further, it can be seen that each Cl\(^-\) ion at the corner is shared between eight unit cells and thus its contribution to one unit cell is \( \frac{1}{8} \). Similarly, each Cl\(^-\) ion on a face is shared by two unit cells, hence its contribution to one unit cell is \( \frac{1}{2} \).

Total number of Cl\(^-\) ions per unit cell = \( \left( \frac{1}{8} \times 8 \right) + \left( 6 \times \frac{1}{2} \right) = 1 + 3 = 4 \)

Thus, the number of NaCl units per unit cell is 4. This type of structure is exhibited by most of the alkali metal halides, alkaline earth oxides earth oxides and sulphides, NH\(_2\)Cl, NH\(_2\)Br, NH\(_2\)I, AgC, AgBr and AgI.
Ferrous oxide also has sodium chloride type structure in which O\(^2\) ions are arranged in ccp and Fe\(^{3+}\) ions occupy octahedral holes. However, this oxide is always non-stoichiometric and has the composition Fe\(_{\text{avg}}^{3+}\); it can be explained on the assumption that some of the Fe\(^{3+}\) ions are replaced by Fe\(^{2+}\) ions.

**Zinc Blende (Zns) Type Structure**

The zinc sulphide crystals are composed of equal number of Zn\(^{2+}\) and S\(^{2-}\) ions. The radii of the two ions (Zn\(^{2+}\) = 74 pm and S\(^{2-}\) = 184 pm) led to the radius ratio (\(r/r'\)) as 0.40 which suggest a tetrahedral arrangement.

\[
\frac{r_{\text{Zn}}}{r_{\text{S}^2-}} = \frac{74 \text{ pm}}{184 \text{ pm}} = 0.40
\]

The unit cell of zinc blende structure is shown in Figure 12.20. The salient features of this structure are as follows:

- The sulphide ions are arranged in ccp arrangement, i.e., sulphide ions are present at the corners and at the centre of each face of the cube.

![Zinc Blende Structure](image)

**Fig. 12.20 Unit Cell Representation of Zinc Blende Structure**

The Zn\(^{2+}\) ions occupy tetrahedral holes.

In a close packed lattice since there are two tetrahedral holes per atom (ion), only half of the tetrahedral holes are occupied by Zn\(^{2+}\) ions so that the formula of zinc sulphide is ZnS; i.e., the stoichiometry of the compound is 1 : 1.

Note that only alternate tetrahedral holes are occupied by Zn\(^{2+}\).

Since the void is tetrahedral, each zinc ion present in the void is surrounded tetrahedrally by 4 sulphide ions and each sulphide ion is surrounded tetrahedrally by 4 zinc ions. Thus the co-ordination number of Zn\(^{2+}\) and S\(^{2-}\) ions in zinc blende is 4. This is called 4 : 4 co-ordination.

For exact fitting of Zn\(^{2+}\) in the tetrahedral holes of the closely packed arrangement of S\(^{2-}\) ions, the radius ratio \(\frac{r_{\text{Zn}}}{r_{\text{S}^2-}}\) should be 0.225. However, the actual (larger) radius ratio value (0.40) points out that the arrangement of S\(^{2-}\) ions is not actually close packed.
There are four Zn$^{2+}$ ions and four S$^{2-}$ ions is not actually close packed. There are four Zn$^{2+}$ ions and four S$^{2-}$ ions per unit cell as calculated below:

No. of S$^{2-}$ ions = \( \left( \frac{1}{8} \right) \times \left( \frac{1}{2} \right) = 1 + 3 = 4 \)

No. of Sn$^{2+}$ ions = 4 (within the body) \times 1 = 4

Therefore, the number of zinc sulphide units in a unit cell of zinc sulphide is four.

Some more examples of ionic solids having the zinc blende structure are CuCl, CuBr, CuI, silver iodide and beryllium sulphide.

**The Wurtzite Structure:** It is an alternative form in which zinc sulphide occurs in nature. The unit cell of Wurtzite structure is shown in Figure 12.21.

![Fig. 11.21 Unit Cell Representation of Wurtzite Structure.](image)

The structure of Wurtzite is very similar to the structure of zinc blende. The only difference is in the arrangement of close-packed layers of S$^{2-}$ ions. In zinc blende, the S$^{2-}$ ions are arranged in ccp type of packing (i.e., there is ABC ABC … sequence of layers) while in Wurtzite S$^{2-}$ ions are arranged in HCP (Hexagonal Close-Packed) manner (i.e., there is ABABA … sequence of layers).

Other examples of this type of structure are ZnO, CdS, AlN, NH$_3$F, AgI, BeO, etc.

**The Structure Of Cesium Chloride:** The cesium chloride crystal is composed of equal number of cesium ions, Cs$^+$ and chloride ions, Cl$^-$. The radii of the two ions (Cs$^+$ = 160 pm, and Cl$^-$ = 181 pm) led to radius ratio of \( r_{Cs^+} \) to \( r_{Cl^-} \) as 0.884 which suggests:

\[
\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{160 \text{ pm}}{181 \text{ pm}} = 0.884
\]

A body centered cubic structure having a cubic hole, the unit cell of cesium chloride is shown in Figure 12.22. The salient features of this structure are as follows.
The chloride ions form the simple cubic arrangement and the cesium ions occupy the cubic interstitial holes. In other words, the Cl⁻ ions may be regarded as lying at the corners of a cube and the cesium ions are present at the body centre of each cube.

Each cesium ion is surrounded by 8 chloride ions and each chloride ion is surrounded by 8 cesium ions. Thus the co-ordination number of each ion is eight.

It may be noted that the structure of CsCl is usually described as Body Centered Cube (BCC). But actually it is a misnomer because the body centered cubic structure is one which has the same atoms at the corners as well as at the body centre of the cube.

For exact fitting of Cs⁺ ions in the cubic voids, the radius ratio \( \frac{r_{Cl^-}}{r_{Cs^+}} \) should be equal to 0.732. However, the actual value (0.884) indicates that packing of Cl⁻ ions slightly opens up to accommodate Cs⁺ ions.

The unit cell of CsCl has one Cs⁺ ion and one Cl⁻ ion as calculated below.

No. of Cl⁻ ions = 8 (at corners) \( \times \frac{1}{8} = 1 \)

No. of Cs⁺ ions = 1 (at the body centre) \( \times 1 = 1 \)

Thus the number of CsCl units per unit cell is 1.

Other common examples of this type of structure are CsBr, CsI, TiCl and TiBr.

Higher coordination number in CsCl (8:8) suggests that the cesium chloride lattice is more stable than the sodium chloride lattice in which coordination number is 6:6. Actually, the cesium chloride lattice is found to be 15 more stable than the sodium chloride lattice. Then the question arises why NaCl and other similar compounds do not have CsCl-type lattice. This is due to their smaller radius ratio. Any attempt to pack 8 anions around the relatively smaller cation (Li⁺, Na⁺, K⁺ and Rb⁺) will produce a state in which negative ions will touch each other sooner than they approach a positive ion. This causes instability to the lattice.
12.6.2 Structure of Ionic Compounds of Type $AX_2$

**Fluorite Structure (Calcium Fluoride)**

The unit cell or calcium chloride is shown in Figure 12.23. The salient features of fluorite structure are as follows:

- The Ca$^{2+}$ ions are arranged in CCP arrangement, i.e. these ions occupy all the corners and centres of each face of the cube. Recall that this arrangement is also called FCC arrangement.
- The F$^-$ ions occupy all the tetrahedral holes.
- Since there are two tetrahedral sites for each Ca$^{2+}$ ion; and F$^-$ ions occupy all the tetrahedral holes, there will be two F$^-$ ions for each Ca$^{2+}$ ion, thus, the stoichiometry of the compound is $1:2$.
- Each Ca$^{2+}$ ion is surrounded by 8 F$^-$ ions for each F$^-$ ion is surrounded by 4 Ca$^{2+}$ ions. The co-ordination number of Ca$^{2+}$ ion is eight and that of F$^-$ ion is four; this is called $8:4$ arrangement.
- Each unit cell has 4 calcium ions and 8 fluoride ions as explained below:

  \[
  \text{No. of Ca}^{2+} \text{ ions} = \left[ 8 \text{ (at corners)} \times \frac{1}{8} \right] + \left[ 6 \text{ (at face centres)} \times \frac{1}{2} \right] = 1 + 3 = 4 \\
  \text{No. of F}^- \text{ ions} = 8 \text{ (within the body)} \times 1 = 8 \\
  \]

  Thus the number of CaF$_2$ units per unit cell is 4. Other examples of this type of structure are SrF$_2$, BaF$_2$, HgF$_2$, PbF$_2$, CuF$_2$, SrCl$_2$, BaCl$_2$, etc.

![Fig. 12.23 Unit Cell Representation of Calcium Fluoride](image)

**NOTES**

**Rutile Structure (Titanium dioxide, TiO$_2$)**

The unit cell of the crystal of TiO$_2$ is shown in Figure 12.24 circles with positive sign represent. Ti$^4+$ ions while the circles having negative sign represent oxide ions ($O^{2-}$). The crystal structure of TiO$_2$ molecule can be discussed under the following headings:
NOTES

**Fig. 12.24** Crystal Structure of Titanium Dioxide TiO₂ (Rutile structure). Circles with Positive Sign Represent Ti⁺⁺ Ions and those with Negative Signs Represent O⁻⁻ Ions

Arrangement of Ti⁺⁺ and O⁻⁻ ions in the unit cell. Ti⁺⁺ ions are present at all the eight corners and at the body centre of a distorted cube. The cube is distorted because one of the axis of the cube is shorter than the other by 30%. Therefore, we can say that Ti⁺⁺ ions have a body-centered distorted cubic arrangement. Oxide ions (O⁻⁻ ions) occupy positions of three fold coordination.

Coordination number of Ti⁺⁺ and O⁻⁻ ions. It may be seen from the figure that each Ti⁺⁺ ion is surrounded octahedrally by 6 O⁻⁻ ions and each O⁻⁻ ion is surrounded by three Ti⁺⁺ ions which are disposed towards the corners of an equilateral triangle. Thus the coordination numbers of Ti⁺⁺ and O⁻⁻ ions are 6 and 3 respectively, i.e., TiO₂ crystal is a 6 : 3 ionic crystal.

**Beta Cristobalite Structure**

The mineral B-cristobalite is a high temperature polymorph of silica. this means that it has the same chemical formula as quartz, SiO₂, but a distinct crystal structure. Cristobalite occurs as while octahedral in acidic volcano rocks (Refer Figure 12.25).

**Fig. 11.25** B-cristobalite structure

Silica SiO₂ exists in six different crystalline forms as quartz, cristobalite and tridymite, each with an α and β form. B-cristobalite is related to zinc blende, with two interpenetrating close-packed lattices, one lattice arising from Si occupying
the S⁺ positions, and the other lattice from Si occupying the Zn²⁺ positions (i.e.,
the tetrahedral holes in the first lattice). The oxygen atoms lie midway between the
Si atoms, but are shifted slightly off the line joining the Si atoms, so the bond angle
Si–O–Si is not 180°. The radius ratio predicts a coordination number of 4, and
this is a 4 : 2 structure.

Check Your Progress
10. What does sodium chloride structure consists of?
11. What does zinc sulphide crystals composed of?

12.7 LAYER STRUCTURES

Cadmium Iodide, CdI$_2$

It is a chemical compound of formed with cadmium and iodine, notable for its
crystal structures with strong polarization effects. In CdI$_2$, the iodide ions form a
HCP packed arrangement while the cadmium cation fill all the octahedral sites in
the alternate layers. The structure thus formed law layered lattice. This same
structure is forms in many other salts and minerals. It is mostly ironically bonded
but with partial covalent character.

The radius ratio for CdI$_2$ is 0.45, and this indicates a coordination number
of 6 for cadmium. The structure is made up of electrically neutral layers of Cd²⁺
ions with layers of I⁻ ions on either side – rather like a sandwich where a layer of
Cd²⁺ corresponds to the mass in the middle, and layers of I⁻ correspond to the
bread on either side. this is called a layer structure, and it is not a completely
regular ionic structure. In CdI$_2$, two sheets of I⁻ ions are separated by Cd²⁺ and
two I⁻ layers are in contact. Whilst there is strong electrostatic bonding between
Cd²⁺ and I⁻ layers, there are only weak van der Walls forces holding the adjacent
layers of I⁻ together. The packing of layers in the crystal structure is not completely
regular, and the solid is flaky, and it cleaves into two parallel sheets quite easily.
In cadmium iodide, the third layer of I⁻ ions is directly above the first layer, so the
repeating pattern is ABABAB… The I⁻ ion may be regarded as an approximately
hexagonal close packed arrangement. The Cd²⁺ ions occupy half of the octahedral
sites. Rather than half filling the octahedral sites in a regular way throughout the
whole structure, all of the octahedral sites are filled between two I⁻ layers, and
none of the octahedral sites is filled between the next two layers of I⁻ ions. All of
the octahedral holes are filled between the next two layers of I⁻ ions, none between
the next pair, and so on (Refer Figure 12.26).
NOTES

**Fig. 12.26** Part of Two Layers of Cadmium Iodide (CdI₂) Structure

**Nickel Arsenide (NiAs) Structure**

In nickel arsenide structure, the arsenic atoms form a hexagonal close packed type of lattice with the Ni atoms occupying all the octahedral sites between all the layers of arsenic atoms.

In the nickel arsenide structure each atom has six nearest neighbours of the other type of atom. Each arsenic atom is surrounded by six nickel atoms at the corners of a trigonal prism. Each nickel atom is surrounded octahedrally by six arsenic atoms, but with two more nickel atoms sufficiently close to be bonded to the original nickel atom. This structure is adopted by many transition elements combined with one of the heavier elements from the p-block (Sn, As, Sb, Bi, S, Se, Te) in various alloys. These are better regarded as intermetallic phase rather than true compounds. They are opaque, have metallic luster, and sometimes have a variable composition (Refer Figure 12.27).

**Fig. 12.27** Nickel Arsenide Structure.

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**Check Your Progress**

12. What is cadmium iodide?
13. What is nickel arsenide?
12.8 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. True solids have definite shape and volume and do not lose their shape and volume on standing. There are rigid and have sharp melting point. Common examples include solids like NaCl, KCl, Fe, Cu sugar, etc.; on the other hand pseudo solids do not have definite shape and volume and are less rigid. These melt over a range of temperature and common examples are glass and pitch.

2. Plane of symmetry is an imaginary plane which can divide the crystal into two halves such that one is the image of the other. A cubic crystal for example, has two types of plane of symmetry.

3. The smallest repeating pattern (unit) from which the lattice is built is known as a unit cell.

4. In simple or primitive unit cell the points (i.e., atoms, ions or molecules) are present only at the corners of the unit cell.

5. In face centered unit cell the type, points are present at the corners as well as at the centre of each of the six faces.

6. Hexagonal Close Packed (HCP), Cubic Close Packed (CCP), Body Centered Cubic (BCC).

7. In a Body Centered Cubic arrangement, the atoms occupy corners of a cube with an atom at its centre. Thus each atom is in contact with eight other atoms (four atoms in the layer just above and four atoms in the layer just below) and hence the coordination number in this type of arrangement in only eight.

8. Trigonal site (CN of cation = 3) is a vacant space formed when three spheres representing anions are placed at the corners of an equilateral triangle is known as trigonal site; this site is occupied by a cation is an ionic crystal and the radius of the cation is the size (radius) of the trigonal site.

9. Cubic site (CN of Cation = 8) is consider an ionic crystal having CN of cation eight such as CoCl₂. Since the CN of cation and anion is eight, i.e., each ions is surrounded by 8 ions of opposite change, the cubic arrangement of 8 anions is obtained by placing the 8 anions at the eight corners of a cube in such way that they touch each other and the cation is put at the body centre of the cube.

10. The sodium chloride structure consists of Na⁺ and Cl⁻ ions.

11. The zinc sulphide crystals are composed of equal number of Zn²⁺ and S²⁻ ions. The radii of the two ions (Zn²⁺ = 74 pm and S²⁻ - 184 pm) led to the radius ratio (r⁺/r⁻) as 0.40 which suggest a tetrahedral arrangement.
12. Cadmium Iodide, CdI₂, is a chemical compound of formed with cadmium and iodine, notable for its crystal structures with strong polarization effects. In CdI₂, the iodide ions form a HCP packed arrangement while the cadmium cation fill all the octahedral sites in the alternate layers.

13. In nickel arsenide structure, the arsenic atoms form a hexagonal close packed type of lattice with the Ni atoms occupying all the octahedral sites between all the layers of arsenic atoms.

12.9 SUMMARY

- Solids have both definite shape and volume. There are characterized by rigidity, in compressibility, slow diffusion and chemical strength. These characteristics are because the constituent particles (atoms, molecules or ions) are closely packed and held together by strong attractive forces.
- True solids have definite shape and volume and do not lose their shape and volume an standing. There are rigid and have sharp melting point. Common examples include solids like NaCl, KCl, Fe, Cu sugar, etc.
- Pseudo solids do not have definite shape and volume and are less rigid. These melt over a range of temperature and common examples are glass and pitch.
- Polycrystalline solids are the solids which occur as powder and resemble amorphous solids, but their individual particles have all the characteristics of crystalline solids.
- Plane of symmetry is an imaginary plane which can divide the crystal into two halves such that one is the image of the other. A cubic crystal for example, has two types of plane of symmetry.
- Rectangular plane of symmetry are the planes situated midway and parallel to the opposite faces. Since a cubic crystal has six faces, i.e., three pairs of opposite faces, so it has three rectangular plane of symmetry.
- Axis of symmetry is such an imaginary line within the crystal that if the crystal is rotated about this line, the crystal will have the same appearance more than once during the course of a complete rotation. A cubical crystal like NaCl can have in all 13 axes of symmetry.
- The smallest repeating pattern (unit) from which the lattice is built is known as a unit cell.
- The unit cells are repeated over and over again in three dimensions and result into the whole of the space lattice of the crystal. Thus the unit cell, in fact, is the smallest sample that represents the picture of the entire crystal.
- Points located at the corners of a unit cell. since such point lies at the corner of a unit cell, it is shared between eight such unit cells. thus only 1/8th part of each such point contributes to any one cell.
• In Hexagonal Close Packed (HCP) structure atoms are located at the corners and centre of two hexagons placed parallel to each other, three move atoms are placed in a parallel plane midway between these two planes.
• In Cubic Close Packed (CCP) or Face Centered Cubic (FCC) structure atoms are arranged at the corners and at the centers of all the six faces of a cube.
• It has hour sets of parallel close packed layers. Hence the chances for slipping of one layer over the other are more in the CCP arrangement that in the HCP arrangement. Hence metals having CCP structure (for example, Cu, Ag, Au and Pt) are highly malleable and ductile.
• In Body Centered Cubic (BCC) arrangement of spheres (or atoms) is not exactly close packed. This structure can be obtained if spheres in the first layer (A) of close packing are slightly opened up.
• As a result none of these spheres are in contact with each other. The second layer of spheres (B) may be placed on top of the first layer so that each sphere of the second layer is in contact with four spheres of the layer below it. Successive building of the third layer will be exactly like the first layer.
• Ions in a crystal should be arranged in such a way that forces of attraction are maximum and the forces of repulsion are minimum. Hence, for maximum stability the oppositely charged ions should be as close as possible and similarly changed ions as for away as possible from one another.
• In nickel arsenide structure, the arsenic atoms form a hexagonal close packed type of lattice with the Ni atoms occupying all the octahedral sites between all the layers of arsenic atoms.

12.10 KEY WORDS

• **Pseudo solids**: Pseudo Solids do not have definite shape and volume and are less rigid. These melt over a range of temperature and common examples are glass and pitch.
• **Polycrystalline solids**: Polycrystalline solids are the solids which occur as powder and resemble amorphous solids, but their individual particles have all the characteristics of crystalline solids.
• **Plane of symmetry**: It is an imaginary plane which can divide the crystal into two halves such that one is the image of the other.
• **Axis of symmetry**: It is such an imaginary line within the crystal that if the crystal is rotated about this line, the crystal will have the same appearance more than once during the course of a complete rotation.
• **Unit cell**: The smallest repeating pattern (unit) from which the lattice is built is known as a unit cell.
12.11 SELF ASSESSMENT QUESTIONS AND EXERCISES

NOTES

Short Answer Questions
1. Write a short note on classification of solids.
2. Write a brief note on axis of symmetry.
3. What is unit cell and how can we describe it?
4. Brief a note on lattice point.
5. Write short note on BCC.
7. Write a short note on Wurtzite structure.

Long Answer Questions
1. Write a descriptive note on crystal structure of solids mentioning about classification of solids and elements of crystal symmetry.
2. Explain about space lattice and unit cell in detail.
3. Describe in detail about the packing of ions in ionic crystals explaining about HCP, FCC and BCC.
4. Elaborate a detailed note on interstitial sites or voids in ionic crystals.
5. Write in detail about the structure of ionic crystals.
6. Give a detailed note on layer structures of CdI₂ and Nickle arsenite structure.

12.12 FURTHER READINGS


UNIT 13 DEFECTS IN CRYSTALS

13.0 INTRODUCTION

Crystal defect, imperfection in the regular geometrical arrangement of the atoms in a crystalline solid emerges from deformation of the solid, rapid cooling from high temperature, or high-energy radiation striking the solid. Point defects include the Frenkel type, the Schottky type, and the impurity type. The Frenkel defect involves a single ion, which is displaced from its normal lattice point and shifts to a nearby interstice, or space, between atoms in the lattice. In Schottky defect, two ions of opposite sign leave the lattice. Impurity defects are foreign atoms that replace some of the atoms making up the solid or that squeeze into the interstices; they are important in the electrical behaviour of semiconductors, which are materials used in computer chips and other electronic devices.

In this unit, you will study about Schottky and Frenkel defect, stoichiometric and non-stoichiometric crystals, defects in crystals, point defects, stoichiometric defects, consequences of Schottky and Frenkel defects, non-stoichiometric defects, consequences of metal deficient defects in detail.

13.1 OBJECTIVES

After going through this unit, you will be able to:

- Discuss Schottky and Frenkel defect and the consequences of Schottky and Frenkel defects
- Discuss the defects in crystals, point defects
- Explain stoichiometric and non-Stoichiometric defects
- Learn consequences of metal deficient defects
13.2 DEFECTS IN CRYSTALS

According to the definition of crystalline solids, an ideal crystal is one which has a regular repeating arrangement of unit cell throughout the crystal. This type of perfectly ordered arrangement is observed in the crystals formed at absolute zero. However, in practice, almost all the crystals suffer from defects of one kind or the other. The defect increases with the rise in temperature. The defects or imperfections in crystals may arise due to any one of the following reasons:

- One of the constituent particle is missing from the crystal lattice. It creates a vacancy or hole in the crystal.
- Displacement of atom or ion from its lattice site to the interstitial position.
- Presence of impurity at the lattice site.
- Presence of an impurity in the void or the interstitial site.

Such defects when developed in the crystal lattice, alter the properties of the solids, for example, change in density, conduction of current, coloration and shining (metallic lusture) in the crystals, etc.

Stoichiometric and Non-Stoichiometric Crystals

Stoichiometric ionic crystals are those in which the ratio of positive and negative ions present in the compound are the same as required by the ideal formula of the compound. On the other hand, non-stoichiometric compounds are those in which the ratio of positive and negative ions present in the compound differ from that which is required by ideal chemical formula of the compound. For example, vanadium (II) oxide is non-stoichiometric oxide, since it has the formula VO$_x$ where $x = 0.6 – 1.3$. Similarly iron (II) oxide samples contain more oxygen atoms than iron atoms, while samples of zinc (II) oxide usually has excess of zinc atoms than oxygen atoms. In each case electrical neutrality is maintained.

Defects in Crystals

In an ideal crystal the arrangement of constituent ions is perfect. The defect in crystals means that the perfect arrangement of the constituent ions is destroyed due to the presence of cationic and anionic vacancies in the lattice points, dislocations of ions in the lattice, the presence of the same type of ions in the different oxidation states and the presence of impurities in the lattice points. Such defects when developed in crystal lattice, alter the properties of the crystals, such as change in density, conduction of current, colorations, mechanical strength and shining in crystals, etc. A brief classification of these defects is shown in Figure 13.1.
13.2.1 Point Defects

Point defects are produced in an ionic crystal when equal number of cations and anions are missing from their regular lattice positions and thus an equal number of cation and anion vacancies are produced in the structure of the crystal or when an ion (cation or anion) of an ionic crystal is missing and is shifted to a vacant interstitial site existing in the structure of the crystal. Point defects may occur in stoichiometric as well as non-stoichiometric crystals. The point defects found in stoichiometric crystals are called **stoichiometric defects** while the point defects in non-stoichiometric crystals are known as **non-stoichiometric defects**.

13.2.2 Stoichiometric Defects

The compounds in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae are called stoichiometric compounds. The defects do not disturb the stoichiometry (the ratio of numbers of positive and negative ions) are called stoichiometric defects. Point defects occurring in stoichiometric defects are of the following types:

- Interstitial defect
- Schottky defect
- Frenkel defect

**Interstitial Defect**: This type of defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystals.

**Schottky Defect**: This defect was discovered by the German scientist, Schottky in 1930. When one positive ion and one negative ion, from any site in the crystal
lattice, are missing from their respective sites then it creates a pair of holes or vacancies. Such paired cation-anion vacancies in ionic crystals is termed as Schottky defect as shown in Figure 13.2.

**NOTES**

![Schottky Defect Diagram](image)

**Fig 13.2 Schottky Defect**

Schottky defect is generally developed in highly ionic compounds with either one or both of the following characteristics:

(i) With high co-ordination number in crystal structure.

(ii) Where sizes of cation and anion are almost equal.

Crystal structure of NaCl, KCl, KBr and CsCl usually exhibit this type of defect. Crystallographic studies have shown that in NaCl crystal one paired vacancy is observed in 10^10 lattice sites at room temperature. The increase of temperature increases the vacancies, i.e., defect becomes more prominent at high temperature.

**Frenkel Defect:** This defect occurs when some of the ions (usually cations) shift from their normal lattice sites to the interstitial positions in the crystal lattice, then the vacancies are developed at the original sites. Since cations are generally smaller in size than anions, cations can easily be displaced to the voids as depicted in Figure 13.3.

![Frenkel Defect Diagram](image)

**Fig 13.3 Frenkel Defect**

This type of defect is generally found in crystals in which

(i) Anion is much larger in size than the cation.

(ii) Low co-ordination number is shown between anions and cations.

Therefore, during shifting of cation to interstitial site, lesser amount of energy is required to overcome the forces of attraction. Crystal structure of ZnS, AgBr and AgCl are good examples for illustrating Frenkel defect. The Table 13.1 differentiates between Schottky and Frenkel defects.
Table 13.1 Differences between Schottky and Frenkel Defects

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Schottky Defect</th>
<th>Frenkel Defect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>In this defect, the ion pair (cation as well as the anion) are missing from their respective lattice sites in the crystal.</td>
<td>In Frenkel defect, the ion takes the interstitial position rather than its original lattice site.</td>
</tr>
<tr>
<td>2.</td>
<td>In occurs in highly ionic compounds with high coordination number</td>
<td>It occurs in compounds showing less coordination number amongst ions.</td>
</tr>
<tr>
<td>3.</td>
<td>This defect is observed in compounds in which cations and anions are of almost same size.</td>
<td>Frenkel defect is shown by compounds having large difference between the size of cation and anion.</td>
</tr>
<tr>
<td>4.</td>
<td>In Schottky defect, the density of the crystal decreases.</td>
<td>No change in density is observed due to Frenkel defect in the crystal.</td>
</tr>
<tr>
<td>5.</td>
<td>The stability of crystal decreases and the electrical conductivity increases due to the formation of voids.</td>
<td>Decrease in stability and increase in electrical conductivity is observed. Due to the presence of ions in interstitial position (void), this defect increases the dielectric constant of the crystals.</td>
</tr>
</tbody>
</table>

Consequences of Schottky and Frenkel Defects:

- It is due to the presence of these defects that the crystal is able to conduct electricity through it when an electric field is applied on it. This tendency of the crystal can be explained as follows. When an electric field is applied on a crystal, having both types of defects, a nearby ion moves from its position to occupy a hole. This results in creating a new hole and another nearby ion moves into it and so on. This process continues and a hole, thereby, moves from one end to the other end. Thus it conducts electricity across the whole crystal.
- Density of the crystals, having Schottky defects, decrease, as expected.
- The presence of holes also decreases the lattice energy or the stability of the crystal. The presence of too many holes decreases the stability of the crystal to such an extent that a partial collapse of the lattice energy may take place.
- We have seen that in a crystal having Schottky defect, the similar ions (charges) come closer to each other and hence the dielectric constant of the crystal increases.

13.2.3 Non-Stoichiometric Defects

When the ratio of the cations and anions present in the imperfect ionic solid differs from that required by the ideal or perfect chemical formula of the compound, the defect is known as non-stoichiometric defect. This defect is caused either by excess cation (anion vacancies) or by excess anion (cation vacancies) in the crystal. The crystal becomes electrically neutral by acquiring either extra electrons or extra
positive charge on the cation. The ionic compounds having such defects are called as non-stoichiometric or Berthollide compounds. The chemical composition of such compounds varies from the ideal chemical formula and the variation depends upon the amount of impurities present in the crystal.

The non-stoichiometric defects are classified into the following types:
- Metal excess defect due to anion vacancies
- Metal excess defect due to interstitial cation
- Metal deficiency defect due to cation vacancies
- Cation deficiency defect due to impurities

**Metal Excess Defect due to Anion Vacancies:** This type of defect is developed when some of the anions are missing from their respective lattice sites creating holes. These vacant anion positions (holes) are occupied by the electrons in order to maintain the electrical neutrality of the crystal as shown in the Figure 13.4.

The vacant sites occupied by electrons are termed as F-centres (F stands for Farbe, meaning colour). The presence of F-centres impart colour to the otherwise colourless ionic crystal. Greater the number of such F centres greater will be the intensity of coloration.

Electron at the anion site

![Electron at the anion](image)

**Fig. 13.4 Metal Excess Defect due to Anion Vacancies**

This type of defect of anionic vacancies is usually found in crystals likely to possess Schottky defect. In alkali halides this defect is developed when alkali halide crystal is heated in an atmosphere of alkali metal vapours. The alkali metal atoms condense on the surface of the crystal where these combine with halide ion of the lattice by diffusion. The electrons released during oxidation of metal atoms to ions diffuse into crystal lattice and occupy the sites vacated by anions.

\[ M + X^- \rightarrow M^+ + X^- + e^- \]

The consequences of anion vacancies or F-centre defect are as follows:
- Crystals with F-centres are paramagnetic because the trapped electrons in the anionic vacancies are unpaired.
- Excess of metal ions impart colour to the crystal, for example, excess of Li in LiCl gives pink colour to crystal and the excess of K in KCl crystal turns it to violet.
- The crystals with F-centres on irradiation with light becomes photoconductors.

**Metal Excess Defect due to Interstitial Cation:** This type of defect is observed in crystals containing extra positive ion in the interstitial position. The electrical neutrality is maintained by the electrons also occupying the interstitial sites as illustrated in the Figure 13.5.

![Fig. 13.5 Metal Excess Defect due to Interstitial Cation Vacancy](image)

This type of defect is usually observed in crystals which are likely to develop ‘Frenkel defect’. The example illustrating this kind of defect is the crystal of ZnO. When ZnO is heated, it loses oxygen reversibly and turns yellow. The excess of the Zn\(^2+\) ions formed on heating ZnO is accommodated in the interstitial site and the electrons in the neighbouring interstitial position.

\[
2\text{ZnO} \xrightarrow{\text{Heating}} 2\text{Zn}^{2+} + \text{O}_2 + 4e^-
\]

Crystals having this type of defect show increased electrical conductivity due to the presence of free electrons in the interstitial position.

**Metal Deficiency Defect due to Cation Vacancies:** This type of defect is generally found in ionic solids in which metal ions have variable valency. This defect is developed in the crystal when a positive ion is missing from its lattice site and the charge is balanced (i.e., electrical neutrality is maintained) by oxidation of some of the cations to higher oxidation states as shown in the Figure 13.6. The crystal lattice shows the deficiency of metal ion.
Fig. 13.6 Metal Deficiency Defect due to Cation Deficiency

The metal deficient ionic compounds, as shown in the above figure, are classified as p-type semiconductors. These conduct electricity through positive hole conduction mechanism.

Illustrative examples of this type are FeO, FeS, NiO and TiO. In FeS crystal, one Fe\textsuperscript{2+} lattice site is vacant and the other two cation sites are occupied by Fe\textsuperscript{3+} ions (produced by oxidation of Fe\textsuperscript{2+} ions), in order to maintain the electrical neutrality. The existence of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} ions side by side results in free exchange of electrons between two such sites. So it gives metallic lustre to the crystal.

**Cation Deficiency Defect due to Impurity:** This type of defect arises due to the presence of impurity cation (foreign atom), of almost same size but of higher oxidation state, at the lattice site instead of host cation. It results in the formation of vacant site, for example, the presence of Cd\textsuperscript{2+} ion impurity in the crystal lattice of AgCl as shown in Figure 13.7.

Cation vacancy

Fig. 13.7 Silver Chloride Crystal having Cd\textsuperscript{2+} Ion as Impurity

In the crystal lattice of AgCl, two Ag\textsuperscript{+} ions are missing from their lattice sites; one of the vacant site is occupied by Cd\textsuperscript{2+} ion (impurity cation) and the other remains vacant. The vacant site helps in conduction of electricity through AgCl. The mechanism of conduction of electricity involves the migration of Ag\textsuperscript{+} ion from lattice point into the vacant site creating a new vacancy. This kind of movement of vacancy in the opposite direction to the movement of Ag\textsuperscript{+} makes the crystal p-type of semiconductor.
Consequences of Metal Deficient Defects: Crystals having metal deficient defects are semiconductors. The conductivity is due to the movement of an electron from one cation to the other cation. When an electron moves from one cation, it is changed into a cation with higher positive oxidation state. The movement of a cation is also called the movement of a positive hole and the substances are called p-semiconductors.

Check Your Progress
1. What is the difference between stoichiometric and non-stoichiometric compounds?
2. What is meant by the defect in crystals?
3. What are point defects?
4. What do you understand by Schottky defect?
5. What do you understand by Frenkel defect?

13.3 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS
1. Stoichiometric ionic crystals are those in which the ratio of positive and negative ions present in the compound are the same as required by the ideal formula of the compound. On the other hand, non-stoichiometric compounds are those in which the ratio of positive and negative ions present in the compound differ from that which is required by ideal chemical formula of the compound.

2. The defect in crystals means that the perfect arrangement of the constituent ions is destroyed due to the presence of cationic and anionic vacancies in the lattice points, dislocations of ions in the lattice, the presence of the same type of ions in the different oxidation states and the presence of impurities in the lattice points.

3. Point defects are produced in an ionic crystal when equal number of cations and anions are missing from their regular lattice positions and thus an equal number of cation and anion vacancies are produced in the structure of the crystal or when an ion (cation or anion) of an ionic crystal is missing and is shifted to a vacant interstitial site existing in the structure of the crystal.

4. When one positive ion and one negative ion, from any site in the crystal lattice, are missing from their respective sites then it creates a pair of holes or vacancies. Such paired cation-anion vacancies in ionic crystals is termed as Schottky defect.

5. Frenkel defect occurs when some of the ions (usually cations) shift from their normal lattice sites to the interstitial positions in the crystal lattice, then the vacancies are developed at the original sites.
13.4 SUMMARY

- An ideal crystal is one which has a regular repeating arrangement of unit cell throughout the crystal.
- Stoichiometric ionic crystals are those in which the ratio of positive and negative ions present in the compound are the same as required by the ideal formula of the compound.
- When the ratio of the cations and anions present in the imperfect ionic solid differs from that required by the ideal or perfect chemical formula of the compound, the defect is known as non-stoichiometric defect.
- In an ideal crystal the arrangement of constituent ions is perfect. The defect in crystals means that the perfect arrangement of the constituent ions is destroyed due to the presence of cationic and anionic vacancies in the lattice points, dislocations of ions in the lattice, the presence of the same type of ions in the different oxidation states and the presence of impurities in the lattice points.
- Such defects when developed in crystal lattice, alter the properties of the crystals, such as change in density, conduction of current, coloration, mechanical strength and shining in crystals, etc.
- When the ratio of the cations and anions present in the imperfect ionic solid differs from that required by the ideal or perfect chemical formula of the compound, the defect is known as non-stoichiometric defect.
- Point defects are produced in an ionic crystal when equal number of cations and anions are missing from their regular lattice positions and thus an equal number of cation and anion vacancies are produced in the structure of the crystal or when an ion (cation or anion) of an ionic crystal is missing and is shifted to a vacant interstitial site existing in the structure of the crystal.
- Schottky defect is generally developed in highly ionic compounds with either one or both of the following characteristics, i.e., with high co-ordination number in crystal structure or where sizes of cation and anion are almost equal.
- The stability of crystal decreases and the electrical conductivity increases due to the formation of voids.
- Non-stoichiometric defects the ratio of the cations and anions present in the imperfect ionic solid differs from that required by the ideal or perfect chemical formula of the compound, the defect is known as non-stoichiometric defect.
- This defect is caused either by excess cation (anion vacancies) or by excess anion (cation vacancies) in the crystal. The crystal becomes electrically neutral by acquiring either extra electrons or extra positive charge on the cation.
The ionic compounds having such defects are called as non-stoichiometric or Berthollide compounds.

- The chemical composition of such compounds varies from the ideal chemical formula and the variation depends upon the amount of impurities present in the crystal.

### 13.5 KEY WORDS

- **Ideal crystal**: An ideal crystal is one which has a regular repeating arrangement of unit cell throughout the crystal.

- **Point defects**: Point defects are produced in an ionic crystal when equal number of cations and anions are missing from their regular lattice positions and thus an equal number of cation and anion vacancies are produced in the structure of the crystal or when an ion (cation or anion) of an ionic crystal is missing and is shifted to a vacant interstitial site existing in the structure of the crystal.

- **Schottky defects**: When one positive ion and one negative ion, from any site in the crystal lattice, are missing from their respective sites then it creates a pair of holes or vacancies. Such paired cation-anion vacancies in ionic crystals is termed as Schottky defect.

- **Frenkel defect**: This defect occurs when some of the ions (usually cations) shift from their normal lattice sites to the interstitial positions in the crystal lattice, then the vacancies are developed at the original sites.

- **Non-stoichiometric defect**: When the ratio of the cations and anions present in the imperfect ionic solid differs from that required by the ideal or perfect chemical formula of the compound, the defect is known as non-stoichiometric defect.

### 13.6 SELF ASSESSMENT QUESTIONS AND EXERCISES

**Short Answer Questions**

1. What are the main reasons for the defects or imperfections in crystals?
2. Describe Stoichiometric defects.
3. What is point defect?
4. Differentiate between Schottky and Frenkel defects.
5. What are the consequences of Schottky and Frenkel defects?
Defects in Crystals

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13.7 FURTHER READINGS


Long Answer Questions

1. Discuss in detail about non-Stoichiometric defects.
2. Give a detailed account of defects in crystals.
3. Explain about Schottky and Frenkel defects in detail.
4. Distinguish between Schottky and Frenkel Defects.
UNIT 14 ELECTRICAL PROPERTIES OF SOLIDS

Structure
14.0 Introduction
14.1 Objectives
14.2 Band Theory of Solids
14.3 Electrical Properties of Solids
  14.3.1 Good Conductors
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14.0 INTRODUCTION

Solids can be categorized into conductors, semiconductors or insulators by their ability to conduct electricity. A conductor is an object or type of material that allows the flow of an electrical current in one or more directions. Materials made of metal are common electrical conductors. Electrical current is generated by the flow of positively charged electrons, positively charged holes, and positive or negative ions in some cases. A solid substance that has a conductivity between that of an insulator and that of most metals, either due to the addition of an impurity or because of temperature effects. Devices made of semiconductors, notably silicon, are essential components of most electronic circuits. An electrical insulator is a material whose internal electric charges do not flow freely; very little electric current will flow through it under the influence of an electric field. This contrasts with other materials, semiconductors and conductors, which conduct electric current more easily. The property that distinguishes an insulator is its resistivity; insulators have higher resistivity than semiconductors or conductors. Electron band theory explains differences in conduction.

In solid-state physics, the electronic band structure (or simply band structure) of a solid describes the range of energies that an electron within the solid may have (called energy bands, allowed bands, or simply bands) and ranges of energy that
it may not have (called band gaps or forbidden bands). Band theory derives these bands and band gaps by examining the allowed quantum mechanical wave functions for an electron in a large, periodic lattice of atoms or molecules. Band theory has been successfully used to explain many physical properties of solids, such as electrical resistivity and optical absorption, and forms the foundation of the understanding of all solid-state devices (transistors, solar cells, etc.).

The imperfections (defects) in solids (crystal) give some characteristic changes in the properties of ionic compounds. These properties of solids are directly related to their composition, their lattice structure and the nature of bonds.

In this unit, you will study some of the properties of solids like, electrical properties, magnetic properties and dielectric properties. All these properties depend on the structure, nature of bonds and the composition of the solids.

14.1 OBJECTIVES

After going through this unit, you will be able to:

- Explain electrical properties of conductors, semiconductors and insulators
- Discuss the band theory of solids
- Understand Superconductivity and Covalent Crystals
- Interpret magnetic and dielectric properties of solids
- Describe structure of diamond and graphite

14.2 BAND THEORY OF SOLIDS

The band theory of solids is explained on the basis of Molecular Orbital Theory. The salient features of band theory of solids are as follows:

- Materials in the solid state do have very large aggregation of atoms (or ions) and are arranged in regular close-packed structures.
- The constituents (ions or atoms) of solids are bound together by a cohesive force and as a result, the atomic orbitals of valence electron shells interact and overlap with each other and give rise to molecular orbitals.

When two atomic orbitals (half-filled) overlap, two molecular orbitals of different energy levels are formed as shown in Figure 14.1. As seen in the Figure 14.1 one of the Molecular Orbitals (MO) gets stabilized due to pairing up of electrons and acquires lower energy state, which is called ‘Bonding Molecular Orbital’ (BMO), while the other empty molecular orbital is destabilized (higher energy) and is known as ‘Antibonding Molecular Orbital’ (ABMO).
**Fig. 14.1 Overlap of Two Molecular Orbitals (MO)**

When a $2N$ number of valence atomic orbitals of constituent atoms (or ions) overlap with each other in solids, they give rise to the ‘$N$’ number of closely spaced bonding molecular orbitals and as well to ‘$N$’ number of antibonding molecular orbitals.

For very large aggregation of atoms (or ions), a very closely spaced energy levels (σ MOs and σ* MOs) of extremely small energy difference results in the formation of ‘bands’ in solids and evidently, these ‘energy bands’ appear to be continuous as shown in Figure 14.2.

**Fig. 14.2 Formation of Energy Bands in Solids**

The energy gap between the ABMO and BMO (i.e. $\sigma^*$ and $\sigma$ bands) or the magnitude of the separation of these bands depends on the nature of the constituents, the inter-nuclear distances of atoms (ions) and the orientation of the valence electron orbitals in a particular crystal structure.

However, in few cases, the energy bands of atoms in solid may also overlap and gives rise to a continuous half-filled energy bands.

A ‘band’ is a group of infinitesimal energy levels is a solid that gives a continuous appearance.
**Types of energy Bands:** There are mainly two types of energy bands:

(i) **Overlapping energy Bands:** Some energy bands in a solid way overlap, as shown in Figure 14.3. In such a case there is then a continuous distribution on allowable energies for its electrons.

The extent of overlapping of atomic orbitals of a nucleus with the atomic orbital of the surrounding depends upon its distance from these surrounding nuclei, i.e., the internuclear distance. If the internuclear distance increases, there is lesser overlapping and, thus there is less of perturbation and orbitals remain essentially atomic. As the internuclear distance decreases, the amount of overlapping of atomic orbitals with atomic orbitals of neighbouring nuclei increases. Thus, there is more of perturbation and overlapping orbitals become molecular orbitals. The filling of these bands and the width of forbidden zones determine whether a substance is a conductor, insulator, or a semi-conductor.

(ii) **Non-overlapping Bands:** In many solids, the higher energy band does not overlap the lower filled (or half-filled) energy level band and evidently, there is an energy gap between the two bands of energy levels. This energy gap is known as a forbidden energy gap (Refer Figure 14.4)
14.3 ELECTRICAL PROPERTIES OF SOLIDS

The electrical property of a solid is defined as its ability to conduct current through it. Many solids conduct electricity while the other do not. On the basis of the value of electrical conductivity of solids, these have been classified as:

- Good Conductors
- Insulators
- Semiconductors

14.3.1 Good Conductors

The electrical conductivity of good conductors is of the order of $10^0$ ohm$^{-1}$ cm$^{-1}$ and they allow the maximum portion of the applied electric field to flow through them. Some common electrical conductors are as follows:

1. Electrical Conductivity of Metals: Metals are good conductors of electricity, since according to electron sea theory, the metallic crystals have mobile or delocalized (free) electrons. When an electric field is applied between the two ends of a metal, the mobile electrons begin to move towards the positive pole and the new electrons from negative pole take their position. Thus with the movement of electrons, the electric current starts to flow in the metal and the metal, therefore, acts as a good conductor of electricity.

   It has been observed that the electrical conductivity of most of the metals decreases with the increase of temperature. This is because of the fact that with increase of temperature the positive metal ions also begin to vibrate and their motion hinders the free movement of the mobile electrons between the positive metal ions. Thus the vibrating positive metal cores create resistance to the flow of the electrons towards the positive pole and hence the movement of the electrons towards the positive pole falls and so does the electrical conductivity of the metals at higher temperature.

2. Electrical Conductivity of Ionic Solids:

   - Ionic solids are poor or bad conductors of electricity, since they do not allow the electric current to pass through them. This is because of the fact that, due to the electrostatic force of attraction, the positive and negative ions present in the ionic crystals are fixed in their position and hence cannot move even if an external electric field is applied on them.

   - Ionic solids in their fused (melted) state conduct electricity because the positive and negative ions now become free to move under the applied electric field.

   - An ionic solid in water conducts electricity because it reacts with water and gives free ions in solution.
The ionic solids having defects, conduct electricity because the ion moves from its lattice site to occupy a vacancy. This results in creating a new vacancy and another nearby ion moves into it and so on. This process continues and a vacancy, thereby, migrates from one end to the other end. Thus it conducts electricity across the whole of the ionic crystal.

**Electrical Conductivity of Covalent Solids**

- At low temperature (0°K) covalent solids like silicon and germanium do not conduct electricity because the electrons present in the localized covalent bonds are fixed in their position and hence are not free to move. At high temperature, these elements act as semiconductors (see below).
- Because of its unique structure with free electrons, graphite conducts electric current.
- Hydrogen chloride dissolved in water (hydrochloric acid) conducts electricity, since it reacts with water to form \( \text{H}^+ \) ions.

**14.3.2 Insulators or Poor Conductors**

The electrical conductivity of insulators is of the order \( 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1} \) and they do not practically allow electric current to flow through them. The common electrical insulators are polythene, bakelite, silica, urica, PVC and rubber.

**14.3.3 Semiconductors**

Semiconductors are those crystals which are perfect insulators at absolute zero, but conduct electric current (although partial) at room temperature. Their electrical conductivity is \( 10^{-7} \) to \( 10^2 \text{ ohm}^{-1} \text{ m}^{-1} \) which is intermediate between the good conductor and an insulator. The materials which have a forbidden gap of about 2-3 eV or less are called semiconductors, while those with more than 3eV of forbidden energy are known as insulators.

**Ionic compounds** are nonconductors in solid state at room temperature because the electrons in these compounds are fixed and are unable to move freely under applied electrical field. However, when the temperature is raised the electrical conductivity usually increases. For example, the conductivity of sodium chloride at its melting point (1073 K) is \( 10^7 \) times higher than at 298 K. Similar conducting properties are noticed in ionic compounds containing either impurities or some other defects.

The detailed studies related to the preparation of semiconductors became necessary because of their remarkable applications in electronic industry. Silicon and germanium are two important elements used as semiconductors. Pure samples (= 99.999% pure) of these elements are obtained by zone refining and some impurity is added deliberately by a process called doping. There are two types of semiconductors.
• Intrinsic Semiconductors
• Extrinsic Semiconductors

(a) Intrinsic Semiconductors

When an insulator conduct electric current either at higher temperature or on irradiation with electromagnetic wave, it is termed as intrinsic semiconductor. These do not contain any added impurities. As depicted in Figure 14.5, the width of the forbidden gap is small (1.1 eV for silicon) in semiconductors. The thermal energy excites some of the electrons of nonconductors to cross over the forbidden gap resulting in vacant electron site (holes) in the valence-band. These holes in the valence-band move in the direction opposite to that of the electrons conducting the current.

![Figure 14.5 Forbidden gap in an insulator and semiconductor.](image)

(b) Extrinsic semiconductors

When impurity is added to the insulator to assist the conduction of current then it is called extrinsic semiconductor. The impurity makes availability of either electrons or holes for electric conduction. Therefore, the extrinsic semiconductors are of two types,

• n-Type semiconductors (n stands for negative)
• p-Type semiconductors (p stands for positive)

• n-Type Semiconductors: This type of semiconductor is formed when the atoms of the impurity provide more number of electrons than the parent atom forming the insulator. An impurity of group 15 element (P or As) will provide five valence electrons in place of four valence electrons of silicon atom (group 14 element). Therefore, when the trace amount of As is added to extremely pure silicon then one electron on each As atom remains unused after bonding. Such free electron moves under the influence of an electrical field, conducting current. This process of adding impurity of P or As (even one in millions) to the extremely pure Si or Ge is termed as doping. The n-type semiconductors developed by this process is represented in Figure 14.6.
Electrical Properties of Solids

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Fig. 14.6 Silicon With an Impurity (n-type semiconductor)

- **p-Type Semiconductors**: The semiconductors formed by the introduction of impurity atoms containing one electron less than the parent atoms of insulators are termed as p-type semiconductors. An impurity of group 13 element will provide only three valence electrons when substituted in place of atom of group 14 (four valence electrons). In this one valence electron of silicon remains non-bonded. It develops electron vacancy or commonly known as positive hole in the semiconductor. A semiconductor containing Ga atoms as impurity in silicon is shown in Figure 14.7.

Fig. 14.7 Silicon with Ga Impurity (p-type semiconductor)

Unlike metals, the conductivity of semiconductors increases with increase in temperature. This is due to the fact that extra electron or positive hole (as the case may be) is bound weakly with the crystal and when energy is supplied in the form of heat, they become free from the crystal lattice for the conduction of electricity.

**Applications of Semi-conductors**: A large variety of semiconductors have been prepared by the following types of combinations.

- Elements of group 14 (Si, Ge) and group 15 (P, As, Sb)
- Elements of group 13 (B, Ga) and group 14 (Si, Ge)
Elements of group 13 and group 15, for example, InSb, AIP
Elements of group 12 and group 16, for example, ZnS, CdS, CdSe, HgTe
Properties of semiconductors are considerably charged depending on the nature of the impurity. Semiconductors are used in transistors and in exposure meters as photo electric devices combination of p- and n-type semiconductors (known as p-n junction) allows the electric current from outside to flow through it in one direction. This type of p-n junction is known as rectifiers and is used for converting alternating current to direct current.

Conduction in semiconductors
The band diagrams for the conduction in semiconductors is shown in Figure 14.8. In case of intrinsic semiconductors like Si, each atom of Si is surrounded by four neighbouring atoms when a small energy is given, an electron.

Fig. 14.8 Conduction in Semiconductors

14.3.4 Superconductivity
Superconductivity may be defined as a phenomenon in which metals, alloys and chemical compounds become perfect conductors with zero resistivity at temperatures approaching absolute zero. This phenomenon was first discovered by Kamerlingh Onnes in 1913 where he found that mercury becomes superconducting at 4 K. The temperature at which a substance starts behaving as superconductors is called transition temperature which lies between 2 and 5 K in most of the metals exhibiting this phenomenon.

Until 1987, the only known superconductors (which included metals, some oxides, and some halides) needed to be cooled to below about 20 K before they became superconducting. However, in 1987 the first ‘high temperature’ superconductors were discovered; then superconduction is well established at 120 K and spasmodic reports of even higher temperatures have appeared. We will not consider these high-temperature materials at this stage but sketch the ideas behind the mechanism of low-temperature superconduction.

The central concept of low-temperature superconduction is the existence of a Cooper pair, a pair of electrons that exists on account of their interaction indirectly through vibrational displacements of the atoms in the lattice. Thus, if one electron is in a particular region of a solid, the nuclei there move toward it to give a distorted local structure (Refer Figure 14.9). Since that local distortion is rich in
positive charge, it is favourable for a second electron to join the first. Hence, there is a virtual attraction between the two electrons, and they move together as a pair. The local distortion can be easily disrupted by thermal motion of the ions, so the virtual attraction occurs only at very low temperatures.

![Fig 14.9 Close Packing of Spheres in One Plane](image)

A cooper pair undergoes less scattering than an individual electron as it travels through the solid, since the distortion caused by one electron can attract back the other electron should it be scattered out of its path in a collision. This has been likened to the difference between the motion of a herd of cattle, with members of the herd that are deflected from their path.

**Check Your Progress**
1. What is a bonding molecular orbital (BMO)?
2. Define the phenomenon of superconductivity.
3. What is an insulator?
4. What is an iconic conductor?

### 14.4 MAGNETIC PROPERTIES OF SOLIDS

Depending upon the behaviour of different solids in magnetic field, these are classified as paramagnetic substances, diamagnetic substances and ferromagnetic substances.

**(i) Paramagnetic Substances:** The substances which are weakly attracted when placed in the external magnetic field are termed as paramagnetic substances. The paramagnetic property of the solid is due to the presence of ions, atoms or molecules containing unpaired electrons. The unpaired electrons have magnetic moment (electron spin) but their randomly orientation cancel each other’s effect. However, in the presence of external magnetic field these unpaired electrons are aligned and show temporary magnetism.

From the valence band is shifted to the conduction band, leaving behind a positively charged hole. This +ve hole can travel to an adjacent atom by accepting an electron ‘e’ from the latter one in a repeated manner. Consequently, the hole can move from one site of crystal lattice to another. Thus ‘e’ and holes in equal numbers are the charge carriers is intrinsic semiconductors.
In case of n-type semiconductors, small amount of phosphorous impurity is added to silicon (4-valence electrons) the fifth valence electron remains unshared and is a surplus electron which moves through the crystal under the influence of the electric field. This gives an n-type semiconductor. These surplus electrons occupy a delocalized level called the donor impurity level which is just below the empty conduction band of Si crystal. These ‘e’ can very easily be excited to empty e and action bands by application of electric thermal energy so the crystal of Si becomes a semiconductor.

p-type semiconductors are formed by an impurity having lesser electrons than the parent insulator atoms like B or Al, which forms the covalent band with 3-Si atoms and the fourth Si atom is linked to the B-atom by an incomplete bond (containing 1 – e). Thus, in this bond in lattice there is an electron deficiency which creates a +ve hole in the valence band of Si. There are as many +ve holes as boron atoms. These holes occupy the level close to the filled valence band called acceptor impurity level. The positive holes so formed in the crystal lattice conduct current, when electric field is applied. The movement of holes through the crystal of a p-type semiconductor is nothing but movement of positive electric charge.

Wide variety of substances exhibit paramagnetic properties due to the presence of unpaired electrons in them. Some examples are:

Molecules NO and O₂
Transition metals Cr, Mn, Ni, Co, Fe, etc.
Metal ions Cu²⁺, Ni²⁺, Fe³⁺, etc.
Metal oxides VO₂ and CuO

The substance showing diamagnetism include N₂, NaCl, TiO₂, Zn, Cd, Cu⁺, etc.

(ii) Ferromagnetic Substance: The substances possessing unpaired electrons are further classified in three different groups based on the alignment of magnetic moments of unpaired electrons

• Ferromagnetic Substances
• Antiferromagnetic Substances
• Ferrimagnetic Substances

Ferromagnetic Substances: The substances which are strongly attracted by magnetic field are termed as ferromagnetic substances. This type of substances have alignment of all the unpaired electrons in the same direction (orientation). These substances are permanently magnetised i.e., these substances show magnetism even in the absence of magnetic field. Examples are Ni, Fe, Co and CrO₂.
Electrical Properties of Solids

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Fig 14.10 Orientation of Unpaired Electron Spin in External Magnetic Field

**Antiferromagnetic Substances:** When equal number of unpaired electrons are aligned in opposite directions, their magnetic moment (electron spin) will compensate each other’s magnetic moment. Such substances are termed as antiferromagnetic substances. For example, MnO, Mn₂O₃ and MnO₂.

**Ferrimagnetic Substances:** When unequal number of unpaired electrons are aligned in opposite directions, the net magnetic moment is not zero. Such substances are termed as ferrimagnetic substances. For example, ferrite, Fe₃O₄.

It has been observed that the ferromagnetic, ferrimagnetic and antiferromagnetic substances show paramagnetic nature at higher temperatures. This arises due to randomization of spins at higher temperature e.g., Fe₃O₄ is ferrimagnetic at room temperature but becomes paramagnetic at 850K.

### 14.5 DIELECTRIC PROPERTIES

A substance through which there is no net flow of electric charge when placed under an applied electric field is defined as dielectric material. This is due to the fact that the electrons in the dielectric material are tightly held by individual atoms or ions. However, the applied field polarizes the dielectric material and thus results in the creation of dipoles. The electrical dipoles are developed in the polar bonds with two equal and opposite charges. Such electrical dipoles interact with the applied external field in the following manners.

- These dipoles may align themselves in such a manner that the dipole moments cancel each other completely giving no net dipole moment in the crystal.
- The dipoles are so orderly oriented that these result in a net dipole moment in the crystal.

The crystals of second type, having some net dipole moment show the undermentioned electrical properties.

- **Piezoelectricity:** When the crystals, in which dipoles are oriented in an ordered manner, are subjected to mechanical stress or pressure, piezoelectricity is produced. Such crystals are termed as piezoelectric crystals. In piezoelectric crystals, electricity is produced due to displacement of ions from their orderly arrangement by the application of mechanical stress.

  Such crystals are used as pickups in record players where they produce electrical signals by application of pressure.
- **Pyroelectricity**: Upon heating, if the orderly arrangement of ions or atoms in the crystal is displaced and electricity is produced then the property of the crystal is termed as pyroelectricity.

- **Ferroelectricity**: Certain piezoelectric crystals show permanent alignment of dipoles even in the absence of an electric field. When the electric field is applied on such crystals, then the direction of polarization of ions is altered. Such solids are called ferroelectric substances and the phenomenon is termed as ferroelectricity. Sodium potassium tartrate (Rochelle salt), potassium dihydrogen phosphate (KH₂PO₄) and barium titanate (BiTiO₃) are examples of ferroelectric solids.

- **Antiferroelectricity**: If the crystal is having the alternate electrical dipoles pointing in opposite directions then it shall not exhibit ferroelectric properties. The net dipole moment in such solids is zero and such crystals are termed as antiferroelectric crystals. Lead zirconate (PbZrO₃) is a typical antiferroelectric solid.

### 14.6 COVALENT CRYSTALS

Covalent crystals are made up of neutral atoms of the same or different kind, which are held together by electron pair covalent bonds. A covalent crystal is made up of a large network of atoms, covalently linked to one another. Common examples of covalent crystals include diamond, graphite, silicon carbide, boron nitride, silicon dioxide, quartz etc. Covalent crystals are saturated and covalent bands are oriented in definite direction. This leads to looser packing than in ionic and metallic crystals i.e., covalent crystals have open structure. The covalent bond is very strong so large amount of energy is required to break it. Thus, covalent crystals are usually very hard, possess high melting points and low volatility and are insoluble in most of the solvents. These solids are generally bad conductors of electricity (except graphite). This is because they are not made up of ions and do not have any free electrons available for electric conduction, all the electrons being involved in covalent bonding.

Diamond and graphite, two common covalent crystals are discussed below.

#### 14.6.1 Diamond

Diamond is the purest crystalline allotropic form of carbon, occurring in nature in the free-state. Diamond are found in South Africa, Russia, Australia and Brazil. In nature diamond occurs as octahedral crystal.

**Preparation**: The artificial diamonds were prepared by heating pure sugar charcoal and iron in a graphite crucible at 3000°F in an electric furnace. At this high temperature, carbon dissolved in iron. Now when the molten mass was cooled rapidly by plunging it into a bath of molten lead and then treated with conic HCl crystals of artificial diamond were obtained.
**Structure**: X-ray analysis has shown that the crystal of diamond is made up of a number of tetrahedral units. Each tetrahedral unit contains C-atoms at its centre and this C-atom, is linked with other four C-atoms placed at the four corners of the tetrahedron. C-atoms of each tetrahedron are also linked by strong C – C covalent bonds with C-atoms of each of the neighbouring tetrahedrons (See Figure 14.11). Each C-atom is sp$^3$ hybridised. C – C bond distance in diamond is equal to 1.54 Å. Which is the normal distance of C – C covalent bond.

![Diagram of C-atoms and Neighbouring Tetrahedrons](image)

**Fig 14.11 C-atoms of Neighbouring Tetrahedrons**

- Tetrahedral unit of C-atoms in diamond crystal.
- Structure of diamond crystal in which a number of tetrahedral units are linked together. White circles indicate the C-atom placed at the centre of each tetrahedron while black circles indicate carbon atoms placed at the four corners of each tetrahedron.

Since diamond consists of a number of tetrahedral units. It is a giant molecule. Since each C-atom forms four covalent bonds. It produces a repetitive three-dimensional structure, using only covalent bonds.

Silicon, germanium and grey tin also crystallize in the same way as diamond.

**Properties**: The structure of diamond, discussed above, explains the following properties of diamond.

- It is insoluble in all solvents.
- Due to the giant molecular nature of the structure of diamond, it is a very hard substance. In fact diamond is the hardest natural substance known so far. Due to its great hardness, diamond is used for making glass cutters and rock borers.
- Since all the four electrons of the valence-shell of each C-atom are used up in making four covalent bonds with other C-atoms, there is no free electron left in diamond crystal to carry electricity or heat in the crystal. Thus diamond is a bad conductor of electricity and heat.
14.6.2 Graphite

Graphite is found in Ceylon.

**Manufacture:** Graphite is obtained by Acheson’s process which consists of heating a mixture of sand (SiO₂) and coke anthracite in the presence of iron oxide as catalyst at a temperature of 3000°C in an electric furnace. The furnace is fitted with two carbon electrodes joined by a thin carbon rod through which an alternating current is passed. The reaction between SiO₂ and coke proceeds as:

\[
s\text{SiO}_2 + 3\text{C} \xrightarrow{\text{heat, } 3000^\circ\text{C}} \text{SiC} + 2\text{CO}
\]

\[
\text{SiC} \xrightarrow{\text{heat}} \text{Si} + \text{C} \quad \text{(graphite)}
\]

**Structure:** The structure of graphite consists of a large number of flat parallel layers (or sheets) of C-atoms. Each layer is composed of flat hexagonal rings of C-atoms. In each layer, each C-atom is joined to only three C-atoms by C–C covalent bonds. Thus each C-atom is sp² hybridised. The C–C distance in each hexagonal ring is 1.42 Å and the distance between the two adjacent layers of C-atoms is 3.40 Å. Such a large distance between the two layers suggests that these layers are not joined together by covalent bonds. The layers are in fact joined together by weak van der Waals forces. The presence of hexagonal rings in each layer is supported by the fact that with alkaline KMnO₄ solution, graphite is oxidized to mellitic acid, \( \text{C}_n(\text{COOH})_n \) and oxalic acid. Mellitic acid on distillation with lime gives \( \text{C}_n\text{H}_6 \). Structure of graphite is given in Figure 14.12.
**Properties and Uses:**

- Since the van der Walls forces, by which layers of C-atoms are held together, are very weak, these layers in graphite can easily slide over one another and hence graphite is a soft substance and has lubricating properties. Thus, graphite is used as a lubricant for the fast moving parts of machinery. Since graphite is non-volatile, it can also be used for lubricating the machinery parts which operate at a very high temperature. It is a greasy substance.

- Since in each layer, each C-atom is linked to other three C-atoms only, one electron on each C-atom is free to carry heat and electricity in the structure of graphite. Thus, graphite is a good conductor of electricity and heat. Due to its good thermal and electrical conductivity, graphite is used for making carbon electrodes or graphite electrodes. The electrical conductivity increases with the increase of temperature.

- Due to the fact that graphite is soft and black in colour, it is used for making lead pencils.

- It is due to the strong C–C covalent bonding within the sheets that graphite has high melting point (≈ 3700⁰) and hence is used for making refractory crucibles, which are used for melting metals in industry.

- At 700⁰–800⁰, graphite burns in air, to give CO₂.

- It reacts with conc. HNO₃ of conc. H₂SO₄ below 100⁰ to form graphitic acid (C₄₄H₂O₇).

- Graphite is used for lining and for making electrodes of electric furnaces.

- Graphite is also used as a moderator, i.e., for reducing the speed of fast moving neutrons in an atomic reactor.
Table 14.1: Differences Between the Properties of Diamond and Graphite

<table>
<thead>
<tr>
<th>Diamond</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>• It occurs in nature in the free-state.</td>
<td>• It occurs naturally and is also manufactured artificially.</td>
</tr>
<tr>
<td>• It is the hardest natural substance.</td>
<td>• It is soft and greasy to touch.</td>
</tr>
<tr>
<td>• It has high relative density (1.35).</td>
<td>• Its relative density is 2.3.</td>
</tr>
<tr>
<td>• It is transparent and has high refractive index (&gt; 2.45). It is a non-conductor of heat and electricity.</td>
<td>• It is black, opaque and a good conductor of heat and electricity.</td>
</tr>
<tr>
<td>• It burns in air at 900°C to give CO₂.</td>
<td>• It burns in air at 700°C – 800°C to give CO₂.</td>
</tr>
<tr>
<td>• It occurs as octahedral crystal.</td>
<td>• It occurs as hexagonal crystal.</td>
</tr>
<tr>
<td>• It is insoluble in all solvents.</td>
<td>• It is insoluble in all ordinary solvents.</td>
</tr>
</tbody>
</table>

Check Your Progress
5. What are paramagnetic substances?
6. What do you understand by a dielectric material?
7. What is a covalent crystal?
8. At what temperature diamond burns in air to give CO₂?

14.7 Answers to Check Your Progress Questions

1. When two atomic orbitals (half-filled) overlap, two molecular orbitals of different energy levels are formed, one of the molecular orbitals (MO) gets stabilized due to pairing up of electrons and acquires lower energy state, which is called ‘bonding molecular orbital’ (BMO).
2. Superconductivity may be defined as a phenomenon in which metals, alloys and chemical compounds become perfect conductors with zero resistivity at temperatures approaching absolute zero.
3. The electrical conductivity of insulators is of the order $10^{-22}$ ohm$^{-1}$ cm$^{-1}$ and they do not practically allow electric current to flow through them. The common electrical insulators are polyethylene, bakelite, silica, urica, PVC and rubber.
4. Ionic compounds are nonconductors in solid state at room temperature because the electrons in these compounds are fixed and are unable to move freely under applied electrical field.
Electrical Properties of Solids

5. The substance which are weakly attracted when placed in the external magnetic field are termed as paramagnetic substances.

6. A substance through which there is no net flow of electric charge when placed under an applied electric field is defined as dielectric material.

7. A covalent crystal is made up of a large network of atoms, covalently linked to one another. Common examples of covalent crystals include diamond, graphite, silicon carbide, boron nitride, silicon dioxide, quartz etc.

8. Diamond burns in air at 900° to give CO₂.

14.8 SUMMARY

- Solids can be categorized into conductors, semiconductors or insulators by their ability to conduct electricity. A conductor is an object or type of material that allows the flow of an electrical current in one or more directions. Materials made of metal are common electrical conductors.

- The band theory of solids is explained on the basis of Molecular Orbital Theory. The salient features of band theory of solids are as follows: 1. Materials in the solid state do have very large aggregation of atoms (or ions) and are arranged in regular close-packed structures. 2. The constituents (ions or atoms) of solids are bound together by a cohesive force and as a result, the atomic orbitals of valence electron shells interact and overlap with each other and give rise to molecular orbitals.

- Types of energy Bands: There are mainly two types of energy bands: (i) Overlapping energy bands and (ii) Non-overlapping bands.

- The electrical property of a solid is defined as its ability to conduct current through it.

- Metals are good conductors of electricity, since according to electron sea theory, the metallic crystals have mobile or delocalized (free) electrons.

- Ionic solids are poor or bad conductors of electricity, since they do not allow the electric current to pass through them.

- Semiconductors are those crystals which are perfect insulators at absolute zero, but conduct electric current (although partial) at room temperature.

- There are two types of semiconductors: Intrinsic semiconductors and extrinsic semiconductors.

- Superconductivity may be defined as a phenomenon in which metals, alloys and chemical compounds become perfect conductors with zero resistivity at temperatures approaching absolute zero.

- Depending upon the behaviour of different solids in magnetic field, these are classified as paramagnetic substances, diamagnetic substances and ferromagnetic substances.
• A substance through which there is no net flow of electric charge when placed under an applied electric field is defined as dielectric material. This is due to the fact that the electrons in the dielectric material are tightly held by individual atoms or ions.

• Covalent crystals are made up of neutral atoms of the same or different kind, which are held together by electron pair covalent bonds. A covalent crystal is made up of a large network of atoms, covalently linked to one another. Common examples of covalent crystals include diamond, graphite, silicon carbide, boron nitride, silicon dioxide, quartz etc.

• Diamond and graphite, two common covalent crystals.

14.9 KEY WORDS

• Intrinsic semiconductors: When an insulator conduct electric current either at higher temperature or on irradiation with electromagnetic wave, it is termed as intrinsic semiconductor.

• Extrinsic semiconductors: When impurity is added to the insulator to assist the conduction of current then it is called extrinsic semiconductor.

• Ferromagnetic substances: The substances which are strongly attracted by magnetic field are termed as ferromagnetic substance.

• Piezoelectricity: When the crystals, in which dipoles are oriented in an ordered manner, are subject to mechanical stress or pressure, piezoelectricity is produced. Such crystals are termed as piezoelectric crystals.

• Solid: A solid is a state of matter characterized by particles arranged such that their shape and volume are relatively stable.

14.10 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions
1. Describe band theory of solids.
2. Write a short note on conductors.
3. What are energy bands? Discuss.
4. Write a short note on insulators.
5. What are n-type and p-type semiconductors?
6. Write properties of diamond.
7. Write properties of graphite.
### Long Answer Questions

1. Give a detailed account of electrical properties of solids.
2. Discuss magnetic properties of solids giving suitable examples.
3. Describe covalent crystals with suitable examples.
4. Write a short note on the following:
   a. Superconductivity
   b. Paramagnetic substances
   c. Dielectric Properties of solids
   d. Covalent Crystals
5. Explain dielectric properties of solids.
6. Differentiate between diamond and graphite.

### 14.11 Further Readings


