

Unit - 1

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1.0 Objectives of the unit

After studying this unit you are able to.

- ❖ Explain the Periodicity and the Periodic Properties of elements
- ❖ Identify the differences between Atomic and ionic radii
- ❖ Define the Ionization energy (IE) and its variation along the period and group
- ❖ Define the Electron affinity (EA) and its variation along the period and group
- ❖ Define the Electronegativity and its variation along the period and group
- ❖ Explain the octet rule and its importance
- ❖ Identify the Hypervalent and Subvalent compounds
- ❖ Predict the shape of the molecules using Valence bond theory
- ❖ Explain the formation of sigma (σ) and pi (π) bonds with the help of Overlap of atomic orbitals
- ❖ Recognize the limitations of VBT

1.1.Introduction

In 1861, for the first time Mendeleef attempted to classify the existing elements in some order that could explain their properties. He arranged the elements in the increasing order of their atomic weights in the form of a table later it was called as Mendeleef periodic table. He found that

Periodic Properties of elements in modern periodic table

Atomic number of an element is equal to the number of electrons in an atom. It is the fundamental property of an element it decides the properties of an element. The elements show similar chemical properties are arranged in periodic table in a vertical columns called “groups” and horizontal rows called “periods”

Modern periodic law and Long form of periodic table

It states that, “physical and chemical properties of elements are periodic of their respective atomic number”. The table of elements or chart of elements in which elements are arranged in the increasing order of atomic number such that elements having similar properties will fall in the same vertical column is called modern periodic table or long form of periodic table.

The structure of long form of periodic table is as follows

1. Elements are arranged in increasing order of their atomic numbers such that there will be periodic repetition of elements.

2. It is based on electronic configuration of elements.
3. Vertical columns of elements are called groups. There are 18 groups (1-18). Each group contains elements with similar electronic configuration in the outermost orbit or valence shell. Elements in a group will show similar chemical properties and are called a family generally named after the first element in the group or by a special name.

Ex: 1. First group elements are called alkali metals.

2. Second group elements are called alkaline earth metals or alkaline earths.

3. 11th group metals are called coinage metals.

4. 13th group elements are called metalloids.

5. 16th group elements are called chalcogens.

6. 17th group elements are called halogens.

7. 18th group elements are called rare gases or noble gases.

4. Horizontal rows in the periodic table are called periods. There are seven periods (1 -7th period)
Period contains a series of elements having the same principal quantum number with the same but related configuration. Each period begins with a highly electropositive alkali metal and ends with a highly electro negative noble gas (except 1st period). Each period corresponds to filling up of definite number of orbitals. The first period contains only two elements and is called very short. The second period contains eight elements and is called short period. Principal quantum number $n = 2$ and electrons are filled into 2s and 2p sub energy levels with a maximum capacity of $2+6=8$ electrons. The third period also contains eight elements and is called short period. Principal quantum number $n = 3$ and electrons are filled into 3s and 3p sub energy levels with a maximum capacity of $2+6=8$ electrons. The fourth period contains 18 elements and is called long period. Principal quantum number $n = 4$ and electrons are filled into 4s, 3d, and 4p sub energy levels. The maximum capacity is $2 + 10 + 6 = 18$ electrons. The fifth period also contains 18 elements and is called long period. Principal quantum number $n = 5$ and electrons are filled into 5s, 4d, and 5p sub energy levels with maximum capacity of $2+10+ 6 =18$ electrons. The sixth period contains 32 elements including fourteen "Lanthanides". Electrons are filled into 6s, 4f, 5d, and 6p sub energy levels with maximum capacity of $2 + 14 +10 + 6 = 32$ electrons. It is called very long period. The seventh period contains 25 elements (Two normal elements + 9 Transitional metals + 14 Actinides) Electrons are filled into 7s, 5f, 6d and 7p sub energy levels.

In the sixth period after Lanthanum with electronic configuration $[\text{Xe}] 5d^1, 6s^2$ after the entry of one electron into 5d sub energy level, energy of 4f sub energy level decreases. Therefore in the next fourteen elements from cerium with atomic number = 58 to Lutetium with atomic number = 71 electrons are filled into 4f sub energy level. These 14 elements are called lanthanides.

In the seventh period after Actinium with atomic no = 89 electrons are filled into 5f sub energy level. The next fourteen elements from Thorium with atomic number 90 to Lawrencium with atomic no 103 are called Actinides.

1.2 Periodicity and the Periodic Properties

The repetition of elements having similar properties after some interval with the increase in atomic number is called periodicity.

The periodic properties are

1. Atomic and ionic radii
2. Ionization energy
3. Electron affinity
4. Electronegativity

a. Atomic and ionic radii

The term atomic or ionic radius is generally used for distance between the nucleus and the outermost shell of electrons of the atomic or ionic particle. Since it is impossible to isolate an individual atom or an ion it is not possible to measure the atomic or ionic radius. These quantities are however generally derived in an indirect manner from the measured distance between the nuclei of two bonded atoms in a gaseous molecule or between the nuclei of two ions in crystals (solids). In the former case these distances are called internuclear distances (or bond lengths or bond distances) and in the latter case these are called interionic distances.

The internuclear distances (in covalent substances) and inter ionic distances (in ionic substances) are generally determined by X-ray diffraction, electron diffraction, NMR spectroscopy techniques etc.,

Classification of atomic radii

Atomic radii are sub divided into three classes

- i) Covalent radii as in non-metals and in covalent molecules in general
- ii) Metallic (or crystal) radii as in metals, alloys, or inter-metallic compounds and
- iii) Van der Waals radii

ii) *Covalent Radius*

It is defined as half of the distance between the nuclei of two like atoms bonded together by a single covalent bond. Thus covalent radii are essentially single bond covalent radii (SBCR)

For example, in a homo-nuclear diatomic molecule A_2 in which two A and A molecule bonded together by a covalent bond, the two like atoms are regarded as effective spheres in close contact with each other. Then according to the definition of covalent radius, the distance between the nuclei of these two atoms (ie bond length or internuclear distance d_{A-A}) should be equal to the sum of single-bond covalent radii of both the atoms.

Thus $d_{A-A} = r_A + r_A$

$$\text{Or } r_A = \frac{d_{A-A}}{2}$$

Where r_A = single-bon covalent radius of atom A.

In case of hetero- nuclear diatomic molecule, for example, AB the two atoms A and B are bonded together by purely covalent bond, then the inter nuclear distance (bond length) d_{A-B} is equal to the sum of r_A and r_B . Suppose the electronegetavity of atom A (x_A) and atom B (x_B) are equal, then d_{A-B} is equal to r_A+r_B

$$d_{A-B} = r_A + r_B \text{ [when } x_A = x_B]$$

If x_A is not equal to x_B in such cases experimental value of d_{A-B} is less than the sum of r_A and r_B .

The following examples illustrate the above fact,

$$\begin{aligned} \text{i) } (d_{C-I})_{\text{expt}} &= 2.14 \text{ \AA} \\ (d_{C-I})_{\text{cal}} &= r_C + r_I = 0.77 + 1.33 = 2.10 \text{ \AA} \end{aligned}$$

Similarly

$$\begin{aligned} \text{ii) } (d_{S-Br})_{\text{expt}} &= 2.27 \text{ \AA} \\ (d_{S-Br})_{\text{cal}} &= r_S + r_{Br} = 1.02 + 0.14 = 2.16 \text{ \AA} \end{aligned}$$

The factors responsible for observed deviation are

- i) Electro negativity difference between the bonded atoms A and B (or due to the increasing ionicity of the A-B bond)
- ii) Multiplicity of the bond between A and B.

The ionic character of A-B bond {Schomaker and Stevenson 1941} is compensated as follows the inter atomic distance d_{A-B} for a bond A-B is taken as the sum of covalent radii r_A and r_B and

subtracted with a correction term $-0.09 (x_A - x_B)$. Where x_A and x_B is the absolute values of electronegativity of A and B

$$\text{Thus } d_{A-B} = r_A + r_B - 0.09 (x_A - x_B)$$

Types of covalent radii

Covalent radii may be single bond, double bond and triple bond covalent which involve single, double, and triple bond respectively. The double bond and triple bond covalent radii are called multiple covalent radii.

Metallic Radius (Crystal Radius)

This is used for metal atoms which are assumed to be closely packed sphere in the metallic crystal. The metal atoms are supposed to touch one another in the crystal and the crystal radius is defined as *one-half of the distance between the nuclei of two adjacent metal atoms in the metallic close packed crystal lattice in which metal exhibits a co-ordination number of 12* eg, the inter nuclear distance between two adjacent sodium atoms in a crystal of sodium metal is 3.80 \AA only the atomic radius (or metallic radius) of Na metal = $3.80/2 = 1.90 \text{ \AA}$. Metallic radii are about 10 to 15 % higher than the single bond covalent radii.

The metallic radii are smaller than the Vander waals radii since the bonding forces in the metallic crystal lattice are much stronger than the Vander waals forces.

Van der waals radius or Collision radius

In the solid state the non-metallic elements usually exist as aggregations of molecules. The bonding within non-metallic molecule is largely covalent in character and the individual molecules are held together by attractive force called Van der waals forces of attraction. When two molecules approach each other without forming a chemical bond, there will be a slight attraction between them due to a mutual distortion of their electron clouds this force is called Van der Waals force. These forces are absent in gaseous condition.

Van der Waals radius is half of the distance between the nuclei of two non-bonded neighboring atoms of two adjacent molecules.

Comparison between Van der Waals and Covalent radii

Consider two molecules of chlorine viz $\text{Cl}_2(1)$ and $\text{Cl}_2(2)$ in close contact with each other (not bonded). Let X and Y be the two nuclei of the two chlorine atoms of $\text{Cl}_2(2)$ molecule and X' and Y' be the those of the two chlorine atoms of $\text{Cl}_2(1)$ molecule. The half of the distance between the nuclei Y and X' of the two non-bonded neighbouring chlorine atoms of adjacent molecules

$\text{Cl}_2(1)$ and $\text{Cl}_2(2)$ is Van der Waals radius of chlorine atom while half of the distance between the two nuclei X and Y in the same molecules $\text{Cl}_2(2)$ is the covalent radius of chlorine atom. In case of chlorine, Van der Waals radius = $3.60/2 = 1.8 \text{ \AA}$ while covalent radius = $1.99/2 = 0.99 \text{ \AA}$ thus covalent radius is smaller than the Van der Waals radius.

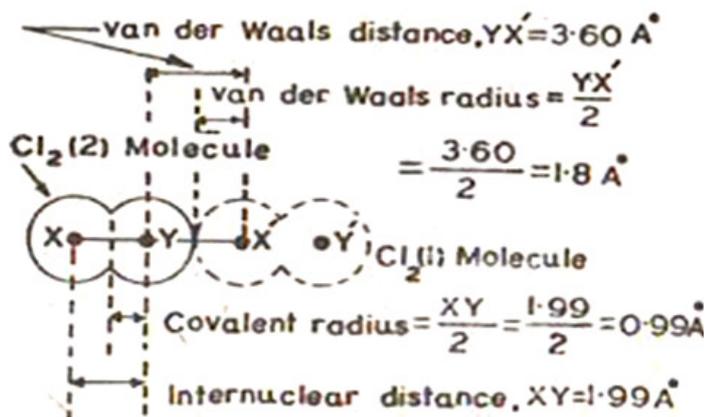


Figure 2. Comparison between covalent and Van der Waals radius in chlorine atom. $\text{Cl}_2(1)$ and $\text{Cl}_2(2)$ are two chlorine molecules in close contact with each other (no bond formation) X and Y are the two nuclei of the two chlorine atoms of $\text{Cl}_2(2)$ molecule while X' and Y' are those of $\text{Cl}_2(1)$ molecule.

Noble gases do not form covalent bonds. Thus in crystals of noble gases no chemical forces operate between the atoms. It is only the Van der Waals attractive forces prevailing in these atoms. Thus for noble gases in the solid state the crystal radii (atomic radii) are Van der Waals radii.

b) Ionic radii

Ionic radius is defined as the distance between the nucleus of an ion and the point up to which the nucleus has influence on its electron cloud.

Periodicity

1. along a period ionic radius decreases with increase in atomic number and down a group ionic radius decrease with the increase in atomic number.
2. Removal of an electron from the outermost orbit of a neutral atom forms a positively charged particle called cation. The net nuclear force of attraction on the remaining electrons increases and the external electron cloud shrinks. Therefore size of a cation is smaller than that of the corresponding neutral atom.
3. Addition of an electron on to the outermost orbit or valence orbit of a neutral atom forms a negatively charged particle called anion. Nuclear force of attraction on the outermost electron

cloud decreases and external electron cloud expands. Therefore size of anion is larger than that of neutral atom.

Isoelectronic ions

They are ions of different elements containing the same number of electrons. Examples are listed in the below table.

Ions	F ⁻	O ²⁻	N ³⁻	Na ⁺	Mg ⁺	Al ³⁺
No of electrons	10	10	10	10	10	10
No of proton	9	8	7	11	12	13

In isoelectronic ions external electron cloud shrinks with the increase in nuclear charge the outermost electrons are subjected to more nuclear force of attraction. Therefore ionic size decreases.

Examples: 1) $H^- > Li^+ > Be^{2+}$

2) $N^{3-} > O^{2-} > F^-$

3) $Na^+ > Mg^{3+} > Al^{3+}$

Factors influencing ionic size (ionic radii)

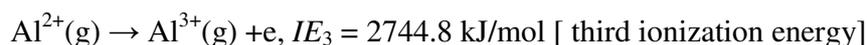
Following factors are influencing the ionic radii of an ion

1. Nuclear charge or number of protons in the nucleus.
2. Number of orbitals in an orbit.

b) Ionization energy (IE)

Ionization energy of an atom is defined as the amount of energy required to knock out the most loosely bound electron in the outermost shell in an isolated atom in the gaseous phase to generate a singly charged cation is referred to as the first ionization energy of the element.

The ionization energies are expressed in eV per atom or kJ mol⁻¹ (1 eV per atom = 96.48 kJ/ mol = 23 kcal mol⁻¹).



From the above example it is clear that, the higher ionization energies are always greater than the lower ionization energies. This is because removing an electron from a more positively charged species always required more energy therefore $IE_3 > IE_2 > IE_1$

The ionization energies for some molecules are given below.

$\text{CO(g)} \rightarrow \text{CO}^+(\text{g}) + \text{e}$, $IE = 1352 \text{ kJ/mol}$; $\text{N}_2(\text{g}) \rightarrow \text{N}_2^+(\text{g}) + \text{e}$, $IE = 1503 \text{ kJ/mol}$; $\text{NO(g)} \rightarrow \text{NO}^+(\text{g}) + \text{e}$, $IE = 894 \text{ kJ/mol}$; $\text{O}_2(\text{g}) \rightarrow \text{O}_2^+(\text{g}) + \text{e}$, $IE = 1164 \text{ kJ/mol}$.

Periodicity of ionization energy

1. along a period ionization energy increases with the increase in atomic number. This is due to increase in nuclear force of attraction on the outermost electron as electrons are added on to the orbitals of same orbital.
2. Down a group electrons are added on to a new orbit with the increase in atomic number. Therefore electrons are placed more and more away from the nucleus. Therefore nuclear force of attraction decreases. Ionization energy decreases down a group with the increase in atomic number.

Factors deciding ionization energy

i) Atomic size or Atomic Radius

Larger the atomic size lesser the Ionization energy.

ii) Nuclear charge

Increase in nuclear charge increases ionization energy.

iii) Shielding effect of inner orbital electrons

Larger the number of electrons on inner orbitals, smaller the force of attraction on the valence orbit electron. Therefore higher shielding effect means smaller ionization energy

iv) Type of orbital containing outermost electron

The nuclear force of attraction on electrons of the different orbitals is in the order $s > p > d > f$. this is because 's' orbital is closer to the nucleus.

v) Stability of half filled or completely filled orbitals

Either exactly half filled or completely filled orbitals give extra stability to the atom. Ionization energy for such an atom is generally high. Therefore ionization energy of nitrogen is higher than ionization energy oxygen. Ex: EC of N = $1s^2 2s^2 2p^3$



Half filled

EC of Oxygen is $1s^2 2s^2 2p^4$



Incomplete filled

c) Electron affinity (EA)

Electron affinity is defined as the amount of energy released when an electron is added to the valence shell of the isolated gaseous species (which may be an atom or ion or a molecule). The magnitude of electron affinity is positive, which indicates that the process is exothermic [i.e., $X(g) + e \rightarrow X^-(g)$].

The convention accepted in defining the electron affinity apparently contradicts the established convention in thermodynamics. It happens so because in the given definition the term 'Energy release' has been coined but in all electron affinity processes energy release may not occur and in some cases energy absorption may also occur.

For example $F(g) + e \rightarrow F^-(g)$, $\Delta H = -328 \text{ kJ/mol}$ and $EA = 328 \text{ kJ/mol}$,

**Periodicity of electron affinity**

1. Along a period with the increase in atomic number the net nuclear charge increases and hence nuclear force of attraction increases. Therefore electron affinity increases. This is because in a period the effective nuclear charge increases and the size decreases with the increase of atomic number in a period. This is why the electron affinity in general increases in a period.
2. Down a group with the increase in atomic number electrons are placed on to the valence orbit which is away from the nucleus. Therefore the shielding effect on inner orbital electrons decreases. Therefore electron affinity decreases.

d) Electronegativity

Electronegativity is defined as the electron attracting power of an atom towards its nucleus when the atom is covalently bonded in a molecule. Thus the more electronegative element withdraws the bonding electron cloud more towards its own nucleus giving rise to an accumulation of negative charge on it.

From the definition it is evident that the electronegativity of an element is not an inherent property of the element. It depends on its surrounding environment in the molecule in which the electronegativity of the elements is being considered. Thus the electronegativity of S in the compounds H_2S , SF_4 and SF_6 is not the same and it is different in different compounds. Electronegativity of an element is not its inherent property but the electron affinity of an element is an inherent property.

Periodicity of electronegativity

1. Along a period with the increase in atomic number net nuclear force of attraction increases. Therefore electronegativity increases. Fluorine has the highest electronegativity equal to four.
2. Down a group with increase in atomic number. Inner orbital electron repulsive force increases as electrons are added on to a new orbit. Therefore electronegativity decreases.

1.3 The Octet Rule

It is found that when two atoms form covalent bonds, they attain an inert configuration with an octet electrons i.e., $ns^2 np^2$ -configuration is attained. This is known as octet rule.

In most of the cases, through the covalent linkage formation each of the combining species attains the octet i.e., $ns^2 np^6$ configuration. If the species already bears the octet configuration, it will not display any tendency to form covalent linkage. In the case of hydrogen the inert gas configuration of helium i.e., ns^2 is attained. This is very often referred to as the rule of duplet. There are a lot of molecules in which the rule of octet and duplet have been satisfied. For example, $H_2(H-H)$, $N_2(:N\equiv N:)$, $O_2(\ddot{O}=\ddot{O})$, $CO_2(\ddot{O}=C=\ddot{O})$, $H_2O(H-\ddot{O}-H)$, $:NH_3$, CCl_4 , etc....,

Deviation from the octet Rule

There are number of molecules in which the combining species or atoms have less than eight electrons (and they are called incomplete octet) or more than eight electrons (and they are called expansion of octet) in the covalently bonded molecules.

Incomplete Octet

In the molecules such as $BeCl_2$, BBr_3 and $NO (:N=O)$ the central atoms i.e., Be, B and N bear four six and seven electrons respectively. It is important to note that other atoms except the central ones in the above compounds maintain the octet rule. A large number of compounds formed by Be (quartet), M (sextet) where $M = B, Al, Ga$ are known to form incomplete octets. Therefore these compounds are referred as electron deficient compounds and they are characterized by a tendency to receive back a lone pair electron to attain the octet. Hence the electron deficient compounds are called Lewis acids.

Expansion of Octet

In the compounds like PCl_5 , ClF_3 , SF_6 , SiF_6^{2-} etc...., the central elements P, Cl, S and Si are bearing ten, twelve and twelve electrons respectively and display the expansion of octet

Similarly in OsF_8 there are sixteen electrons around Os. Here also except the central atoms all other atoms satisfy the octet rule.

1.5 Sugden's View of singlet linkage bond (2c-1e) in favour of Octet rule

To explain the expression of octet which apparently contradicts the rule of octet, Sugden proposed that to maintain the octet rule some of the bonds may arise by sharing a single electron 2c-1e i.e., two centre one electron bond instead of 2c-2e bonds. This single electron bond ie 2c-1e is very often referred as singlet linkage or half bond. This singlet linkage is represented by a half arrow pointing towards the acceptor. Thus it is believed that in PCl_5 there are two singlet linkages in addition to the three ordinary covalent 2c-2e bonds leading to the octet ie $(2 \times 1) + (3 \times 2) = 8$ at P similarly in SF_6 there are four singlet linkages along with the two ordinary covalent bonds to give the octet ie $(4 \times 1) + (2 \times 2) = 8$ around S.

This concept of singlet linkage is not supported from the experimental facts. In PCl_5 or SF_6 all the bonds are found equivalent. Definitely 2c-1e bonds are weaker than the 2c-2e bonds but no such indication is supported by the fact. Therefore the Sugden's concept of singlet linkage to define the octet theory has no practical importance.

1.5 Sidgwick's rule of Maximum covalency

According to Sidgwick the number of maximum electrons which can be accommodated around an atom in the valence shell depends on the periodic position of the concerned element.

The empirical rule states as: the element ie hydrogen in 1st period can have maximum 2 electrons ie 1 bond for each of the elements in the 2nd period ie Li to F the maximum number of electrons to be accommodated is given by 8 ie 4 bonds similarly for the elements in the 3rd and 4th periods it is limited by 16 i.e., 8 bonds.

Thus the maximum capacity to accommodate the electrons around an atom in its valence shell in a compound is mainly dependent on the number of orbitals available for bonding. This is why the rule of octet is limited only for the elements of the second period. Because of steric and other factors, all the available orbitals for a particular atom may not always participate in bonding to attain in the maximum possible covalency.

1.6 Hypervalent and Subvalent compounds

Compounds in which the number of electrons around an atom generally the central atom exceeds an octet are called Hypervalent compounds. Example: SF_6 , PCl_5 etc....,

Compounds in which the number of valence electrons around an atom is less than an octet are called subvalent compound. Example, $\text{PH}_2 \text{CH}_2 \text{NO NO}_2$ etc....

1.7 Oxidation state or Oxidation number

Oxidation numbers are hypothetical numbers assigned to an individual atom or ion present in a substance using a set of rules. Oxidation numbers (or oxidation states) can be positive, negative, or zero. The oxidation numbers are always reported for one individual atom or ion and not for groups of atoms or ions. Oxidation state shows the total number of electrons which have been removed from an element (a positive oxidation state) or added to an element (a negative oxidation state) to get to its present state.

Rules for assigning oxidation number

- The oxidation state of an uncombined element is zero. Because it hasn't been either oxidized or reduced. This applies whatever the structure of the element for example, Xe or Cl_2 or S_8 , giant structure like carbon or silicon.
- The sum of the oxidation states of all the atoms or ions in a neutral compound is zero.
- The sum of the oxidation states of all the atoms in an ion is equal to the charge on the ion.
- The more electronegative element in a substance is given a negative oxidation state. The less electronegative one is given a positive oxidation state.
- Some elements almost always have the same oxidation states in their compounds:

1.8 Covalent bond

In 1919 Lewis suggested that there are atoms which attain inert gas configuration i.e., $1s^2$ or ns^2p^6 configuration by sharing one or more electron pairs with similar or dissimilar atoms. Each atom contributes one electron to the electron pair and has equal claim on the shared electron pair. Langmuir called the -electron pair bond a covalent bond. Thus the concept of covalent bond is known as Lewis Langmuir concept.

Therefore covalent bond is defined as *a chemical bond formed between two or more atoms in a molecule by sharing two electrons for each bond pair from each atom.*

A covalent bond is expressed in the formula by placing a bar (-) between the atoms bonded together. A covalent bond is non – polar and non – ionized because it is not formed by transfer of electrons from one atom to the other and thus the molecule having the covalent bond does not acquire ions. For this reason covalent bond is also called non-polar bond.

1.9 Types of Covalent bond

Covalent bond may be single covalent bond, double covalent bond or triple covalent bond. Double and triple covalent bonds are called multiple covalent bonds.

Single covalent bonds are formed by the sharing of only one electron pair between the bonded atoms e.g., H-H, Cl-Cl, F-F, ETC...

Double and triple covalent bonds are formed when the atoms bonded together by sharing two or three electron pairs respectively e.g., $N\equiv N$, $O=O$, $HC\equiv CH$, $H_2C=CH_2$, etc...

1.10 Polar and non-polar covalent bonds

In a covalent bond between two similar atoms (A and A) the shared electron pair between them will be shared equally by both the atoms and hence the covalent bond will have no ionic character. Such type of bond is regarded as true covalent bond.

But a covalent bond formed either between two unlike atoms (A and B) or between two like atoms having different neighbors (e.g., C-atoms in H_2C-CCl_3 molecule), the shared bonded electron pair will not be equally distributed among both the atoms. This is because if atom A has a stronger attraction for electron pair (i.e., has greater electronegativity) than atom B, the shared electron pair will be attracted towards A and away from B. This type of permanent displacement of electron pair towards A in the covalent bond will develop a fraction of negative charge δ^- on atom A and a fraction of positive charge δ^+ on atom B. Therefore the molecule AB will be depicted as $A^{\delta-} - B^{\delta+}$ and the bond between A and B has some ionic character and is called polar covalent bond.

The bond between the two like atoms (e.g., in H_2 , Cl_2 etc molecules) is called a non-polar or homo-polar covalent bond or simply covalent bond. Actually covalent bonds also have slight ionic character e.g., the bond H-H in H_2 molecule also has about 2% ionic character which arises from the small contributions of the ionic resonance structures to the total structure of H_2 molecule.

In general when in a molecule AB the electronegativity of atom A = x_A is equal to that of B = x_B this will possible in a molecules having two identical atoms (eg H_2 Cl_2 molecules) then the bond A-B will be pure covalent. When $x_A \neq x_B$ then the covalent bond formed between them will have some ionic character. The amount of ionic character will primarily depend on the value of ($x_A - x_B$). Thus if $x_A > x_B$ the bond will be ionic and represented as $A^- - B^+$ and if $x_A < x_B$ then also

it will be ionic and represented as $A^+ - B^-$ but when $x_A = x_B$ then it is represented as $A \times B$ or $A-B$ and the bond is purely covalent bond.

1.11 Variable covalency or Maximum covalency

Covalency of an element is defined as the number of electrons contributed by it for sharing purpose while forming covalent bond. Generally the covalency of an element which has only s and p orbitals in its valance shell (e.g., H, O, N etc) is a fixed quantity {not always} and is equal to the total number of unpaired electrons in 's' and 'p' orbitals

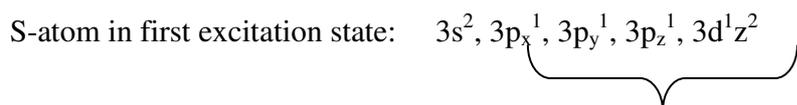
Example, the covalency of the elements viz. H ($1s^1$), F($2s^2, 2p_x^1, 2p_y^2, 2p_z^1$), O ($2s^2, 2p_x^2, 2p_y^1, 2p_z^1$) and N ($2s^2, 2p_x^1, 2p_y^1, 2p_z^1$) is equal to 1, 1, 2 and 3 since these elements have 1, 1, 2 and 3 unpaired electrons respectively.

On the other hand the elements having 'd' orbitals in their valance shell configuration (e.g., S P Cl etc) show variable covalency

For example.

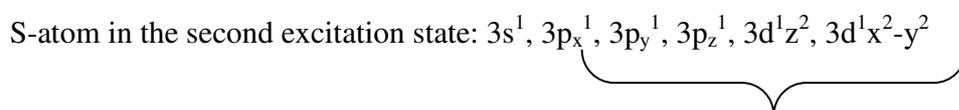
1. Sulphur atom:

- i) Sulphur atom in its ground state has two unpaired electrons ($S \rightarrow 3s^2, 3p_x^2, 3p_y^1, 3p_z^1$) and therefore shows a covalency of two.
- ii) The valence - shell configuration of sulphur atom in the first excitation state is obtained by promoting one of the paired $2p_z$ electrons to the vacant 3d orbital to get four unpaired electrons which result in a covalency of four atom as shown below:



Four unpaired electrons result in
a covalency of four

3. On the same basis the covalency of six of sulphur atom can also be explained.



Six unpaired electrons result in
a covalency of six

2. The variable covalencies equal to 3 and 5 for a phosphours atom and 3 5 and 7 for the halogen atoms (except fluorine) can also be explained on the basis of the arguments mentioned above. It is important to note that the maximum covalency exhibited by an

element is equal to the number of unpaired electrons obtained after unpairing all the s and p electrons.

3. Also it is seen that, the variable covalency is shown only by those elements whose atoms have vacant d orbitals in their valence shell configuration so that unpairing of s and p electrons by promoting them to vacant d orbitals is possible. The elements having no d orbitals (e.g., elements of 2nd period) do not exhibit variable covalency. Therefore the molecules like NCl₅ and OF₆ do not exist.

1.12 Characteristics of Covalent compound

1. Covalent compounds are formed by the sharing of electrons between the atoms. Parts of their crystal lattice are molecules which are held by weak Van der Waals forces.
2. These are generally soluble in organic solvents.
3. Unlike electrovalent compounds which are solids these may be solids, liquids or gases. Their melting and boiling points are low.
4. These are generally soft easily fusible and volatile.
5. The covalent bond is directional and there is a possibility of position isomerism and stereo isomerism amongst these compounds.

Nature of covalent bond

Development of the wave mechanics enables two alternative theories to explain the nature of covalent bond. These two theories are

1. Valence bond theory
2. Molecular orbital theory

1.13 Valence bond theory

This theory is developed by Heitler, London, Pauling and Slater and applied by Heitler and London in 1927 to H₂ molecule

In case of H₂ molecule there is a possibility of interchange of electrons between the two H atoms even though the two H atoms in a H₂ molecule are identical. Suppose H_A and H_B are the two hydrogen atoms in H₂ molecule. Then imagine these two H-atoms, H_A and H_B at an infinite distance from each other so that no appreciable interaction may occur between them. Thus there are two possible equivalent structures of H₂ molecule (I) and (II) shown below are indistinguishable once the bond has been formed.



In structure (I) the nucleus H_A has electron 1 and nucleus H_B has electron 2, in structure (II) these electrons have been exchanged.

Now if ψ_1 and ψ_2 are the wave functions for the structure (I) and (II) respectively then according to VBT $\psi_I = \psi_A(1) \psi_B(2)$ ----- (1)

$$\psi_{II} = \psi_A(2) \psi_B(1) \text{ ----- (2)}$$

Where $\psi_A(1)$, $\psi_B(2)$ and $\psi_A(2)$, $\psi_B(1)$ are the wave functions for the independent H-atoms namely ¹H_A, ²H_B, ²H_A and ¹H_B respectively.

The true wave function ψ for H₂ molecule is given by

$$\psi = C_I \psi_I + C_{II} \psi_{II}$$

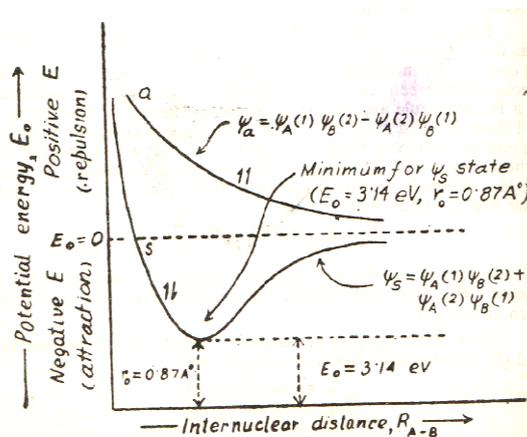
$$\psi = C_I \psi_A(1)\psi_B(2) + C_{II} \psi_A(2)\psi_B(1)$$

Where C_I and C_{II} are the mixing coefficients. For H₂ molecule C_I = ±1. Therefore two possible values of ψ , one corresponding to C_I = 1 and C_{II} = +1 and other corresponding to C_I = 1 and C_{II} = -1. Let these two values of ψ be represented as ψ_s and ψ_a thus

$$\psi_s = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1) \text{ ----- (3)}$$

$$\psi_a = \psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1) \text{ ----- (4)}$$

Equation (3) represents a symmetric combination of $\psi_A(1)$, $\psi_B(2)$ and $\psi_A(2)$, $\psi_B(1)$ since ψ_s remains unchanged by exchange of electron 1 and 2 whereas equation (4) represents an anti symmetric combination, since ψ_a changes its sign by exchange of electrons. The plot of the energy E against the internuclear distance R_{A-B} between the two hydrogen atoms H_A and H_B of H₂ molecule is shown in below figure. It is evident from the plot, curve 'a' represents ψ_a state and in this state the two electrons are in parallel spins. Therefore the energy continues to rise as the two atoms gets close together and no bond is formed. Thus ψ_a is a repulsive or non bonding state.



The energy curve represents the ψ_s state the two atoms have opposed spins, possesses a definite minimum which corresponds to the formation of molecule. It would be evident from curve s representing ψ_s that at minimum the calculated dissociation energy E_0 (or bonding energy) and bond length r_0 are 3.14 eV and 0.87 Å respectively. The corresponding experimental values are 4.7 eV and 0.74 Å.

1.14 Suggested made by Pauling to improvement

The calculations of E_0 by Hitler-London method is improved by Pauling by considering two additional ionic structures for the molecule in which both the electrons 1 and 2 are attached to one atom. These two ionic structures III and IV as shown below:



Ionic structure

Let these structures be represented by wave functions ψ_{III} and ψ_{IV} which are given by

$$\psi_{III} = \psi_A(1) \psi_A(2) \text{ ----- (5)}$$

$$\psi_{IV} = \psi_B(1) \psi_B(2) \text{ ----- (6)}$$

The consideration of the ionic structures (III) and (IV) of H_2 molecule convert equation (3) to

$$\begin{aligned} \psi_s &= \psi_A(1) \psi_B(2) + \psi_A(2) \psi_B(1) + \lambda (\psi_{III} + \psi_{IV}) \\ &= \psi_A(1) \psi_B(2) + \psi_A(2) \psi_B(1) + \lambda [\psi_A(1) \psi_A(2) + \psi_B(1) \psi_B(2)] \end{aligned}$$

$$\text{or } \psi_s = \psi_{cov} + \lambda \psi_{ion} \text{ ----- (7)}$$

Weinbaum used equation (7) and found the values of E_0 and r_0 equal to 3.21 eV and 0.88 Å respectively for $\lambda = 0.158$

The coefficient λ in equation (7) is a measure of the degree to which the ionic forms III and IV contribute to the bonding i.e., λ offers a means of calculating the degree of the ionic character in the covalent bond.

1.15 Important results or postulates of VBT

The overlap of atomic orbitals.

The following points are significant

1. The atoms which involve in forming a molecule are completely retain their identities in the resulting molecule.
2. The formation of a covalent bond is due to overlap of atomic orbitals. If the two atoms each having one unpaired electron come together and overlap, the spins of the two electrons get

mutually neutralized resulting in the formation of a covalent bond which is localized between the two atoms. If the electrons present in the AO's have parallel spins no bond formation will occur ie no molecule will be formed.

3. If the AO's possess more than one unpaired electrons then more than one bond can be formed. Thus in N_2 molecule has three unpaired electrons hence there are three bonds in nitrogen molecule ($N \equiv N$).

4. Electrons which are already paired in the valence shell cannot participate in bond formation. However, they can participate only if they become unpaired without using much energy. It is known that the energy is released when a covalent bond is formed. If this energy exceed the energy needed to unpair the electron (by shifting it to the vacant orbital of slightly higher energy of the same main energy level) then more bonds are formed.

Thus N atom ($2s^2, 2p_x^1, 2p_y^1, 2p_z^1$) shares its three unpaired 2p-electrons with fluorine atom to form NF_3 but cannot form NF_5 since the second main energy level does not possess any other orbital which may accommodate one of the 2s electrons after promotion. On the other hand P ($3s^2, 3p_x^1, 3p_y^1, 3p_z^1, 3d^0$) can form PF_5 since in the third main energy level 3d orbital is also available to accommodate one of the 3s electrons giving five unpaired electrons P ($3s^1, 3p_x^1, 3p_y^1, 3p_z^1, 3d^1$).

5. The strength of the covalent bond is directly related to the extent to which the two AO's can overlap in space. Maximum bonding orbitals overlap leads to more bonding electrons are concentrated between the nuclei, this minimize the nuclear repulsion and maximize the attractive forces between themselves. Hence the greater the overlap between the AO's the greater is the strength of the resulting covalent bond.

The extent of overlap of two AO's the represented by wave function ψ_A and ψ_B is expressed quantitatively by the overlap integral S which is given by

$$S = \int \psi_A \psi_B dr$$

When S is positive (ie $S > 0$) there is a build-up of electron charge (ie electron density) between the nuclei of the two combining atoms and a bond can be formed. When S is negative ie $S < 0$ there is a reduction in the electron density between the nuclei so that the repulsion between them is increased and they tend to move apart. When the overlap is zero (ie $S = 0$) there is no net interaction (ie neither attraction nor repulsion) between the combining atoms.

For example if the radius of an s orbital is equal to 1 unit, then the length of a lobe of p orbital will be equal to $\sqrt{3}$ and the relative magnitudes or strength of the p and s orbitals would be in the ratio of $\sqrt{3}:1$. The bond strength is taken equal to the product of the magnitude of the bond orbitals of the two atoms forming the bond. Thus the strength of the s-s bond (i.e., bond formed by the overlap of s orbitals) is equal to $1 \times 1 = 1$ that of s-p bond equal to $1 \times \sqrt{3} = 1.732$ and that of p-p bond equal to $\sqrt{3} \times \sqrt{3} = 3$.

The relative bond strengths are as follows

$$\text{s-s: } 1 \times 1 = 1, \text{ s-p: } 1 \times \sqrt{3} = 1.732, \text{ p-p: } \sqrt{3} \times \sqrt{3} = 3$$

This shows that p orbitals can overlap with s or p orbitals more effectively than two s orbitals.

1.16 Overlap of atomic orbitals – sigma (σ) and pi (π) bonds

Different types of overlap are possible depending on the type of atomic orbitals involved in bond formation. As a result of these overlap the covalent bond formed may be called as either a σ -covalent bond or a π -covalent bond.

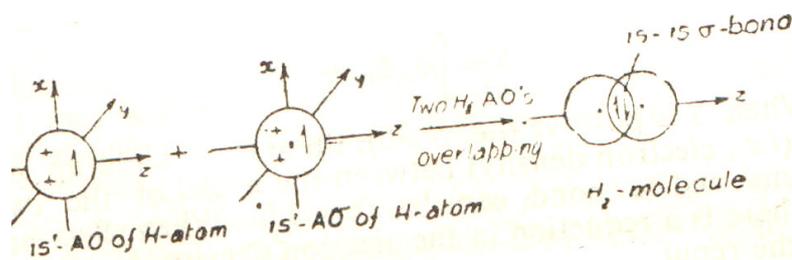
σ -bond

A covalent bond formed between two atoms by end to end or head to head overlap of atomic orbitals along their axes is called a σ -bond. All σ -bonds have axial symmetry. σ -bond is a strong bond, because maximum overlap of two orbitals along their axes.

If z-axis is the molecular axis, σ -bond is given by s-s, s- p_z and p_z - p_z overlaps. These σ -bonds are called (s-s) σ , (s- p_z) σ and (p_z - p_z) σ bonds respectively.

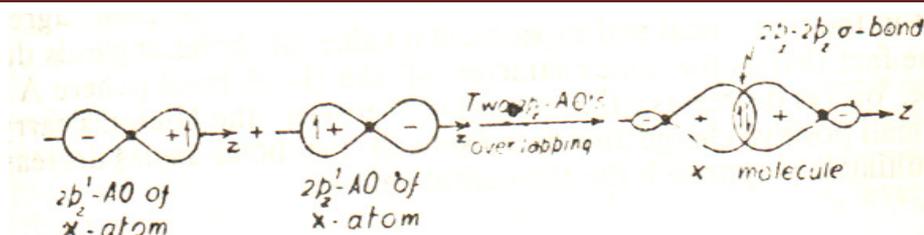
i) s-s overlap and structure of H_2 molecule

1s AO's of the two H atoms in a H_2 molecule overlap with each other and give a covalent bond between them



ii) p_z - p_z overlap and structure of X_2 molecule ($X=F, Cl, Br, I$)

The bond in X_2 molecule can be ascribed to the overlap of $2p_s$ AO's and is linearly directed ($X \rightarrow 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$) as shown in below figure.

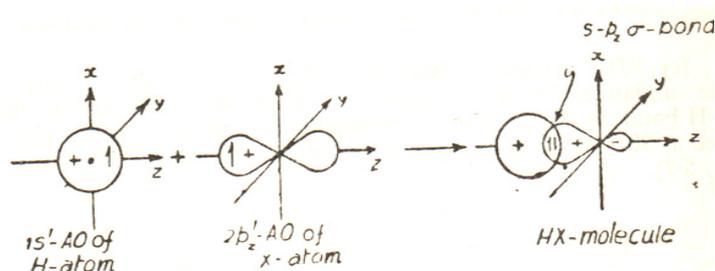


iii) $s-p_z$ overlap

This type of overlap can be exemplified by considering the formation of HX (where X is F Cl Br or I) H_2O and NH_3 molecules.

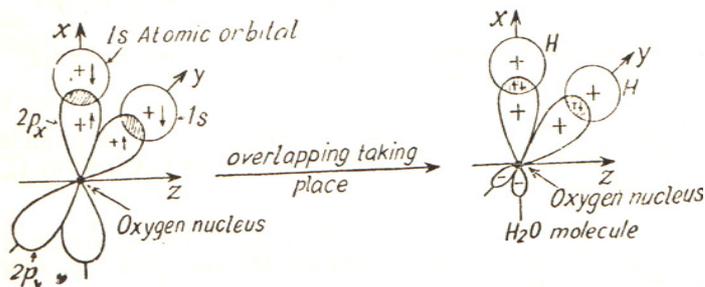
a) HX molecule (X is F, Cl, Br or I)

This molecule is also formed by the overlap of $1s$ – AO of H atom with $2p_z$ AO of X atom. Both the AO's are singly occupied

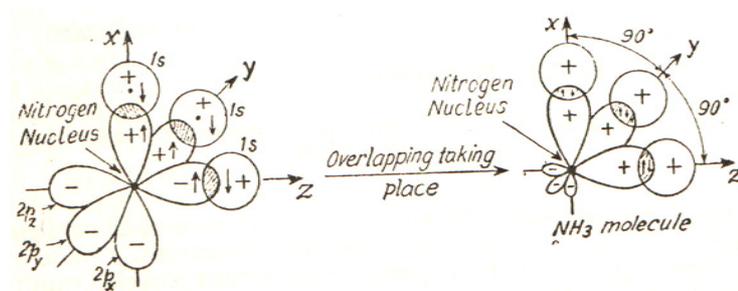


b) Water Molecule (H_2O)

O-atom with its valence shell configuration $2s^2, 2p_x^1, 2p_y^1, 2p_z^2$ has two unpaired p electrons. These two AO's namely $2p_y$ and $2p_z$ overlap with two $1s$ orbitals of two H atoms and thus two $s-p$, σ -bonds are formed. Now since $2p_y$ and $2p_x$ AO's are at right angles to each other an angular structure with two O-H bonds inclined at 90° to each other would be expected, but the actual H-O-H angle, experimentally found in H_2O molecule is 105° . The increase in the bond angle is due to the mutual electrostatic repulsion between the two H atoms which have fractional positive charge on them. This fractional positive charge is caused by the fact that the bond O-H is not purely covalent but has some ionic character. The experimental bond angles in other related molecules is $\text{H}_2\text{S} = 92.2^\circ$ $\text{H}_2\text{Se} = 91.0^\circ$ and $\text{H}_2\text{Te} = 90^\circ$, approach closely the expected theoretical value (i.e., 90°). This close agreement in the theoretical and experimental value of bond angles is due to the fact that as the ionic character of the H-A bond where A is O, Se or Te decreases the repulsion between the H atoms carrying small positive charge also decreases and the bond angles decrease and ultimately approach the theoretical values.

c) NH₃ molecule

There are three unpaired 2p orbital electrons in N ($2s^2, 2p_x^1, 2p_y^1, 2p_z^1$). Thus it is expected to form three N-H bonds in NH₃ molecule perpendicular to each other (i.e., inclined at 90°) which would give a pyramidal shape to NH₃ molecule



The related molecules PH₃, AsH₃ and SbH₃ also have similar structure. The experimental H-N-H bond angle in NH₃ is 108° which is greater than the theoretical value of 90° . The greater value of experimental bond angle is attributed to the mutual repulsion between the two H atoms. Bond angle of the related molecules (PH₃ = 93° , AsH₃ = 92° and SbH₃ = 91°) approach 90° due to the reason that as the repulsion between the two H atoms in these molecules on proceeding from PH₃ → SbH₃ diminishes the bond angle H-A-H where A is P, As or Sb approaches 90° .

 π -bond

A covalent bond formed between two atoms by the overlap of atomic orbitals along a line perpendicular to the molecular axis (side to side or lateral overlap) is called a π -bond.

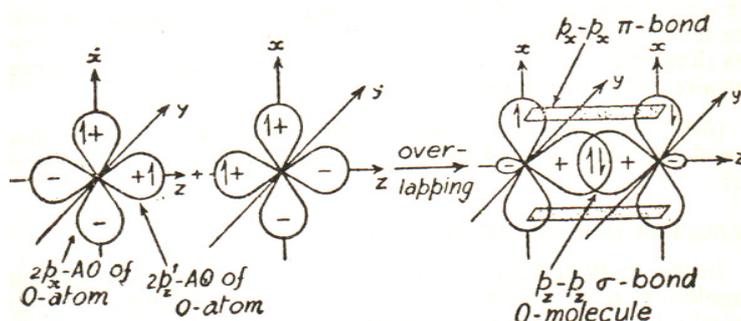
If z axis is assumed to be the molecular axis π -bond is given by p_x - p_x and p_y - p_y overlaps.

p_z and p_y orbitals which on overlapping respectively with p_x and p_y orbitals give π -bonds are referred to p_π -orbitals.

1) O₂ molecule

O-atom has $2s^2, 2p_x^1, 2p_y^2, 2p_z^1$ configuration. Evidently $2p_z$ AO (singly occupied) of one O-atom will overlap with $2p_z$ AO of the other O-atom to give a p_z - p_z , σ -bond and the two $2p_x$ AOs

singly occupied of both the O-atoms will overlap along a line perpendicular to z axis (molecular axis) to give another type of covalent bond known as π -bond. It is a p_x-p_x , π -bond. Thus O_2 molecule has two covalent bonds, one is p_z-p_z σ -bond and the other is p_x-p_x π -bond.



2) N_2 molecule

N atom has $2s^2, 2p_x^1, 2p_y^1, 2p_z^1$ configuration. N_2 molecule has three covalent bonds one is σ -bond ($2p_z-2p_z$) and two π -bonds ($2p_x-2p_x$ and $2p_y-2p_y$)

1.17 Difference between σ -bonds and π -bonds

- σ -bond is formed by the overlap of orbitals by end to end overlap (along bond axes) while π -bond results from side to side overlapping of the orbitals.
- Since the extent of overlapping of orbitals along the bond axes is always greater than the extent of overlapping at an angle 90° , σ -bond is stronger than π -bond.
- Electron cloud of a σ -bond is symmetrical about the line joining the two nuclei while that of a π -bond is unsymmetrical.
- There can be free rotation of the atoms round the σ -bond. Such type of rotation is not possible round the π -bond since the electron clouds overlap above and below the plane of atoms.
- σ -bond determines the direction of the bond and the extent of the internuclear distance. π -bond has no primary effect on the direction of the bond but shortens the internuclear distance

1.18 Limitations of VBT

- Since the two electrons of the shared pair constituting the covalent bond must come from two different atoms, it is evident that this theory does not give any explanation of the formation of a coordinate bond in which one of the bonded atoms furnishes both the electrons.
- The two atoms in O_2 molecule should have close electronic shells resembling those of Ne which would give no unpaired electrons to the molecule and thus will make it diamagnetic.

Actually experiments show that O_2 molecule is paramagnetic indicating the presence of unpaired electrons in oxygen molecule.

3. This theory does not consider the formation of odd electron molecules or ions such as H_2^+ ion where no pairing of electrons occurs.

1.19 Summary of the unit

It is easy to understand that the ions forming ionic bonds are held together by electrostatic force of attraction. Carbon forms thousands of stable compounds, similarly formation of molecules by similar atoms e.g., chlorine molecules, Cl_2 and formation of molecules by dissimilar atoms e.g., Hydrogen chloride, water, ammonia, which do not have properties indicating the presence of ionic constituents. Therefore it is not clear as what holds two or more atoms together in them. Lewis proposed that these elements attain inert gas configurations by sharing of electrons with atoms of similar or dissimilar elements. The electrons are shared in pairs each atom contributing one electron to pair. This theory was considerably extended by Langmuir who introduced the term covalent bond to describe the Lewis electron pair bond.

1.20 Key words

Periodic Properties; Atomic radii; Ionic radii; Ionization energy; Electron affinity; Electronegativity; Octet Rule; Covalent bond; Valence bond theory; σ -bond; π -bond.

1.21 References for further study

- 1) An Introduction to Molecular Orbitals by Y. Jean, F. Volaton, J. Burdett. *Oxford University Press, USA, 1993*.
- 2) Text book of Inorganic chemistry, by Amitt Arora, *Discovery Publishing House, 2005*.
- 3) Advanced Inorganic chemistry by F. Albert Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann; *Wiley-Interscience; 6th Ed. 1999*.
- 4) Concise Inorganic Chemistry by J. D. Lee, *John Wiley & Sons, 5th Ed. 2008*.
- 5) Inorganic Chemistry by Petter Atkins, Fraser Armstrong, Jonathan Rourke, Tina Overton, Mark Welle; *Oxford University Press 5th Ed. 2011*.

1.22 questions for self under standing

- 1) How does the size of atoms vary from left to right in a period and down a group in the periodic table? Explain the reason for these changes.
- 2) What is an atomic radii? Explain its periodicity.

- 3) Explain the reason why decrease in size between Li and B much greater than that between Na and Mg or K and Ca.
- 4) What is meant by the ionization energy of an element?
- 5) How Does Ionization of an element vary along period and a down the group in the periodic table.
- 6) Discuss how the variation of Ionization energy can be related to the electronic structure of the atoms.
- 7) What is the correlation between atomic size and ionization energy?
- 8) Give the reason for the followings
 - a) There is decrease in first ionization energy from Be to B and Mg to Al.
 - b) decrease in first ionization energy from N to O and P to S
 - c) Substantial decrease in first ionization energy is observed between Na and K , similarly Mg and Ca but it is not observed between Al and Ga.
- 9) What is electronegativity and how does it related to the type of bond formed.
- 11) Discuss briefly the periodic variation of electronegativity?
- 11) What is electronaffinity and discuss its periodicity?
- 12) Write a note on octet rule.
- 13) Discuss the advantage of octet rule
- 14) With two examples explain the deviations of octet rule
- 15) Explain Sugden's view of singlet linkage bond (2c-1e) in favour of Octet rule
- 16) Explain Sidgwick's rule of maximum covalency
- 17) What are Hypervalent and Subvalent compounds? Give three examples each.
- 18) Write a note on Oxidation state or Oxidation number
- 19) What are the Rules governing for assigning oxidation number?
- 20) What is Covalent bond?
- 21) Explain different types of Covalent bond?
- 22) What type of atoms are preferably form covalent bonds?
- 23) What is variable covalency or maximum covalency? Explain in brief with example.
- 24) What are the Characteristics of Covalent compounds?
- 25) Discuss briefly Valence bond theory
- 26) What are the postulates of VBT?

- 27) What are the suggestions made by Pauling to improvement VBT
- 28) Discuss overlapping of atomic orbitals.
- 29) What are the necessary conditions for overlapping of atomic orbitals?
- 30) What are sigma and pi bonds?
- 31) What are the difference between σ -bonds and π -bonds?
- 32) What are the limitations of VBT?

Unit - 2**Structure**

- 2.0 Objectives of the unit
- 2.1 Introduction
- 2.2 Concepts of resonance
- 2.3 Resonance and delocalization
- 2.4 Resonance energy
- 2.5 Conditions for effective canonical forms
- 2.6 Formal Charge
- 2.7 Valence shell electron pair repulsion (VSEPR) theory
- 2.8 Applications of VSEPR theory
- 2.9 Prediction of shapes of molecules or ions
- 2.10 Bent's Rule and energetics of hybridisation
- 2.11 Geometry of Molecules having bond pairs and lone pairs of electrons
- 2.12 Limitations of VSEPR theory
- 2.13 Hybridization
- 2.14 Hybridisation Rules
- 2.15 Types of Hybridisation
 - a. sp hybridisation
 - b. sp^2 Hybridisation
 - c. Sp^3 hybridisation
 - d. dsp^2 hybridisation
 - e. sp^3d hybridisation
 - f. sp^3d^2 hybridisation
 - g. sp^3d^3 hybridisation
- 2.16 Ionic character of covalent compound
- 2.17 Summary of the unit
- 2.18 Key words
- 2.19 References for further study
- 2.20 questions for self under standing

2.0 Objectives of the unit

After studying this unit you are able to

- ❖ Explain the concept of resonance
- ❖ Identify the relationship between delocalization and resonance energy
- ❖ Explain the condition for effective canonical forms
- ❖ Calculate the formal charge of an ion
- ❖ Apply the concept of VSEPR theory for different molecule and predict their magnetic property
- ❖ Explain the limitations of VSEPR theory
- ❖ Predict the shape of the molecule using bent's rule
- ❖ Explain the concept of hybridisation and characteristics of different hybrid orbitals
- ❖ Predict the geometry of different molecule based on hybridization theory
- ❖ Reasoning the Ionic character of covalent compound

2.1 Introduction

Atoms having unpaired electrons tend to combine with other atoms which also have unpaired electrons. In this way unpaired electrons from both atoms are paired up. And the atoms involved in this pairing process attain a stable electronic arrangement. Two electrons shared between two atoms constitute a bond between them. The number of bonds formed by an atom is usually equal to the number of unpaired electrons in the ground state. However in some cases the atom may form more bonds than the number of unpaired electrons in the ground state. This happens by excitation of the atom i.e., electrons which were paired in the ground state are unpaired and promoted into suitable empty orbital of higher energy. This increases the number of unpaired electrons and hence the number of bonds formed also increases. The shape of the molecule is primarily determined by the directions in which the orbitals involved in the bond formation are oriented. Electrons in the valence shell of the original atom which are paired are called lone pair. In many cases the usual valency formula does not give a true representation of molecule or ion. For example, carbonate ion can be represented by one neutral oxygen atom is double bonded to carbon while two negatively charged oxygen atoms are single bonded to carbon. The x-ray study however shows that all the oxygen atoms forming the ion are in the same plane. Hence it is thought that actual structure of the carbonate ion is a hybrid structure which lies between the various formulae. Thus the CO_3^{2-} ion is a resonance hybrid and two negative charges are not

located on any particular oxygen atom. The effect of resonance is to decrease the length and increases the stability of the bonds involved.

2.2 Concepts of resonance

The physical interpretation of equation is that the true structure of H_2 molecule cannot be represented by any of the four structures namely I II III and IV but is considered to be resonating between the two extreme structures I and II and ionic structures III and IV ie the actual structure of H_2 molecule is a resonance hybrid of I II III and IV

The double pointing arrows between these structures indicate that these structures are in resonance with one another.

When the properties of a molecule cannot be completely describes by a single structure but by two or more structures, then its true structure is said to be a resonance or mesomeric hybrid of these structures. These various structures between which the resonance occurs are called contributing or resonating structures.

2.3 Resonance and delocalization

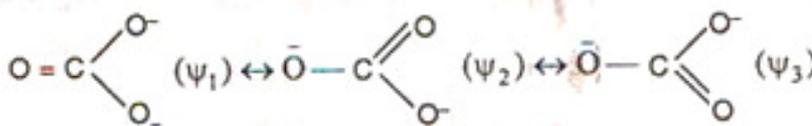
Concept of Resonance according to VBT

In discussing the hydrogen molecule (H_2) in VBT contribution of the ionic form (i.e., H^+H^-) was required to be considered along with the covalent structure (i.e., $H-H$). The actual wave function describing the molecule was expressed as $\psi_{H_2} = (1-\lambda)\psi_{cov} + \lambda\psi_{ion}$ where $\lambda (< 1)$ denotes the mixing coefficient measuring the extent of contribution of the ionic wave function. Thus the true wave function of the molecule can never be expressed by considering only $H-H$ or H^+H^- alone. This phenomenon is referred to as covalent ionic resonance. The wave function dealing with the ionic form becomes important in the heteronuclear species where the electronegativity difference between the combining species is significantly high.

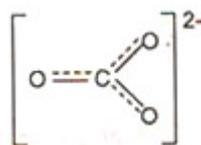
Besides the covalent ionic resonance more than one covalent structure for a particular molecular species can be drawn by considering the electron pair ($2c-2e$) covalent bond in the light of VBT. In drawing such structures the positions of pi bonds are shifted while the sigma bonding pairs are localized between the corresponding nuclei. Each Lewis structure can be expressed by a suitable wave function. Then the actual behaviour of the species called *resonance hybrid* can be expressed as a *linear combination of the separate wave functions expressing the individual structures called canonical forms*. Thus

$$\psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + \dots\dots\dots$$

Thus, no single structure can explain the actual behaviour of the molecule but their linear combination can do the task. This is why no simple Lewis structure can picture the resonance hybrid. To clarify the concept let us take the case of carbonate (CO_3^{2-}) for which the following three canonical forms can be drawn. The canonical forms are related with the double-headed arrows (\leftrightarrow) i.e.,



Thus $\psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3$. Here all the three structures drawn are equivalent. Hence they contribute equally, this means $C_1 = C_2 = C_3$. It is evident that here the pi bonding electron cloud is getting shifted from one position to another. As a result the pi bonding pair is getting delocalized over the whole molecule. Conventionally the resonance hybrid is drawn as follows



Thus the fractional $1/3$ pi bond order in each C-O bond can be nicely explained in the light of MOT by considering the formation of 4 centered π -MOs

2.4 Resonance energy

The energy obtained from the actual wave function which is the linear combination of the wave functions representing the canonical forms is always lower than the energy of the individual canonical forms, i.e. $\psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + \dots$ and $E < E_i$ $i = 1, 2, 3, 4, \dots$. In case canonical forms are not equivalent, i.e., $E_1 \neq E_2 \neq E_3$, then they do not contribute equally. Thus it is evident that the linear combination yields a wave function which gives an extra stability compared to the individual canonical forms. This extra stabilization compared to the most stable canonical form (having the lowest energy which is actually calculated theoretically) gives the measure of resonance energy (E_{res}).

Thus, $E_{\text{res}} = \text{Energy of the most stable canonical form} - \text{energy of the actual molecule} = \text{theoretically calculated energy} - \text{experimentally determined energy}$.

It is illustrated for carbon monoxide (CO). The resonating structures of CO is shown below



Energy of the actual species is obtained from the heat formation and energy of the most stable canonical form is obtained from the bond energy data relevant to the structure. For CO the heat of formation from gaseous atoms is -1072 kJmol^{-1} and lowest energy of the CO structure ie highest bond energy for C=O is -7999 kJmol^{-1} .

Thus, for CO_2 it can be calculated as follows:

$$E_{\text{res}}(\text{CO}) = (1072-799) \text{ kJmol}^{-1} = 273 \text{ kJmol}^{-1}$$

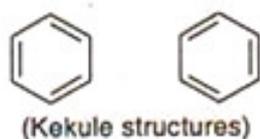
$$E_{\text{res}}(\text{CO}) = [\text{Heat of formation of } \text{CO}_2 \text{ from the gaseous atoms}] - 2E(\text{C}=\text{O}) \approx 154 \text{ kJ mol}^{-1}$$

Where $E(\text{C}=\text{O})$ denotes the C = O bond energy.

The extra stabilization offered by the resonance is rationalized from quantum mechanics with the result of the model particle in a box. The linear combination of the wave functions suggests that the electron cloud can delocalize in a larger dimension embracing more than two nuclei. Thus the resonance energy is basically exchange energy. The resonance energy of carbon dioxide is 154 kJmol^{-1} . It means that the actual molecule is more stable than the theoretically calculated one by 154 kJmol^{-1} .

Note: E_{res} for benzene C_6H_6 can be calculated in the following ways

$$E_{\text{res}}(\text{C}_6\text{H}_6) = [\text{Heat of formation of } \text{C}_6\text{H}_6 \text{ from the gaseous atoms}] - \{6E(\text{C-H}) + 3E(\text{C}=\text{C}) + 3E(\text{C-C})\} \approx 168 \text{ kJmol}^{-1}.$$



From the knowledge of heat of hydrogenation E_{res} can also be calculated. The heat of hydrogenation of cyclohexane is -120 kJmol^{-1} . Assuming benzene as a cyclohexatriene (cf Kekule structure) having three localized double bonds, the calculated heat of hydrogenation is $-3 \times 120 \text{ kJmol}^{-1}$. But the experimental heat of hydrogenation is -209 kJmol^{-1} . This difference i.e., 151 kJmol^{-1} gives the resonance energy of C_6H_6 .

It may be noted that for cyclohexane C_6H_{12} E_{res} is zero i.e., $E_{\text{res}}(\text{C}_6\text{H}_{12}) = [\text{Heat of formation of } \text{C}_6\text{H}_{12} \text{ from the gaseous atoms}] - \{6E(\text{C-C}) + 12E(\text{C-H})\} = 0$

2.5 Conditions for effective canonical forms

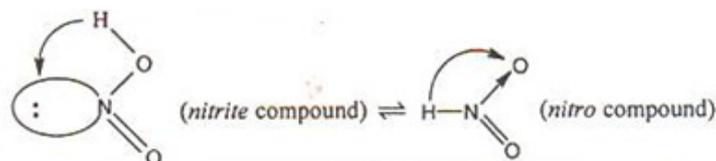
1. Resonance vs tautomerism

Only the position of the pi electrons (the sigma electrons do not get delocalized) is changed from one position to another. Because shifting of an atom leads to tautomerism not resonance structure

and such species are related through the equilibrium sign (\rightleftharpoons). Therefore the proposed canonical forms should not differ in the atomic arrangements.

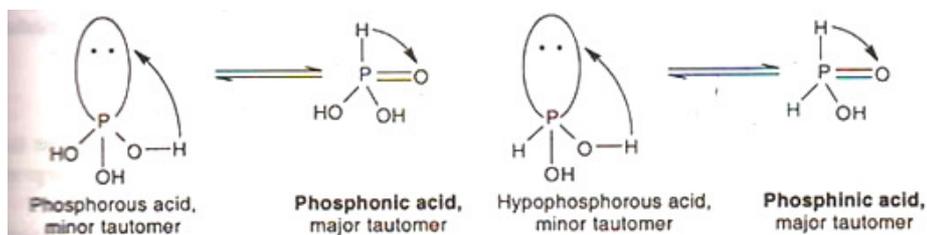
Few examples of tautomerism are mentioned below.

a. The nitrous acid may have two forms in equilibrium.

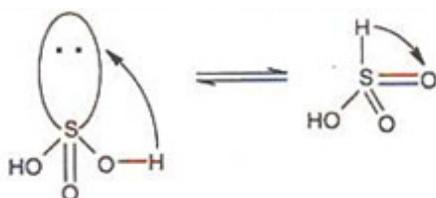


The coloured organic nitrates and some inorganic nitrates such as silver nitrate (pale yellow) mercurous nitrate (pale yellow) probably exist in nitro forms.

b. The phosphorous acid H_3PO_3 and hypophosphorous acid H_3PO_2 exist in tautomeric equilibria as displayed below.



c. Similarly, tautomerism in sulphurous acid is also shown in below figure.



All the examples of tautomerism mentioned above involve the shifting of a proton and this type of tautomerism is referred to as prototropic tautomerism which is very important in organic chemistry eg keto-enol tautomerism

1. Contribution of the canonical forms

The contribution of a canonical form to the resonance hybrid is inversely proportional to its energy. This is why the high energy canonical forms contribute insignificantly.

2. Comparable energy of the canonical forms

The resonating structures should be of comparable energy.

3. *Equivalent canonical forms*

If the resonating structures are equivalent as in the case of CO_3^{2-} the resonance stabilization is very high.

4. *Covalent ionic resonance*

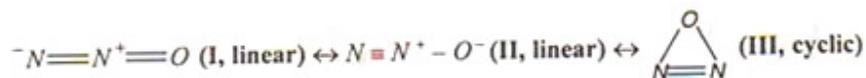
The covalent ionic resonance becomes important in the cases where the combining atoms differ significantly in electronegativity.

5. *Number of covalent linkages*

The canonical forms should have the maximum number of covalent linkages. The reduction in the number of covalent linkages in drawing a canonical form reduces its contribution. For example in the case of carbon dioxide ie $\text{O} = \text{C} = \text{O}$ (I) \leftrightarrow $\text{O} = \text{C}^+ - \text{O}^-$ (II) the canonical form II being deficient of one covalent linkage contributes little.

6. *Geometry of the canonical forms*

The canonical forms should not differ in geometry or bond angle drastically. For example in the case of nitrous oxide the cyclic (3-membered) structure III is not at all promising.

7. *Number of unpaired electrons*

The canonical forms should have the same number of unpaired electrons.

8. *Charge separation*

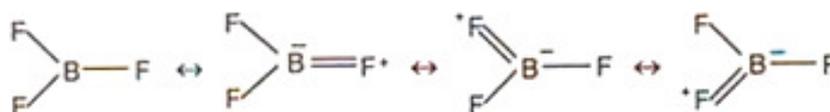
In the case of charge separation, if the adjacent atoms bear the same charge then the electrostatic repulsion will destabilize the structure. On the other hand, placement of opposite charge on the adjacent atoms stabilizes the system through an electrostatic interaction as in the ionic compounds. In the case of undissociated hydrazoic acid the structure II contributes less compared to the structures I and III.

9. *Placement of charge*

The canonical forms in which the negative charge resides on the electronegative atoms contribute more. On the other hand, placement of the negative charge on the electropositive centers destabilizes the system.

10. *Number of covalent linkages*

The canonical forms in which a larger number of covalent linkages exists are more contributing to the resonance hybrid. For example in BF_3 the $p_x - p_x$ bonding places a positive charge on F which is more electronegative than B but this disfavor is compensated due to the formation of an additional π -bond.



In fact due to this type of π bonding, B – F bond has got the double bond character to some extent

11. Requirement of coplanarity

For the delocalization of the pi-electron clouds coplanarity of the involved skeleton is required.

This is why sp and sp^2 hybridisations facilitate the process. This coplanarity is exclusively essential when the pi bonds made of p-orbitals are involved in the processes. But, for the d-orbitals (very often found in inorganic compounds) this coplanarity is not be maintained rigidly. The d-orbitals being diffused can participate in pi bonding even in nonplanar systems

(ex: SO_4^{2-} , ClO_4^- , etc....)

2.6 Formal Charge

Formal charge without considering the effect of electronegativity difference

In the formation of an additive coordinate bond, the donor atom is believed to bear a positive charge while the acceptor bears a negative charge. If both donor and acceptor molecule (or atom) has almost the same electronegativity, then the above consideration would be reasonably true. However in case of distributing the charge, electronegativity difference is not taken into account. Therefore *while calculating the formal charge (q_F) of an atom in a compound, all the constituent atoms are considered to be of the same electronegativity*. To calculate the q_F of an atom in a compound the number of electrons actually owned by the atom in the compound is compared with the number of electrons possessed by the isolated atom in the neutral state. Thus q_F is given by

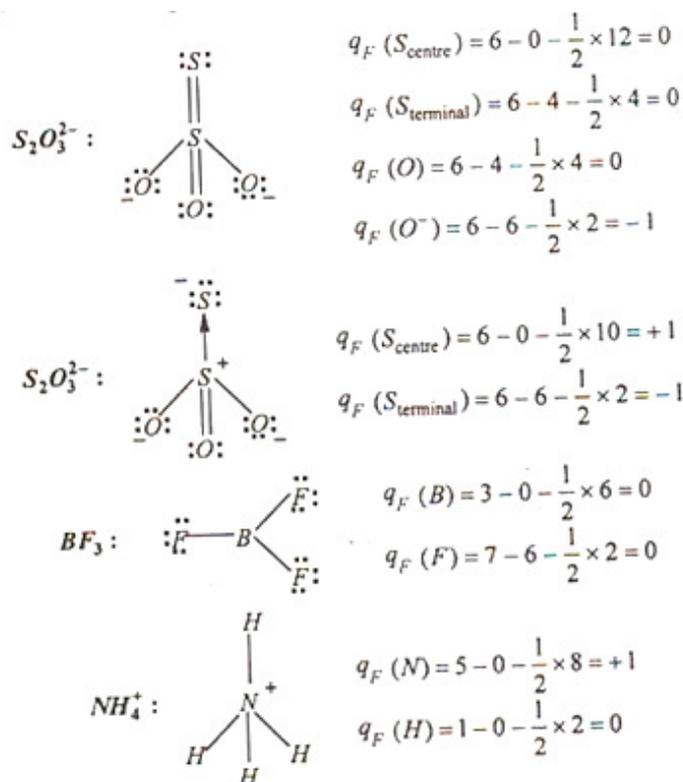
$$q_F = n_A - n_{lp} - \frac{1}{2}n_{nb}$$

where n_A = number of electrons in the valence shell of the atom at the isolated and neutral condition,

n_{lp} = number of lone pair electrons which are completely owned by the atom under consideration,

n_{bp} = number of bond pair electrons which are equally shared by the two combining atoms.

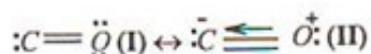
Five examples of formal charge calculation are illustrated below



Application of the concept of resonance in some inorganic compounds

Carbon monoxide (CO)

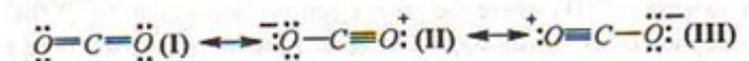
In CO molecule the bond length between carbon(C) and oxygen (O) is 113pm. which is lies in between the bond lengths of C = O (122) pm and C \equiv O (110pm). This intermediate value can be rationalized from the resonating structures i.e.,



The positive charge in the structure (II) is on the more electronegative oxygen atom normally destabilises the structure, but this disfavor is compensated due to the formation of an additional covalent linkage. Interestingly in the structure (I) the bond moment operates towards oxygen, it operates in opposite direction in the structure (II). Because of these two opposing moments the dipole moment of the whole molecule is very small.

Carbon dioxide CO₂

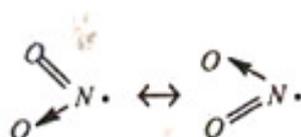
In this molecule the C-O bond length is equal to 115pm again which lies in between the C=O (122pm) and C≡O (110pm) bond lengths. This increased bond order arises due to the contribution of following resonating structures i.e.,



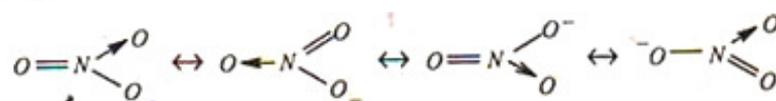
The structure (I) is symmetrical and the other two structures (II) and (III) are unsymmetrical but contribute equally. therefore the molecule overall shows no dipole moment.

Nitrogen dioxide (NO₂)

The canonical forms can explain the partial double bond character of the two equivalent N-O 119pm bonds which are intermediate between N-O 136pm and N=O 115pm. The canonical forms are,

Nitrate ion (NO₃⁻)

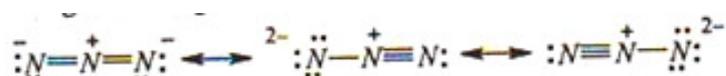
The observed N-O bond length is 121pm can be explained from the contribution of the following canonical structures.

Hydrazoic acid ion (HN₃) and azide (N₃⁻)

In the undissociated acid the bond lengths is H-N 107pm the middle N-N 124pm terminal N-N bond (i.e., remote from H) lengths is equal 115pm. Thus the N-N bond distances in HN₃ are unequal. But in azide all the N-N bond lengths are equal to 115pm. The above facts are explained by considering the resonating structures of both HN₃ and N₃⁻ in HN₃ the corresponding structures are



Here the middle N-N has got the double and single bond character while the terminal N-N has got both the double and triple bond character. This is why the N-N distances in HN₃ are not equal. In N₃⁻ the corresponding resonating structures are,

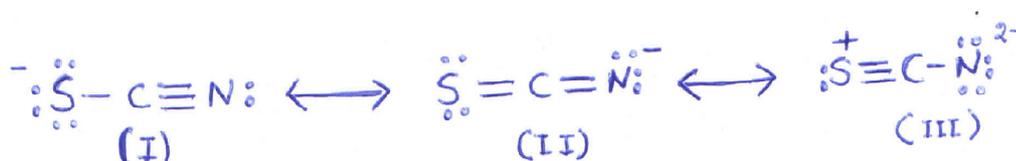


All the N-N bonds are equivalent here.

The enhanced stability of the ionic azides compared to covalent azides is explained on the basis of resonance energy. The covalent azides have the structure like that of the undissociated acid with two nonequivalent resonating structures whereas in the ionic azides the azide ion has three canonical forms in which two forms are equivalent. Thus the resonance stabilization in the ionic azides is greater than that in the covalent azides.

Isosters (N_2O , N_3^- , OCN^- , CNO^- , SCN^- , N_3)

The species having identical outer electronic configurations are called isosters. In isosteric species eg, nitrous oxide (N_2O), azide (N_3^-), cyanate (OCN^-), fulminate (CNO^-) thiocyanate (SCN^-) are also resonance stabilized. Due to the structural similarity, all are linear and they can form the isomorphous alkali salts. The resonating structures of SCN^- can be shown below for an example



Here the structure (III) contributes less as the opposite charges are placed at the largest distance. The most favourable structure is (II) where the most electronegative atom bears the negative charge.

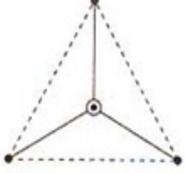
2.7 Valence shell electron pair repulsion (VSEPR) theory

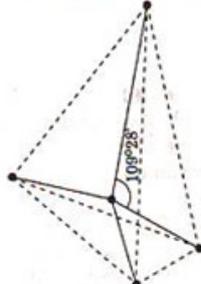
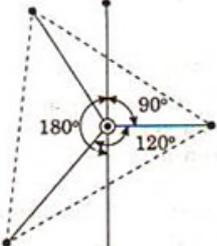
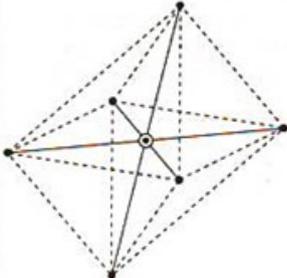
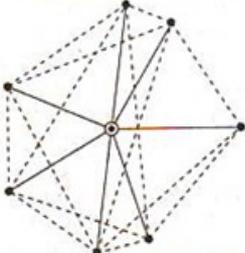
Gillespie and Nyholm in 1957 developed this theory and it is based on the effect of electron repulsion on the bond angles. According to this theory the shape of the molecule (or ion) depends upon the number of bonding electron pairs (bp's) and non-bonding electron pairs or lone pairs lp's in the central atom. The central atom is oriented in such a way that there is minimum repulsion (hence maximum stability) between bonding electron pairs. The molecule has a definite shape because there is only one orientation of orbitals corresponding to minimum energy.

Gillespie postulation of VSEPR theory

Following rules of VSEPR theory was postulated by Gillespie in order to explain the shape and stability of the molecule or ion.

1. If the central atom in a molecule is surrounded by only bonding electron pairs (bp's) and not by non-bonding electron pairs or lone pairs lp's it will have regular geometry or shape. The shapes of the molecules with bond angles are given in the following table.

No. of bp's	Structure	Shape	Bond angle	Examples
1.	Linear		180°	BeF ₂ , HgCl ₂ , CdI ₂ , BeCl ₂
2.	Plane triangular or Trigonal planar		120°	BF ₃ , BCl ₃ , GaI ₃ , SO ₃ , CO ₃ ²⁻

No. of bp's	Structure	Shape	Bond angle	Examples
3.	Planar square or Square planar		90°	[Ni(CN) ₄] ²⁻ , [Pd(CN) ₄] ²⁻
4.	Tetrahedral		109°28'	CH ₄ , NH ₄ ⁺ , ClO ₄ ⁻ , SO ₄ ²⁻ , SnCl ₄ , BF ₄ ⁻
5.	Trigonal bipyramidal		90° & 120°	PCl ₅ , PF ₅
6.	Octahedral		90°	SF ₆ , PF ₆ ⁻ , [SiF ₆] ²⁻
7.	Pentagonal bipyramidal		72° & 90°	IF ₇

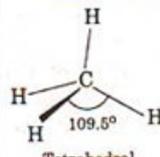
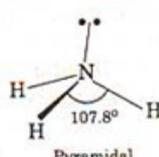
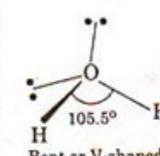
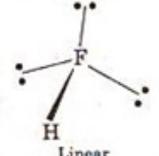
1. If the central atom in a molecule is surrounded by both bp's and lp's, then molecule will have distorted or irregular geometry or shape. Because the lp's repel adjacent electron pairs more strongly than bonding electron pairs. The repulsion increases as follows,

$$(\text{bp-bp}) < (\text{bp-lp}) < (\text{lp-lp})$$

Due to this reason the bond angle decreases in the order of CH_4 (109.5°) > NH_3 (107.8°) > H_2O (105.5°), and the number of lp's increases as $\text{CH}_4(0) < \text{NH}_3(1) < \text{H}_2\text{O}$ (2). Therefore as the number of lp's increases repulsion increases and bond angle decreases (or distortion increases).

This can also be exemplified as follows NO_2^+ (180°) > NO_2 (135°) > NO_2^- (115°)

Effect of Lone Pair of Electrons on Geometry of Molecules

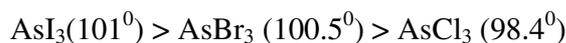
Compound	Number of bond pairs	Number of lone pairs	Structure
CH_4	4	0	 Tetrahedral
NH_3	3	1	 Pyramidal
H_2O	2	2	 Bent or V-shaped
HF	1	3	 Linear

2. Repulsion between bonding pair of electrons is greater if these electron are near the central atom. For example of hydrides of VIA (or 16) group elements of the periodic table with their bond angles

$$\text{H}_2\text{O} (105.5^\circ) > \text{H}_2\text{S} (92.5^\circ) > \text{H}_2\text{Se} (91.0^\circ) > \text{H}_2\text{Te} (89.5^\circ)$$

The size of the central atom increases, its electronegativity decreases. Therefore the bp of electron shifts more and more away from the central atom on moving from H_2O to H_2Te . Thus repulsion between the bp of electron decreasing from H_2O to H_2Te hence bond angle is decreasing from H_2O to H_2Te .

3. If the electronegativity of the central atom decreases the bond angles decreases because bp of electrons shifts away from the central atom. For example, PI_3 ; AsI_3 ; PBr_3 ; AsBr_3 ; PCl_3 ; AsCl_3 . If the electronegativity of the surrounding atoms decreases (central atom remains same) the bond angle increases bp of electron shifts away from the central atom for example, $\text{PI}_3(102^\circ) > \text{PbR}_3$ (105°) > PCl_3 (100°)



4. The multiple bonds do not affect the geometry of the molecules but the bond angles involving single bonds are generally smaller than those of multiple bonds.

2.8 Applications of VSEPR theory

VSEPR theory can apply to decide the shape of the molecules (or ions). One can deduce the regular geometry as well as irregular or distorted geometry in different molecules or ions.

Regular geometry of covalent molecules

Molecules have a regular geometry if it satisfies the following conditions:

1. The central atom of the molecule should be bonded to all similar atoms example; BeH_2 AlCl_3 ; CH_4 ; CCl_4 ; SF_6 etc
2. The central atom of the molecule should be surrounded by only bond pair of electrons.
3. All the bond lengths should be same.
4. The central atom should get bonded to other atom by single covalent bond or same type of bonds. Examples Cl-Be-Cl ; O=C=O , S=C=S etc.

Irregular geometry of covalent molecules

A molecule has irregular (or distorted) geometry if one of the following conditions is satisfied by the molecule.

1. The central atom of the molecule is not bonded with all the similar atoms eg CHCl_3 CH_3Cl etc
2. The central atom of the molecule possesses one or more lone pair of electrons in addition to one or more bond pair of electron eg NH_3 ; PCl_3 ; PH_3 ; SnCl_2 etc
3. The central atom should get bonded with similar atom but different bond length eg in PF_5 molecule 3P-F bond lengths are of 2.04 Å value while 2P-F bond lengths are of 2.19 Å value.
4. The central atom should get bonded with other atom by different type of bonds eg in SO_3 molecule two bonds are covalent and third one is coordinate bond.

2.9 Prediction of shapes of molecules or ions

The shape of the molecule or ion can be predicted as follows

1. Count the number of valence electrons and then write the Lewis structure of the molecule or ion.
2. From Lewis structure calculate the number of lone pair of electrons and bond pair of electrons (the multiple bonds are counted as a single bond).

3. Calculate the number of stereoactive electron pairs by adding the total number of shared pairs and lone pair around the central atom of the molecule.

2.10 Bent's Rule and energetics of hybridisation

According to hybridization atomic orbitals combine through redistribution of their energies to form hybrid orbitals. The hybrid orbital so formed are identical w.r.t energy, shape etc. the shapes of the hybrid orbitals depends upon the contribution of s, p- orbitals.

For example, sp^3 hybridisation, the molecule CH_4 or CCl_4 formed tetrahedral geometry with bond angle 109.5° . But in the case of CH_2F_2 , the F-C-F bond angle is less compare to H-C-H. This is due to the reason that in F-C-F, s-character is less than 25% while in H-C-H it is more than 25%. This can be explained with the help of Bent's rule.

Bent's rule states that "More electronegative substituents prefer hybrid orbitals to have less s-character and more electropositive substituents prefer hybrid orbitals to have more s-character."

in case of formation of PCl_5 , phosphorus atom exhibits sp^3d hybridization in which three hybrid orbitals are on the plane and two hybrid orbitals are above and below the plane. In this $p_zd_z^2$ form linear hybrid orbitals while axially and s, p_x, p_y form trigonal equatorial bonds. Evidently P-Cl bonds which are on the axis are longer ie lesser bond energy than equatorial. But in the case of PCl_3F_2 it is observed that P-F bonds are on the axis and P-Cl bonds are on the equatorial. This is follows the Bent's rule, therefore F-atom is more electronegative hence prefer less s-character and is on the axis ($p_zd_z^2$) while Cl being less electronegative prefer more s-character (sp_xp_y).

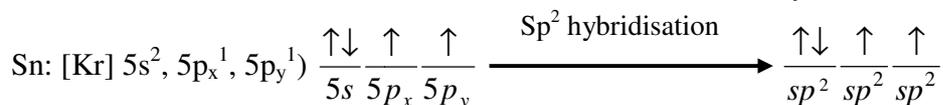
If we consider the case of PF_5 in which P-atom exhibits sp^3d hybridization, by combination of $p_zd_z^2$ hybrids which forms two linear hybrid orbitals bonding axially and sp_xp_y hybrids which forms the trigonal equatorial bonds. The bond lengths in PF_5 are 153.4 pm and 157.7 pm for equatorial bonds (r_{eq}) and axial bonds (r_{ax}) respectively. It clearly indicates that equatorial bonds are stronger than axial bonds. In other words energy of equatorial bonds is higher than that of axial bonds. Similarly way other examples of the type MX_5 M=P, As, Sb, Bi and X=Cl, Br, I can be explained. Thus bent's rule is useful tool in inorganic and organic chemistry. It may be used as a supplement to the VSEPR for interpretation of the structure of many non-metal fluorides.

2.11 Geometry of Molecules having bond pairs and lone pairs of electrons

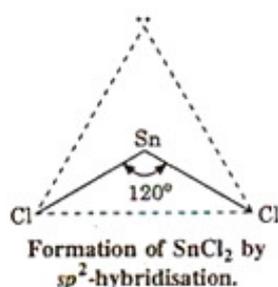
So far we have discussed various types of hybridization with examples, in all those examples central atom does not possess lone pairs of electrons. Now we discuss some examples in which central atom of the molecule possess lone pairs of electrons also.

1. SnCl₂ Molecule

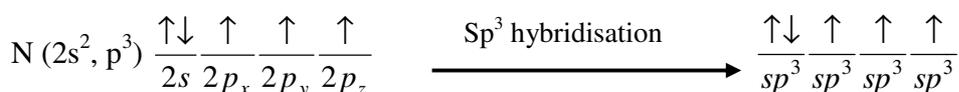
In stannous chloride SnCl₂ molecule tin atom undergoes sp²- hybridisation as follows.



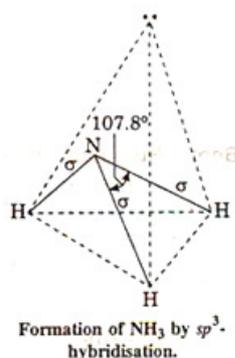
Out of three sp² hybrid orbitals one sp² hybrid orbital is occupied by one lone pair of electrons (lp) and two sp² hybrid orbitals are half filled which overlap with two 3p_z half filled orbitals of two chlorine atoms. Due to sp² hybridisation SnCl₂ molecule is expected to be trigonal planar but it is a bent or V shaped molecule because one lone pair of electrons is present in the molecule.

2. NH₃ Molecule

In ammonia NH₃ molecule nitrogen atom undergoes sp³ hybridisation as follows

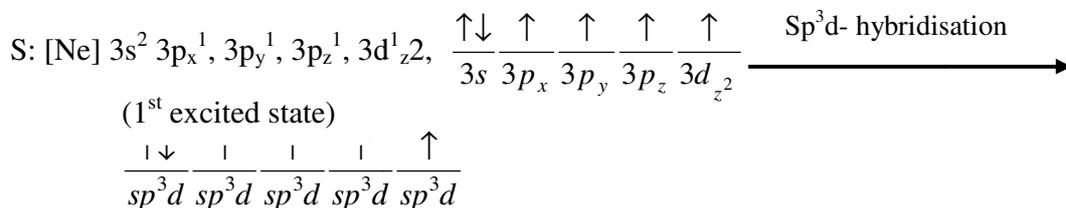


Out of four sp³- hybrid orbitals one sp³ hybrid orbital is occupied by one lone pair of electrons (lp) and three sp³- hybrid orbitals are half filled which overlap with three half filled 1s orbital of three hydrogen atoms and form NH₃. Since there is sp³ hybridisation hence the bond angle should be 109°28' while the bond angle in NH₃ is 107.8° this decrease in value is due to the presence of lp electrons which repels the bp's electron.

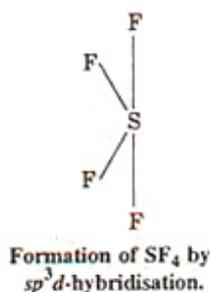


3. SF₄ Molecule

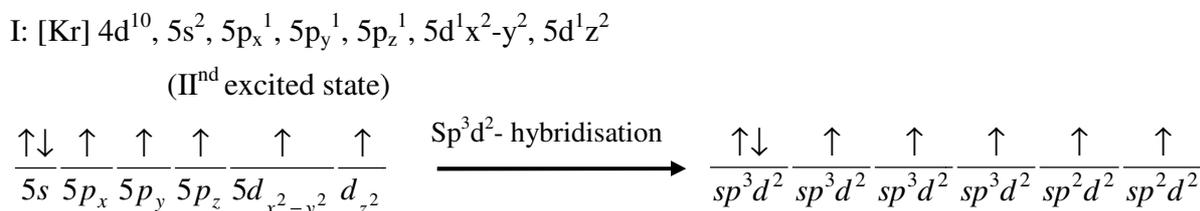
In sulphur tetrafluoride SF₄ molecule sulphur atom undergoes sp³d hybridisation as follows.



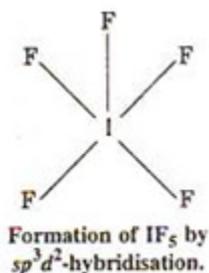
Out of five sp³d hybrid orbitals one sp³d hybrid orbital is occupied by one lone pair of electrons (lp) and four sp³d hybrid orbitals are half filled which overlap with four 2p_z half filled orbitals of four F atoms. Due to sp³d hybridisation SF₄ molecule is expected to be trigonal bipyramidal but it has see-saw geometry.

4. IF₅ Molecule

In iodine pentafluoride IF₅ molecule iodine atom undergoes sp³d² hybridisation as follows.

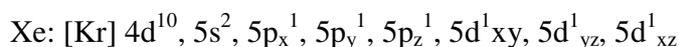


Out of six sp³d² hybrid orbitals one sp³d² hybrid orbital is occupied by one lone pair of electrons (lp) and five sp³d² hybrid orbitals are half filled which overlap with five 2p_z half filled orbitals of five F atoms. It is expected due to sp³d² hybridisation it should be of octahedral geometry but due to one (lp) of electron it has square pyramidal geometry.

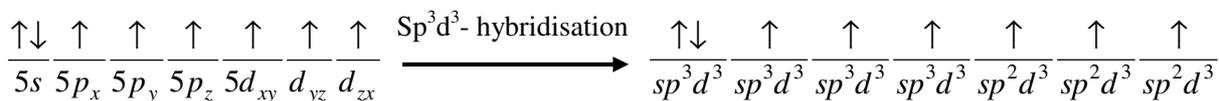


5. XeF₆ Molecule

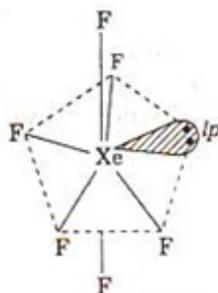
In xenon hexafluoride XeF₆ molecule xenon atom undergoes sp³d³ hybridisation as follows



(IIIrd excited state)



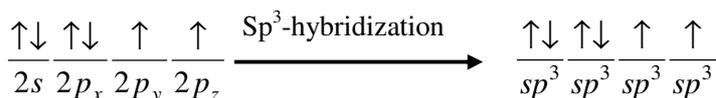
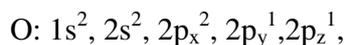
Out of seven sp³d³ hybrid orbitals one sp³d³ hybrid orbital is occupied by one lone pair of electrons (lp) and six sp³d³ hybrid orbitals are half filled which overlap with six 2p_z half filled orbitals of six F atoms. Due to sp³d³ hybridisation it is expected to be pentagonal bipyramidal but due to one lone pair of electrons its geometry is distorted octahedral as shown in the below figure.



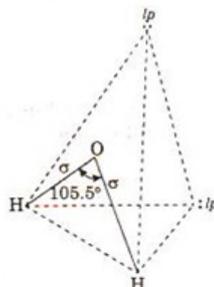
Formation of XeF₆ by sp³d³-hybridisation.

6. H₂O Molecule

In H₂O molecule oxygen atom undergoes sp³ hybridisation as follows



In H₂O molecule oxygen atom undergoes sp³ hybridisation and we get two sp³ hybrid orbitals which are occupied by two lone pairs of electrons (lp's) and two sp³ hybrid orbitals.



2.12 Limitations of VSEPR theory

- i) It does not explain the shapes of the molecules having very polar bonds eg Li_2O and H_2O should have same structure but Li_2O is linear while H_2O is angular.
- iii) It does not explain the shapes of the molecules or ions which are extensive delocalized pi – electron system.
- iv) It does not explain the shapes of some molecules which have an inert pair of electrons.
- v) It does not explain the shapes of certain compounds of transition metals eg the shape of the compound having d8 EC of the central atom is square planar and not tetrahedral as predicted by this theory.

2.13 Hybridization

Consider a methane molecule (CH_4). In methane carbon atom forms 4 covalent bonds with 4 hydrogen atoms. The electronic configuration of carbon is $1s^2 2s^2 2p_x^1 2p_y^1$ i.e., there are only two unpaired electrons hence its valency should be two. The only way obtain tetravalence is to excite the atom, then its configuration becomes $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$. In this configuration also there is one difficulty that three of the electrons have ‘p’ orbitals and the fourth one has ‘s’ orbital. Therefore three bonds should be of one kind and the fourth one should be of a different kind. Also the mutual angles as calculated for p-p bonds and s-p bonds are 90° and $125^\circ 14'$ respectively. But the C-H bonds angle in methane is equivalent and is equal to $109^\circ 28'$. To solve these problems we mix the s and p orbitals and redistribution of energy takes place in such a way that all the four orbitals become equivalent. This phenomenon is known as hybridization. Therefore *mixing of pure atomic orbitals to give equal number of hybrid orbitals is referred to as hybridization*. Since, in this hybridization there are one s and three p orbitals hence it is called as sp^3 hybridisation. The orbitals are known as sp^3 hybrid orbitals.

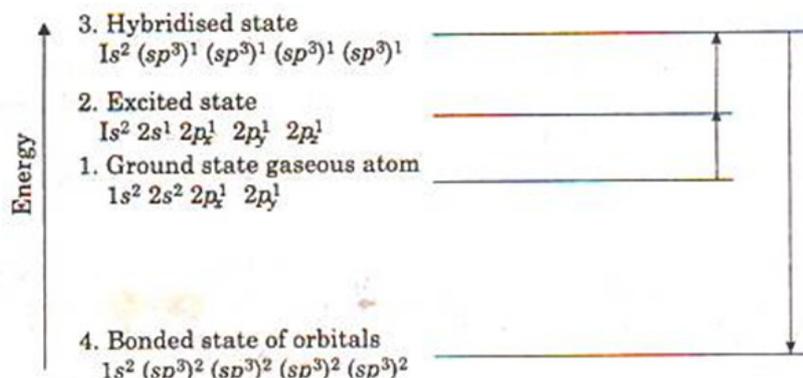
The energy of the hybrid orbitals is higher than the atomic orbitals in excited state but when hybrid orbitals are overlapped by the orbitals of the surrounding atom (ie bond formation takes place) the energy decreases too much and the bond becomes stable.

2.14 Hybridisation Rules

the following are the rules for hybridisation of atomic orbitals.

1. The orbitals of only similar energies belonging to the same atom or ion can be mixed to form hybrid orbitals. Dissimilar energies orbitals may bring hybrids but the exact nature cannot be defined.

- Hybridisation is a process of mixing orbitals of single atom or ion not like molecular orbital formation.
- During hybridization we mix a certain number of orbitals as per requirement.



Hypothetical energy levels of different types of orbitals.

- The number of atomic orbitals mixed together always equal to the number of hybrid orbitals obtained.
- All the hybrid orbitals are similar but they are not necessarily identical in shape. They must differ from one another mainly in orientation shape.
- Once an orbital has been used to build a hybrid orbital is no longer available to hold electrons in its pure form.

2.15 Types of Hybridisation

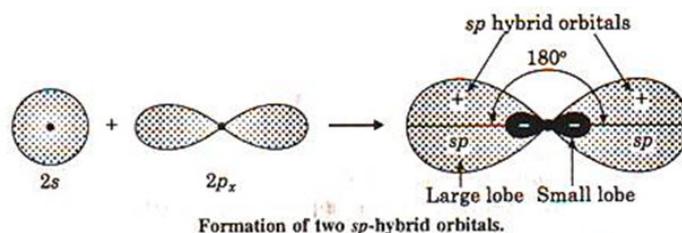
Different types of hybridization are known which are given in the following Table

Hybridisation					
Type of hybridisation	No. of hybrid orbitals obtained	Bond angle	Relative bond strength*	Structure	Examples
sp	2	180°	1.93	Linear	$\text{BeCl}_2, \text{CO}_2, \text{C}_2\text{H}_2, \text{HgCl}_2, \text{CN}^-, \text{N}_3^-, [\text{Ag}(\text{NH}_3)_2]^+$
sp^2	3	120°	1.99	Plane triangle	$\text{SO}_3, \text{BF}_3, \text{AlCl}_3, \text{CO}_3^{2-}$
sp^3	4	$109^\circ 28'$	2.00	Tetrahedral	$\text{CH}_4, \text{C}_2\text{H}_6, \text{SO}_4^{2-}, \text{ClO}_4^-$
sp^2d	4	90°	2.69	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$
sp^3d	5	120° and 90°	Varies	Trigonal bipyramidal	$\text{PCl}_5, \text{PF}_5$
sp^3d^2	6	90°	2.93	Octahedral	$\text{SF}_6, [\text{Fe}(\text{CN})_6]^{4-}$
sp^3d^3	7	72° and 90°	-	Pentagonal bipyramidal	IF_7

*For s and p orbitals its values are 1.00 and 1.73 respectively.

a. sp-hybridisation

Formation for hybrid orbitals by mixing up of one 's' atomic orbital and one 'p' atomic orbital is called sp-hybridisation. In this type of hybridisation one 's' and one 'p' atomic orbital (if x-axis is the molecular axis then it is p_x orbital) of the valence shell of central atom of the given molecule or ion combine form two 'sp' hybrid orbitals as described in below figure.

**Characteristics of sp hybrid orbitals**

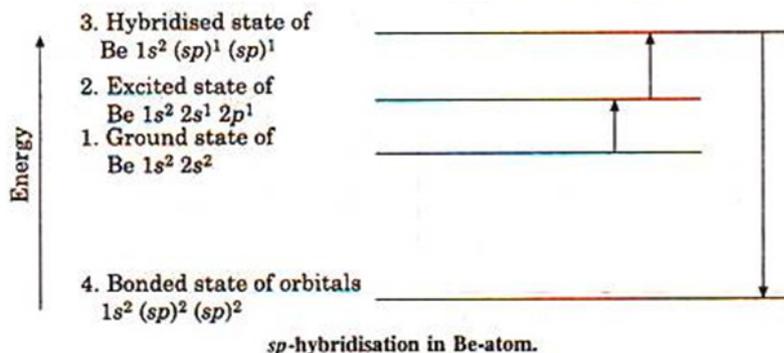
1. Two sp hybrid orbitals [$sp(1)$ and $sp(2)$] are completely equivalent and symmetrical.
2. These are stronger than pure s and pure p orbital from which it is formed after hybridisation. [Its relative power of overlapping is 1.93 with respect to s orbital].
3. These hybrid orbitals are collinear i.e., angle between the hybrid orbitals is 180° .
4. It is oval shaped. In sp hybrid orbital one lobe is bigger while other is smaller. The bigger lobe is very large with respect to p orbital hence it has higher degree of overlapping. Thus it forms stronger bond.
5. The normalized wave function of these hybrid orbitals may be given as follows;

$$\psi_{sp(1)} = \frac{1}{\sqrt{2}} \psi_s + \frac{1}{\sqrt{2}} \psi_{p_x}$$

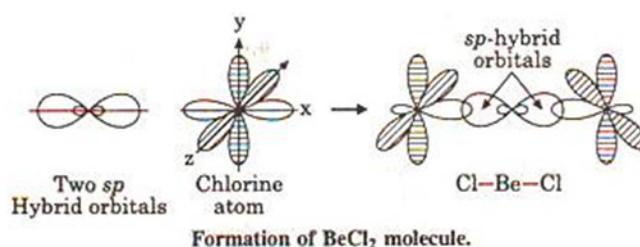
$$\psi_{sp(2)} = \frac{1}{\sqrt{2}} \psi_s - \frac{1}{\sqrt{2}} \psi_{p_x}$$

Example: Formation of BeCl_2 molecule. In this molecule Be is the central atom whose electronic configuration is $1s^2 2s^2$. It does not have any unpaired electron therefore Be should not form compounds of the type BeCl_2 . In order to explain formation BeCl_2 , it is assumed that Be comes in excited state in which its electronic configuration becomes $1s^2, 2s^1 2p_x^1$ now it has two unpaired electrons therefore BeCl_2 can be formed. If BeCl_2 is formed under this condition then the two bonds Be-Cl will be of different nature due to different type of overlapping i.e. s-p and p-p overlapping. But both these bonds are identical (i.e. equal strength and bond length). It is explained by hybridisation. Therefore one 2s and one $2p_x$ orbitals of Be combine to form two

identical sp hybrid orbitals with one electron each. These orbitals have higher energy than excited Be atom. Now these half filled sp hybrid orbitals overlap with two half filled 'p' orbitals



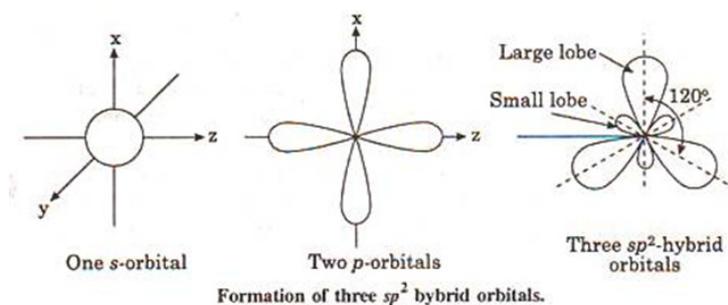
of two chlorine atoms ($1s^2, 2s^2, 2p^6, 3s^2, 3p_x^2, 3p_y^2, 3p_z^1$) to form two Be-Cl bonds by sp - p overlap. Thus hybridisation in $BeCl_2$ explains that two Be-Cl bonds are of equal strength with bond angle 180° . Therefore $BeCl_2$ is a linear molecule.



Other examples of sp hybridization molecules are CO , CO_2 , C_2H_2 , HCN , CN , N_3^- , N_2 etc....,

b. sp^2 – Hybridisation

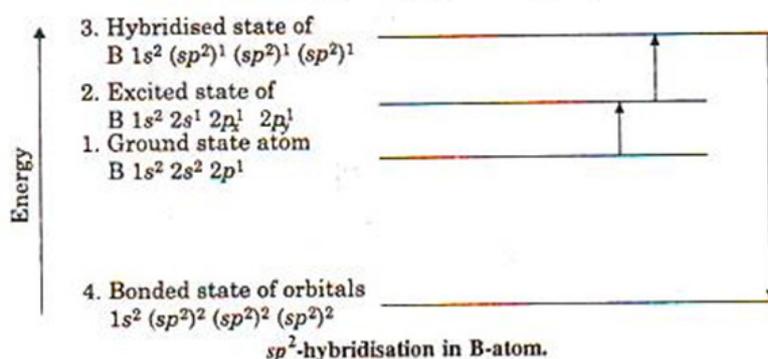
Formation for hybrid orbitals by mixing up of one 's' atomic orbital and two 'p' atomic orbital is called sp^2 -hybridisation. In this type of hybridisation one 's' and two 'p' orbitals of the valence shell of central atom of the given molecule (or ion) combine to form three sp^2 hybrid orbitals as described as follows.



Characteristics of sp^2 hybrid orbitals

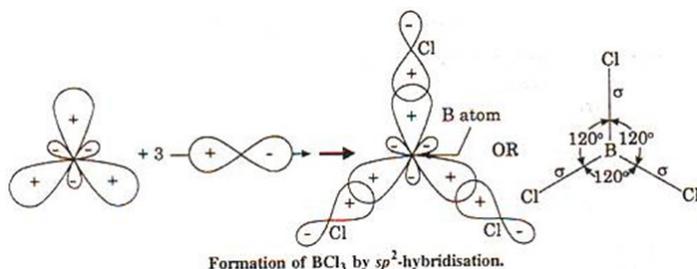
1. Three sp^2 hybrid orbitals $sp^2(1)$, $sp^2(2)$ and $sp^2(3)$ are completely equivalent and symmetrical.
2. These are stronger than pure s and p orbitals from which it is formed after hybridisation.
[Its relative power of overlapping is 1.99 with respect to s orbital].
3. These hybrid orbitals are planar with bond angle 120° .
4. Since in this case contribution of p-orbitals is more hence it is *less oval* than sp -hybrid orbital. As usual in this case also one hybrid orbital is bigger while other one is smaller and it forms stronger bond.
5. The normalized wave function of these hybrid orbitals may be given by,

$$\begin{aligned}\psi_{sp^2}(1) &= \frac{1}{\sqrt{3}} \psi_s + \sqrt{\frac{2}{3}} \psi_{p_x} \\ \psi_{sp^2}(2) &= \frac{1}{\sqrt{3}} \psi_s - \frac{1}{\sqrt{6}} \psi_{p_x} + \frac{1}{\sqrt{2}} \psi_{p_y} \\ \psi_{sp^2}(3) &= \frac{1}{\sqrt{3}} \psi_s - \frac{1}{\sqrt{6}} \psi_{p_x} - \frac{1}{\sqrt{2}} \psi_{p_y}\end{aligned}$$



Example: The formation of BCl_3 molecule. In this case B is the central atom whose electronic configuration is $1s^2, 2s^2, 2p^1$. It has only one unpaired electron therefore B-Cl can easily be formed but formation of BCl_3 compound is not. In order to explain the formation of BCl_3 it is assumed that B atom comes in excited state in which its electronic configuration becomes $1s^2, 2s^1, 2p_x^1, 2p_y^1$. In this state B has three unpaired electrons hence formation of BCl_3 become possible. Suppose BCl_3 is formed under above mentioned condition, one B-Cl bond must be differs from other two B-Cl bonds. This is because of different type of orbitals overlapping [i.e., s-p and p-p overlapping]. But all the three bonds in BCl_3 molecule are identical [ie equal strength and bond length]. It can be explained only by hybridization as follows: one 2s and two 2p orbitals of B atom combine to form three identical sp^2 hybrid orbitals with one electron each. These orbitals have higher energy than excited B atom. Then the half filled sp^2 hybrid orbitals

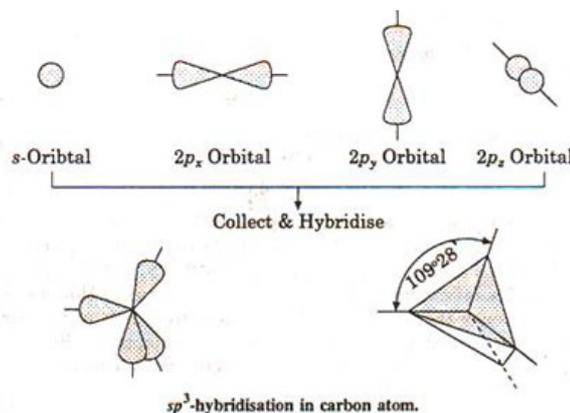
overlap with three half filled p orbitals of three chlorine atoms ($1s^2, 2s^2, 2p^6, 3p_x^2, 3p_y^2, 3p_z^1$) to form three B-Cl bonds by sp^2 -p overlap. Thus hybridisation in BCl_3 explains that three B-Cl bonds are of equal strength with bond angle 120° , it is a planar molecule.



Other examples are CO_3^{2-} , CH_3^+ , C_2H_4 , SO_3 etc...

c. sp^3 hybridisation

Formation for hybrid orbitals by mixing up of one 's' atomic orbital and three 'p' atomic orbital is called sp^3 -hybridisation. In this type of hybridisation one s and 3p orbitals of the valence shell of central atom of the given molecule (or ion) combine to form 4 sp^3 hybrid orbitals as follows:



Characteristics of sp^3 hybrid orbitals

1. All the four sp^3 hybrid orbitals $sp^3(1)$, $sp^3(2)$, $sp^3(3)$ and $sp^3(4)$ are equivalent and symmetrical.
2. sp^3 hybrid orbitals are directed towards the four corners of a regular tetrahedron and the angle between each pair of them is $109^\circ 28'$ or $109^\circ 5'$
3. Their relative power of overlapping is 2.00 therefore sp^3 hybrid orbitals are stronger than sp and sp^2 hybrid orbitals.
4. In sp^3 hybridisation, the contribution of p orbitals is 75% it is still more than that of sp^2 hybridisation. Hence its shape is almost same as that of the parent p orbitals expect that the

bigger lobe in sp^3 hybrid orbital is somewhat more spread and shorter in length than that in the pure p orbitals.

5. The normalized wave function of sp^3 hybrid orbitals are as follows:

$$\Psi_{sp^3}(1) = \frac{1}{2} \Psi_s + \frac{1}{2} \Psi_{p_x} + \frac{1}{2} \Psi_{p_y} + \frac{1}{2} \Psi_{p_z}$$

$$\Psi_{sp^3}(2) = \frac{1}{2} \Psi_s + \frac{1}{2} \Psi_{p_x} - \frac{1}{2} \Psi_{p_y} - \frac{1}{2} \Psi_{p_z}$$

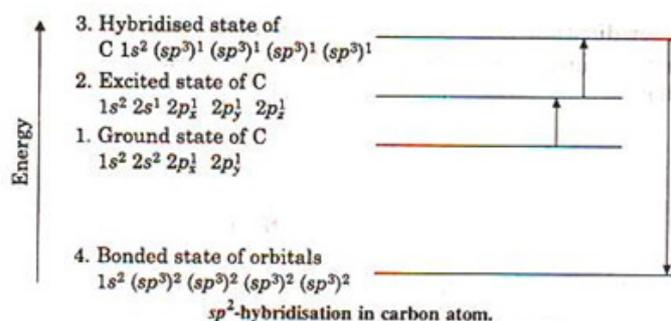
$$\Psi_{sp^3}(3) = \frac{1}{2} \Psi_s - \frac{1}{2} \Psi_{p_x} + \frac{1}{2} \Psi_{p_y} - \frac{1}{2} \Psi_{p_z}$$

$$\Psi_{sp^3}(4) = \frac{1}{2} \Psi_s - \frac{1}{2} \Psi_{p_x} - \frac{1}{2} \Psi_{p_y} + \frac{1}{2} \Psi_{p_z}$$

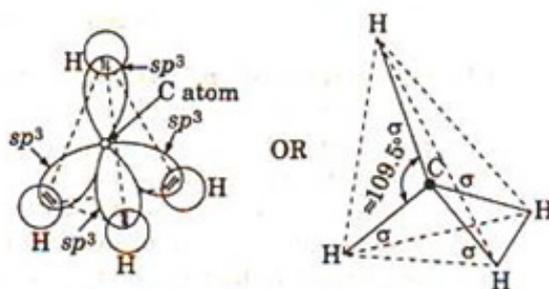
Example: the formation of CH_4 molecule.

In this molecule C atom is the central atom whose electronic configuration is $1s^2, 2s^2, 2p_x^1, 2p_y^1$.

It has only two unpaired electrons therefore CH_2 molecule should be formed.



CH_2 is highly reactive compound or less stable but CH_4 molecule is well known stable compound. In order to explain formation of CH_4 it is assumed that C atom comes in excited state $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$ in this state it has four unpaired electrons. Therefore CH_4 molecule can be formed. However if CH_4 molecule is formed in this manner then one C-H bond differs from rest of the three C-H bonds due to different types of overlapping [ie s-s and s-p overlapping]. The four bonds in CH_4 molecule are identical [i.e. of equal strength and bond length]. It is explained only on the basis of hybridisation as follows: one 2s and three 2p orbitals of C atom combine to form four identical sp^3 hybrid orbitals with one electron each. These orbitals have higher energy than excited C atom. Then these half filled sp^3 hybrid orbitals overlap with four half filled s orbitals of four hydrogen atoms ($1s^1$) and form four C-H bonds by sp^3 -s overlapping. Thus the four C-H bonds CH_4 are equal strength with bond angle $109^\circ 28'$ and it has tetrahedral geometry.

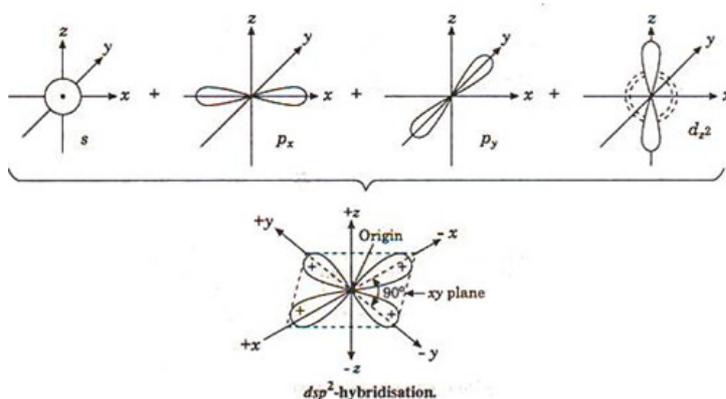


Formation of CH_4 by sp^3 -hybridisation.

Other examples of sp^3 hybrid molecules are C_2H_6 , CCl_4 , SiH_4 , NH_4^+ , SO_4^{2-} , ClO_4^- etc

d. dsp^2 hybridisation

Atoms of the transition metals and of other elements which have d atomic orbitals available can use these d orbitals in hybridization. The hybridization of one s, two p, and one d orbital of the central metal atom gives rise to four hybrid dsp^2 orbitals this is called dsp^2 hybridisation. In this type of hybridisation one d- one s- and two p orbitals of the valence shell of central atom of the given molecule (or ion) combine to form four dsp^2 hybrid orbitals as shown below



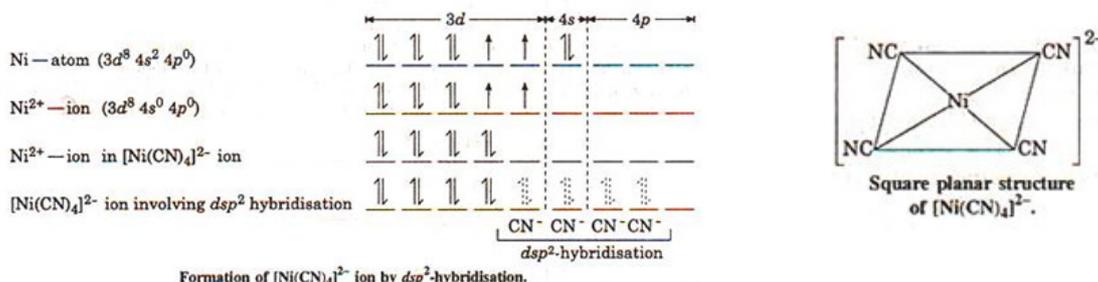
Characteristics of dsp^2 hybrid orbitals

1. All the four dsp^2 hybrid orbitals $dsp^2(1)$, $dsp^2(2)$, $dsp^2(3)$ and $dsp^2(4)$ are completely equivalent and symmetrical.
2. These hybrid orbitals are directed towards the four corners of a square and the angle between each pair is 90° . because the hybrid uses the d_{xy} , s, p_x and p_y orbitals, all of which are in the xy plane.
3. These are coplanar and lie on xy-plane.

Example: The formation of $\text{Ni}(\text{CN})_4^{2-}$ ion.

In this ion Ni^{2+} ion is the central ion. The EC of Ni atom is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8, 4s^2$. It loses two electrons of 4s orbital to become Ni^{++} ion the EC of Ni^{++} is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8$.

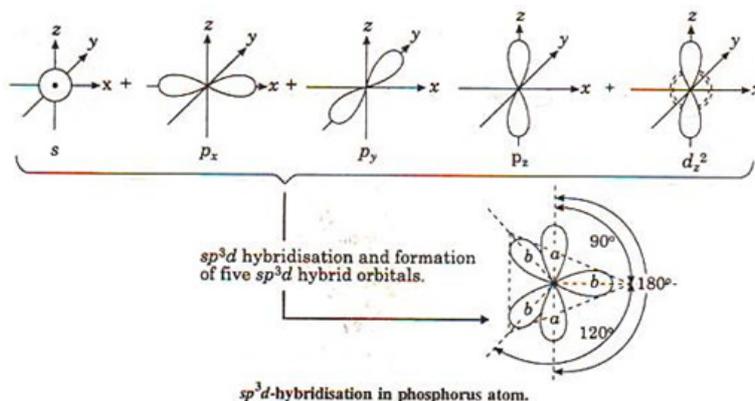
It has two half filled d-orbitals. When four CN^- ions approach to Ni^{2+} ion these unpaired electrons are paired up against Hund's rule because CN^- ion is a strong ligand.



Thus there is one vacant 3d orbital in Ni^{2+} ion. Therefore one d orbital, one s orbital and 2 p orbitals are undergo hybridisation (as dsp^2) and four dsp^2 hybrid orbitals are obtained which are directed toward four corners of the square. All these hybrid orbitals are vacant and thus get four pairs of electrons from four CN^- ions and $[\text{Ni}(\text{CN})_4]^{2-}$ ion is formed. It has square planer geometry.

e. sp^3d hybridisation

Atoms which have d orbitals available can also use them to form other types of hybrid orbitals. The hybridization of one s, one d, and three p orbitals on a central atom gives rise to five dsp^3 orbitals. dsp^3 hybridization gives five orbitals, three equatorial and two axial, because this hybridization uses the d_z^2 , s, and all three of the p orbitals; one of the p orbitals, p_z , is perpendicular to the xy plane.



Characteristics of sp^3d hybrid orbitals

All the five sp^3d -hybrid orbitals $sp^3d(1)$, $sp^3d(2)$, $sp^3d(3)$, $sp^3d(4)$ and $sp^3d(5)$ are not of the same type but they can be divided in two non equivalent sets:

- a. Three hybrid orbitals formed by the combination one s two $2p_x$ and $2p_y$ atomic orbitals to form sp^2 hybrid orbitals. Which are directed towards three corners of an equilateral triangle

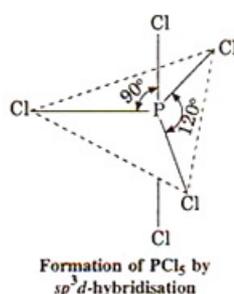
and they are called as equatorial set of orbitals. The angle between each pair of equatorial orbital is 120° .

- b. Another two equivalent hybrid orbitals are directed towards perpendicular to the plane of equilateral triangle and known as axial set of orbitals. These two orbitals are linear therefore angle between these two orbitals is 180° .

Example: Formation of PCl_5 molecule.

In this molecule P atom is the central atom whose EC is $1s^2, 2s^2, 2p^6, 3s^2, 3p_x^1, 3p_y^1, 3p_z^1$. It has three unpaired electrons therefore PCl_3 molecule is expected to be formed. But PCl_5 molecule is also known and it is unstable molecule. The formation of PCl_5 is assumed by excited state of p atom, in which it has five unpaired electrons as follows $\text{Ne } 3s^1, 3p_x^1, 3p_y^1, 3p_z^1, 3d_{z^2}^1$. Now the formation of PCl_5 molecule can be easily explained. However if PCl_5 molecule is formed in this way should have three types of overlapping [ie s-p, p-p and d-p]. But in PCl_5 molecule there are two types of bonds are observed. It is explained only by the hybridisation. Therefore one 3s three 3p and one $3d_{z^2}$ orbitals of P-atom combine to form five sp^3d hybrid orbitals with one electron each. As usual these hybrid orbitals have higher energy than excited P atom. These five hybrid orbitals overlap with $3p_z$ half filled orbitals of five chlorine atoms to form five P-Cl bonds by sp^3d -p overlapping.

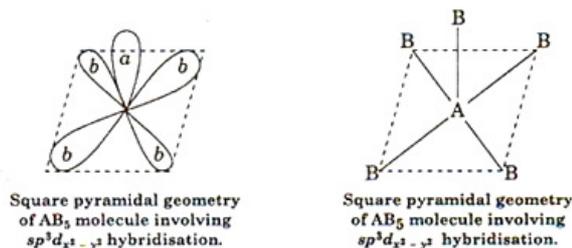
These five hybrid orbitals form trigonal bipyramidal structure. In this geometry axial bonds are slightly longer than the equatorial bonds. This is due to the fact that axial bonds experience greater repulsion from each other than equatorial bonds. This is due to difference in bond angles and bond lengths.



It has unsymmetrical structure therefore it is a reactive molecule or unstable. It splits into PCl_4^+ and PCl_6^- ions in the solid state which have tetrahedral and octahedral structures respectively.

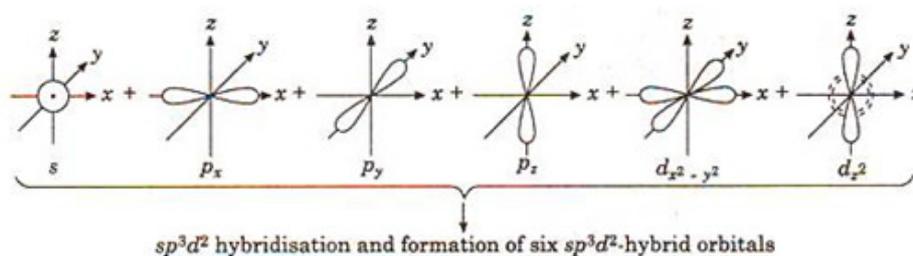
Other examples of sp^3d hybridized molecules are PF_5 SbCl_5 etc.

It is interesting to note that if one s- three p and dx^2-y^2 orbitals of the valence shell of central atom in a molecule (or ion) combine to form five sp^3d hybrid orbitals then these hybrid orbitals form square pyramidal geometry. In this geometry there are four hybrid orbitals are directed towards four corners of the square which are known as basal orbitals, represented by 'b' and one hybrid orbital is directed towards perpendicular to the base called axial orbital represented by 'a'. But this geometry is less stable than trigonal bipyramidal geometry.



f. sp^3d^2 hybridisation

In this type of hybridisation one 's' three 'p' and two 'd' orbitals ($d(x^2-y^2)$ and dz^2) of the valence shell of central atom of the given molecule or ion combine to form six sp^3d^2 hybrid orbitals as shown below.

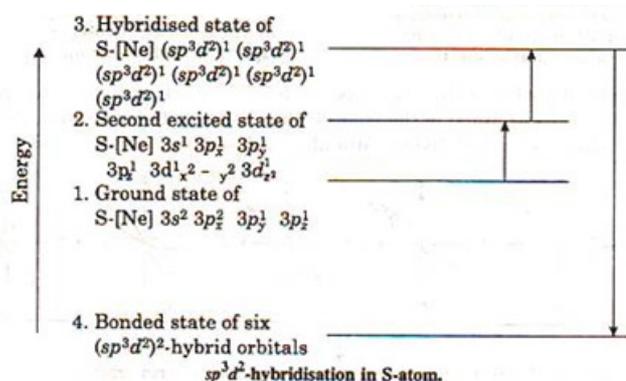
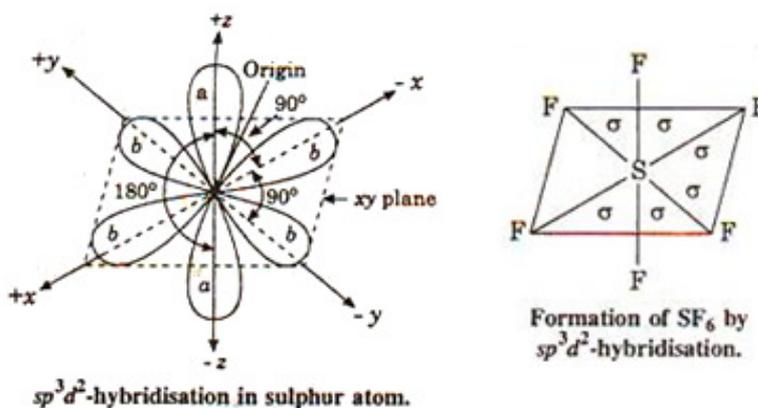


Characteristics of sp^3d^2 hybrid orbitals

1. All the six hybrid orbitals have the same shape and same energy.
2. These six hybrid orbitals are directed towards the six corners of the regular octahedron. Four hybrid orbitals are directed towards four corners of the square and are called as basal orbital 'b' and two hybrid orbitals are directed towards perpendicular of the plane called as axial orbital 'a'
3. The angle between any two orbitals is 90° .
4. The four basal hybrid orbitals are equivalent and similarly two axial hybrid orbitals are equivalent.

Example: The formation of SF_6 molecule.

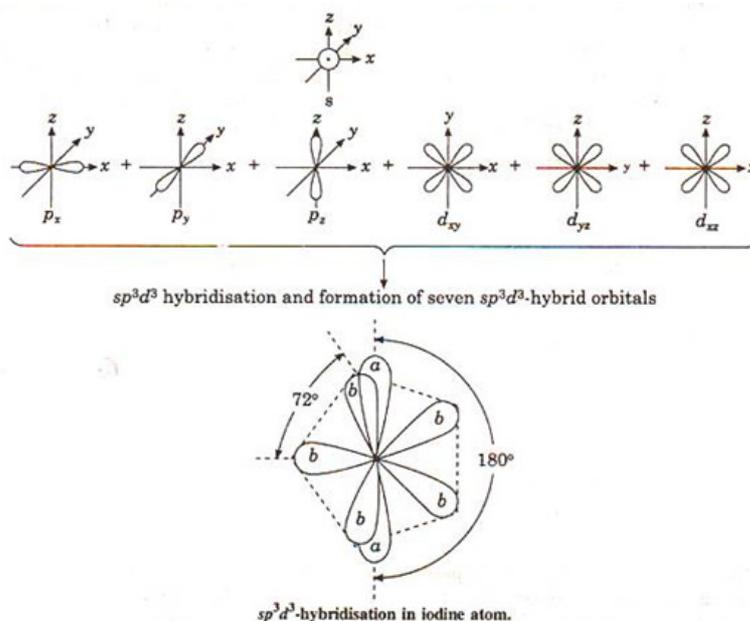
In this molecule S atom is the central atom whose electronic configuration is $Ne\ 3s^2, 3p_x^2, 3p_y^1, 3p_z^1$. It has two unpaired electrons therefore one can expect the formation of SF_2 molecule. But SF_6 molecule is also known. The formation of SF_6 is explained by excited state of S atom in which it has four unpaired electrons as follows; $Ne\ 3s^2, 3p_x^1, 3p_y^1, 3p_z^1, 3d^1z^2$, under this condition the formation of SF_4 molecule only be possible. Therefore it is assumed that S atom comes in second excited state ie $Ne\ 3s^2, 3p_x^1, 3p_y^1, 3p_z^1, 3d^1z^2, 3d^1x^2-y^2$. In this state it has six unpaired electrons and capable to form SF_6 molecule. However if SF_6 molecule is formed in this way, there should be three types of overlapping [ie s-p p-p and d-p]. But in SF_6 molecule all the bonds are identical. It is explained only on the basis hybridisation. Thus one 3s three 3p and two 3d ($3d_{x^2-y^2}$ and $3d_{z^2}$) orbitals combine to form six sp^3d^2 hybrid orbitals with one electron each. These hybrid orbitals have higher energy than the atomic orbitals of excited S atom. These six hybrid orbitals overlap with six half filled $2p_z$ orbitals of fluorine atoms to form six S-F identical bonds by sp^3d^2 -p overlapping. These six hybrid orbitals form octahedral structure. In this geometry the angle between any two hybrid orbitals is of 90° and bond lengths are equal therefore it has symmetrical geometry.



Other examples are AlF_6^{3-} , PF_6^- , TiCl_6^{3-} , SnCl_6^{3-} , AsF_6^- , SeF_6 etc.....,

g. sp^3d^3 hybridisation

In this type of hybridisation one s three p and three d (d_{xy} , d_{yz} and d_{xz}) orbitals of the valence shell of central atom of the given molecule or ion combine to form seven sp^3d^3 hybrid orbitals as follows,



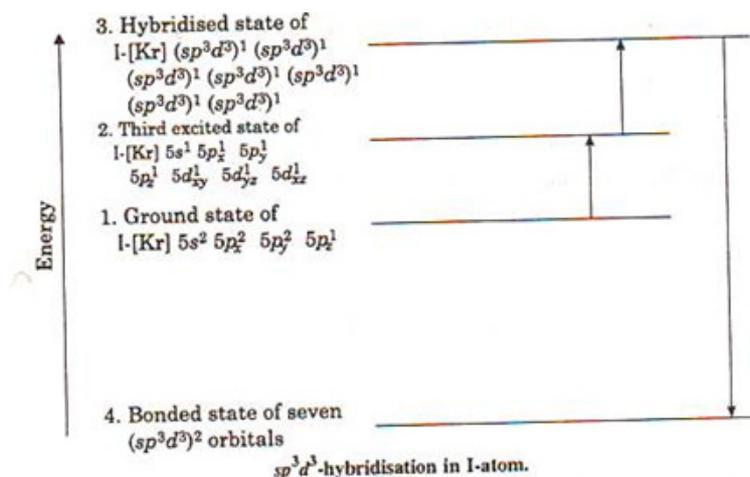
Characteristics of sp^3d^3 hybrid orbitals

12. All the seven sp^3d^3 hybrid orbitals are not same, they are divided in two sets of non equivalent orbitals.

- First set consists of five equivalent hybrid orbitals which are directed towards five corners of pentagon. These five orbitals are known as basal hybrid orbitals and are denoted by 'b'. The angle between any two of these hybrid orbitals is 72° .
- The second set consists of two equivalent hybrid orbitals which are oriented perpendicular to the plane formed by first set of five hybrid orbitals. Thus these two orbitals are linear i.e. 180° . These hybrid orbitals are known as axial hybrid orbitals and are denoted by 'a'.

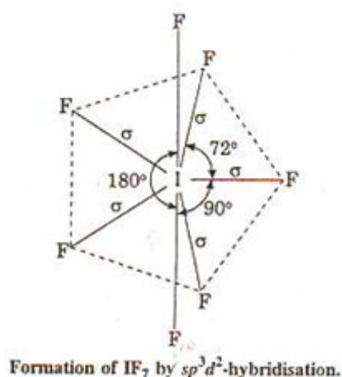
Example: the formation of IF_7 molecule perhaps it is the only example of sp^3d^3 hybridisation molecule. In this molecule I atom is the central atom whose EC is $[\text{Kr}] 5s^2, 5p_x^2, 5p_y^2, 5p_z^1$. Since it has only one unpaired electron hence it should only possible to form IF molecule. But IF_7 molecule is also known. It may be assumed that iodine comes in third excited state and acquire $[\text{Kr}] 5s^1, 5p_x^1, 5p_y^1, 5p_z^1, 5d^{1}_{xy}, 5d^{1}_{yz}, 5d^{1}_{xz}$ configuration. In this state formation of IF_7 can be

explained due to the presence of seven unpaired electrons. However if IF₇ is formed in this way then there will be three types of bonds due to [s-p, p-p and d-p] overlapping. Therefore it is explained by hybridisation. Thus one 5s three 5p and three 5d (5d_{xy}, 5d_{yz} and 5d_{zx}) orbitals combine to form seven sp³d³ hybrid orbitals with one electron each. These hybrid orbitals have higher energy than excited I atom. These seven hybrid orbitals overlap with seven 2p_z half filled orbitals of seven F atoms to form seven I-F bonds by sp³d³ overlapping.



These seven hybrid orbitals form pentagonal bipyramidal geometry. In this geometry axial bonds are slightly longer than the equatorial bonds. This is due to the greater repulsion of equatorial bonds. The five equatorial bonds are at 72° each while axial bonds are at 90° each.

The formation of various types of hybridisation of valence shell orbitals discussed above are given in the following chart with their orientation and bond angle.



2.16 Ionic character of covalent compound

When two atoms of different elements are linked by a covalent bond, the shared electrons are not attracted equally by the two nuclei of bonding atoms. Due to unequal distribution of electron cloud, one end of the molecule acquires partial positive charge and the other end acquires equal partial negative charge. The polarity of bond gives partial ionic character. The percentage of partial ionic character depends upon the difference of E.N. of two atoms join with each other through a covalent bond

For example;

1. HCl molecule:

E.N. of H = 2.1

E.N of Cl = 3.0

Due to difference of E.N., the ability Cl atom to attract shared pair of electron is greater than that of H-atom. Therefore, covalent bond in HCl has ionic character. In HCl, covalent bond is 17% to 18% ionic.

1. HF molecule:

E.N. of H = 2.1

E.N. of F = 4.0

In this example difference of E.N. is greater as compare to HCl. Therefore, ionic character of HF is 64%. Ionic character of covalent compound affects properties of these compounds. For example viscosity, M.P., B.P. of compounds having ionic character are higher than that of non-polar compounds.

2.17 Summary of the unit

There are several theories which explain the electronic structure and shape of molecules, and attempt to predict the structure of unknown molecules. Each theory has its own advantage and also limitations. In many cases all the theories give the correct answer. Octet rule is surprisingly reliable and deal to explain the number of bonds formed in simple molecules. However it did not give indication about shape of the molecules. The shape of the molecule is determined by repulsion between all of the electron pairs present in the valence shell. The lone pair electron takes more space round the central atom than a bond pair, because the lone pair is attracted to one nucleus while the bond pair is shared by two nuclei. Thus presence of lone pair on the central atom causes slight distortion of the bond angles from the ideal shape. The magnitude of

repulsion between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms. During molecule formation orbitals of same energy level (and sometimes different energy levels) can be mixed and reshuffled to produce new orbitals, which are equivalent to each other in all respects. This process is called hybridization. The orbitals produced as a result of hybridization are called hybrid orbitals. In the light of hybridisation we can satisfactorily explain the structure and shape of many molecules.

2.18 Keywords

Resonance; Delocalization; Resonance energy; Canonical forms; Formal Charge; Bent's Rule; VSEPR theory ; Hybridization.

2.19 References for further study

- 1) An Introduction to Molecular Orbitals by Y. Jean, F. Volaton, J. Burdett. *Oxford University Press, USA, 1993*.
- 2) Text book of Inorganic chemistry, by Amitt Arora, *Discovery Publishing House, 2005*.
- 3) Advanced Inorganic chemistry by F. Albert Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann; *Wiley-Interscience; 6th Ed. 1999*.
- 4) Concise Inorganic Chemistry by J. D. Lee, *John Wiley & Sons, 5th Ed. 2008*.
- 5) Inorganic Chemistry by Petter Atkins, Fraser Armstrong, Jonathan Rourke, Tina Overton, Mark Weller; *Oxford University Press 5th Ed. 2011*.

2.20 Questions for self understanding

- 1) What is meant by resonance?
- 2) Write a note on delocalization.
- 3) What is resonance energy?
- 4) What are the conditions for effective canonical forms?
- 5) Explain formal charge.
- 6) Discuss the Valence shell electron pair repulsion (VSEPR) theory with one example.
- 7) What are the applications of VSEPR theory?
- 8) Predict the shape of NH_3 and PCl_5 , molecule using VSEPR theory.
- 9) Write a note on Bent rule.
- 10) What are the limitations of VSEPR theory?
- 11) What is hybridization?

12) With two examples, discuss the geometry of molecules having bond pairs and lone pairs of electrons.

13) Discuss the formation and characteristic of orbitals formed by following types of hybridisation

1. sp hybridization
2. sp^2 Hybridisation
3. Sp^3 hybridisation
4. dsp^2 hybridisation
5. sp^3d hybridisation
6. sp^3d^2 hybridisation
7. sp^3d^3 hybridisation

14) Write a note on Ionic character of covalent compound with one example

Unit - 3

Structure

- 3.0 Objectives of the unit
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- 3.2 Molecular Orbital Theory (MOT)
- 3.3 Basic Principles of MOT
- 3.4 Salient Features of Molecular Orbital Theory
- 3.5 Linear combination of Atomic Orbital (LCAO)
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 - 6. *Beryllium molecule (Be_2)*
 - 7. *Boron Molecule*
 - 8. *Carbon molecule (C_2)*
 - 9. *Nitrogen molecule*
 - 10. *Oxygen molecule (O_2)*
 - 11. *Fluorine Molecule (F_2)*
 - 12. *Neon molecule (Ne_2)*
- 3.11 Molecular orbital diagram of higher period ($n > 2$ valence orbitals) molecule
- 3.12 MO Configuration of Hetero Nuclear Diatomic Molecules
 - 1. *Nitricoxide molecule (NO)*
 - 2. *Carbon monoxide molecule (CO)*
 - 3. *Carbon dioxide molecule (CO_2)*
 - 4. *Molecular orbital diagram of NO_2*
- 3.13 Similarity between Valance bond theory (VBT) and Molecular orbital theory (MOT)
- 3.14 Differences between MOT and VBT
- 3.15 Summary of the unit
- 3.16 Key words
- 3.17 References for further study
- 3.18 questions for self under standing

3.0 Objectives of the unit

After studying this unit you are able to

- ❖ Explain the formation of molecular orbitals.
- ❖ Identify the differences between the Atomic orbitals and Molecular orbitals.
- ❖ Write the molecular orbital energy level diagram for different molecules.
- ❖ Calculate the bond order for different molecules based on energy level diagram.
- ❖ Identify the magnetic properties and strength for different molecules.

3.1 Introduction

Hund and Mulliken have developed an approach to bond formation which is based upon the effects of the various electron field upon each other and which employs molecular orbital rather than atomic orbitals. Each such orbital characterizing the molecule as a whole is described by a definite combination of quantum numbers and possesses a relative energy value.

In molecular orbital theory, we postulate that the combination of atomic orbitals on different atoms forms molecular orbitals (MOs) so that electrons in them belong to the molecule as a whole. Valence bond and molecular orbital theories are alternative descriptions of chemical bonding. They have strengths and weakness, so they are complementary. Valence bond theory is descriptively attractive, and it lends itself well to visualization. Molecular orbital (MO) theory gives better descriptions of electron cloud distributions, bond energies and magnetic properties, but its results are not as easy to visualize. The valence bond picture of bonding in the O_2 is paramagnetic therefore it has unpaired electrons, thus the valence bond structure is inconsistent with experiment and cannot be accepted as a description of bonding. Molecular orbital theory accounts for the fact that O_2 has two unpaired electrons. This ability of MO theory to explain the paramagnetism of O_2 gave it credibility as a major theory of bonding. We shall develop some of the Ideas of MO theory and apply them to some molecules and polyatomic ions.

3.2 Molecular Orbital Theory (MOT)

Like atomic orbitals in an atom, there are molecular orbitals in a molecule. The difference between the atomic orbitals and molecular orbitals is that molecular orbitals are polycentric while atomic orbitals are mono-centric i.e., in an AO the movement of an electron is influenced by only one positive nucleus, while electron in a MO is influenced by two or more nuclei depending on the number of atoms combined in the molecule .

According to MOT the atomic orbitals of the individual atoms are combined to give rise to molecular orbital in which the identity of both the atomic orbitals is lost. The number of molecular orbitals formed is equal to the number of atomic orbitals involved in the combination. Thus two atomic orbitals produced two molecular orbitals. All the electrons pertaining to both the atoms are considered to be moving along entire molecule under the influence of all the nuclei.

3.3 Basic Principles of MOT

1. When nuclei of two atoms come close to each other, their atomic orbitals interact resulting in the formation of molecular orbitals (M.O). Atomic orbitals of atoms in molecule lose their identity after the formation of molecular orbitals.
2. Each MO is associated with a definite energy value. The total energy of the molecule is the sum of the energies of the occupied M.O.
3. Filling up of electrons in the M.O. follows the same way as they filled in the atomic orbitals. i.e., they obey Aufbau principle, Hund's rule and Pauli's exclusion principle.
4. Each electron in a M.O. belongs to all the nuclei present in the molecule.
5. Each electron moving in the M.O. is having clockwise or anticlockwise (i.e, $+\frac{1}{2}$ or $-\frac{1}{2}$) spin.

3.4 Salient Features of Molecular Orbital Theory

i) When two isolated atomic orbitals (A.Os) of two atoms having similar energy and symmetry combine linearly with each other by linear combination of atomic orbital (LCAO) method, two M.Os are obtained.

If both the atoms are of the same element that is called homo-nuclear diatomic molecule or ion (e.g. H_2 , H_2^+ , H_2^- , N_2 , O_2 , O_2^+ , O_2^- etc). If both the atoms are of the different elements that is called hetero-nuclear diatomic molecular or ion (e.g. CO, NO, HF, CN^- , NO^+ , NO^- etc)

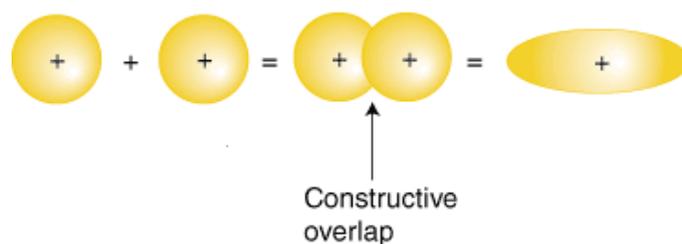
When three A.Os of similar energy and symmetry are combining with one another, three M.Os are obtained. Therefore the number of M.Os obtained is always equal to number of A.Os combining together.

3.5 Linear combination of Atomic Orbital (LCAO)

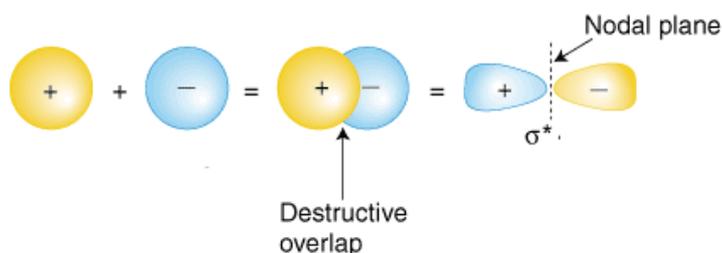
The molecular orbitals are obtained by the methods of LCAO. Suppose two atoms A and B form AB molecule. Their A.Os are represented by ψ_A and ψ_B respectively. There are two ways of their combination.

(c) *Additive overlap*

It is also called as positive overlap or ++ overlap. In this type of linear combination, the positive lobe (i.e. the lobe having + sign) of ψ_A overlaps with the positive lobe of ψ_B thus a molecular orbital is formed. This molecular orbital has lower energy than that of atomic orbitals of atoms A and B due to attraction between the nuclei of A and B. Such type of molecular orbitals are known as bonding molecular orbital (BMO) and represented by ψ_b or σ_b

(d) *Subtraction overlap*

It is also known as negative overlap or +- overlap. In this type a molecular orbital is formed by linear combination the positive lobe of ψ_A overlapping with the negative lobe of ψ_B . This molecular orbital has higher energy than that of two atomic orbitals of atoms A and B due to repulsion between the nuclei. Such type of molecular orbitals are known as anti-bonding molecular orbitals (ABMO) and represented as ψ_a or ψ^* or σ^*

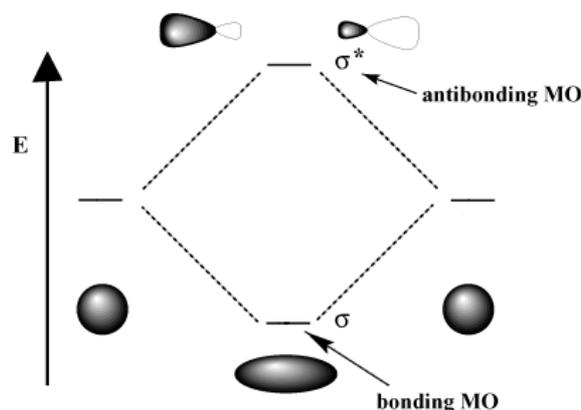


The formation of BMO and ABMO by the linear combination of ψ_A and ψ_B may be represented as:

$$\psi_b = \psi_A + \psi_B \text{ (++ overlap or constructive overlap)}$$

$$\psi_a = \psi_A - \psi_B \text{ (+- overlap destructive overlap)}$$

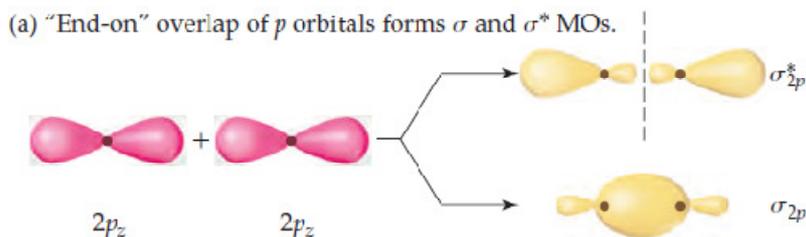
The relative order of the energy of ψ_A , ψ_B , ψ_b and ψ^* is shown in figure 3.



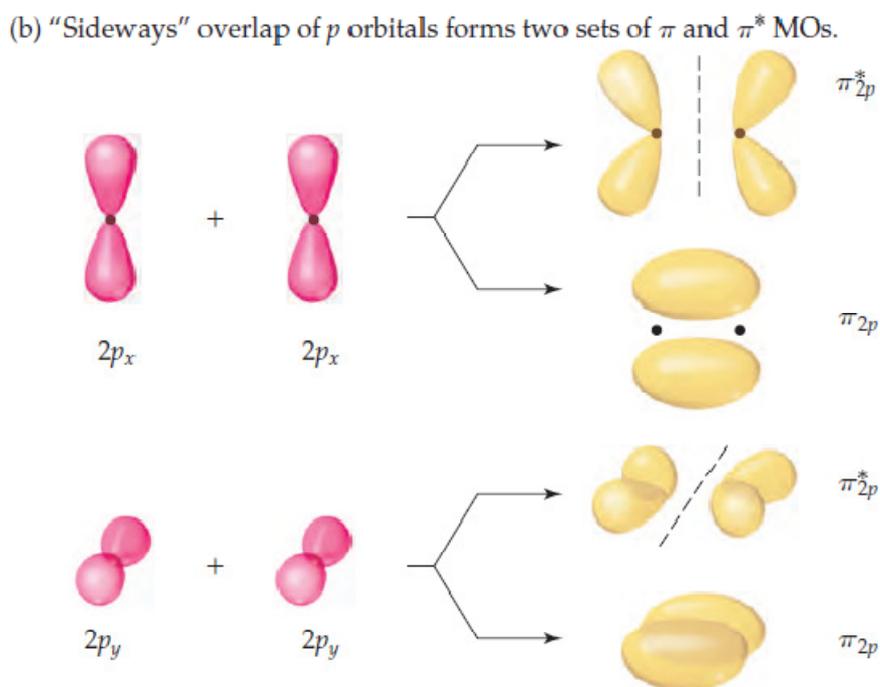
3.6 Conditions for the combination of atomic orbitals

Any pair of atomic orbitals, one from each atom will combine to form two molecular orbitals [one bonding and one anti-bonding]. The combinations of AOs are subject to the following conditions.

- i) The combining orbitals have comparable magnitude of energies. According to this a homonuclear diatomic molecule will not be formed by the combination of 1s-orbital of one atom with 2s-orbital of another atom. Similarly 2s-orbital of one atom will not combine 2p-orbital of another atom because 1s and 2s and 2p-orbitals have very different energies. This is however possible in a heteronuclear diatomic molecule.
- ii) The orbitals must overlap as much as possible. The greater the overlap of atomic orbitals, the greater is the build-up of charge between the nuclei.
- iii) The orbital must have the same symmetry with respect to the molecular axis. According to this, z-axis is generally taken as the molecular (ie, inter-nuclear) axis and x- and y-axes will be perpendicular to the molecular axis.
 - a) Overlap of two s-orbitals: the combination of two s-orbitals (1s or 2s) is exactly like discussed above. Thus their combination gives two σ molecular orbitals (one BMO and another ABMO).
 - b) Overlap of $2p_z$ -orbitals: Like two 2s orbitals, the two $2p_z$ orbitals will also give two σ molecular orbitals (one BMO and another ABMO). Both the overlaps take place along the molecular axis as shown in figure.



- c) Overlap of two $2p_x$ and $2p_y$ orbitals: $2p_x$ orbital of one atom overlaps with $2p_x$ orbital of the other atom along the x -axis, which is perpendicular to the molecular axis. Hence they give two π -molecular orbitals i.e., π_x^b and π_x^* . Similarly, the overlap of two $2p_y$ orbitals also give two π -molecular orbitals i.e., π_y^b and π_y^* .

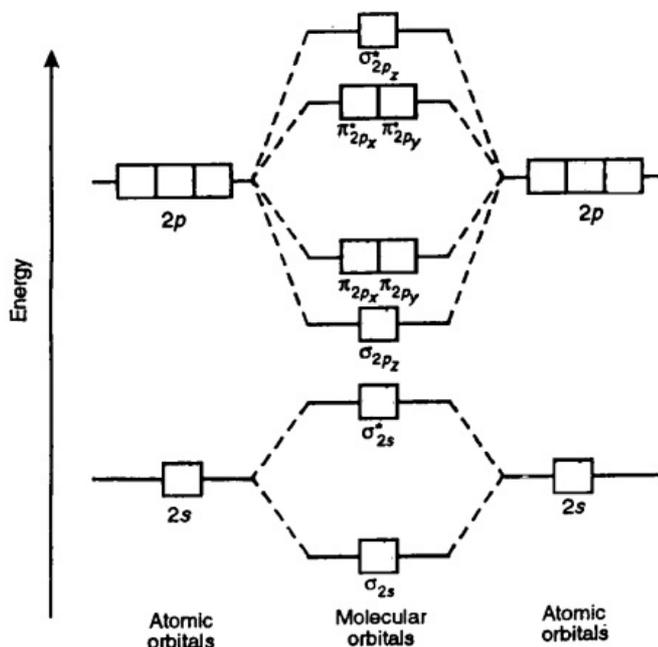


Thus we find that $2s$, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals on one atom on combining with $2s$, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals on the another atom give eight molecular orbitals which are σ ($2s$), σ^* ($2s$), σ ($2p_z$), σ^* ($2p_z$), π ($2p_x$), π ($2p_y$), π^* ($2p_x$), π^* ($2p_y$).

3.7 Energy level diagram for Molecular Orbitals

The energy level of molecular orbitals has been determined experimentally from spectroscopic data. The order of their increasing energy is as follows

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



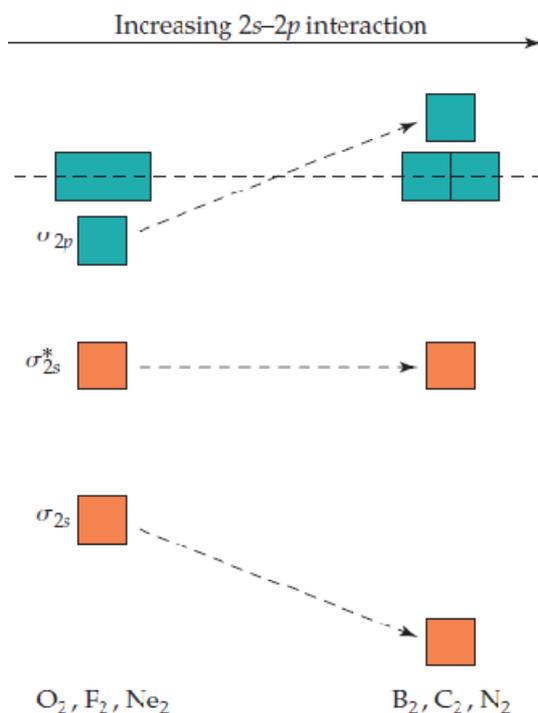
σ and σ^* molecular orbital are symmetric to rotation about the inter nuclear axis, while π and π^* molecular orbitals are unsymmetric to rotation. From the above order it is noted that the π_x and π_y molecular orbitals has same energy and are called degenerate orbitals. Similarly π_x^* and π_y^* molecular orbitals are also degenerate.

It is observed that for some elements (Li, Be, B, C, and N) the above energy level is not correct. For these elements the energy level $\sigma(2p_z)$ MO is higher than $\pi(2p_x)$ or $\pi(2p_y)$ MOs. This is due to the mixing of $2s$ and $2p_z$ AOs as follows.

3.8 Mixing of orbitals

We know that due to the head to head combination of 's' AOs of two atoms forms one $\sigma(s)$ and one $\sigma^*(s)$ MOs are formed.

In the same way by the head to head combination of p_z AOs of two atoms one $\sigma(p_z)$ and one $\sigma^*(p_z)$ are formed. But if the combination of 's' and 'p' AOs is smaller, then there is possibility of the mixing of 's' and 'p' AOs to acquire sp character. Under this condition neither $\sigma(s)$ and $\sigma^*(s)$ MOs retain pure 's' character nor $\sigma(p_z)$ and $\sigma^*(p_z)$ MOs retain pure p character. Due to this s-p mixing the energies of these MOs change in such a way that $\sigma(s)$ and $\sigma^*(s)$ become more stable (hence attain lower energy level) and $\sigma(p_z)$ and $\sigma^*(p_z)$ become less stable (attain higher energy level) as shown in figure.



Because $\pi(p)$ orbitals are not involved in mixing therefore their energy level remain unchanged as shown in the figure. Due to this fact a new sequence of energy of MOs is obtained which is as follows,

$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2p_x) = \pi(2p_y) < \sigma(2p_z) < \pi^*(2p_x) < \pi^*(2p_y) < \sigma^*(2p_z)$
 the above energy level of different MOs is shown in the figure

it is very important to note that the difference in energy levels between 2s and 2p AOs for these atoms is lower while that for O and F is very large as shown in the table-1.

Table-1 energy difference of 2s and 2p_z AOs of some elements.

3.9 Bond order (Bond multiplicity)

Atoms	Li	Be	B	C	N	O	F
Difference between energies of 2s and 2p _z AOs(kJmol ⁻¹)	178	262	449	510	570	1430	1970

The electrons in the bonding molecular orbitals help in the formation of bonds while those in the antibonding molecular orbitals oppose to formation of bond. Therefore as number electrons in the boning orbitals are more compare to antiboning orbitals, then the molecule is stable. Bond order is nothing but number of covalent bonds between the combing atoms. Bond order is equal

to one-half of the difference between the number of electron in bonding molecular orbitals (n_b) and in the anti-bonding molecular orbitals (n_a). Thus,

$$\text{Bond order} = \frac{1}{2} (n_b - n_a)$$

Where n_a = number of electrons in the bonding molecular orbitals and

n_b = number of electrons in the anti-bonding molecular orbitals.

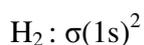
3.10 Molecular orbital configuration of some homonuclear diatomic molecules

Using the relative energy order of the various molecular orbitals discussed in previous sections we can now determine the molecular orbital configuration of molecules and calculate the bond between the atoms in a molecule with the help of Molecular orbital energy level diagram.

1. Hydrogen Molecule (H_2)

The electronic configuration of hydrogen atom is $1s^1$. When hydrogen molecule is formed by the combination of two hydrogen atoms we have two electrons of same energy which occupy $\sigma(1s)$ MO. According to Pauli's exclusion principle these two electrons should have opposite spin ($\downarrow\uparrow$).

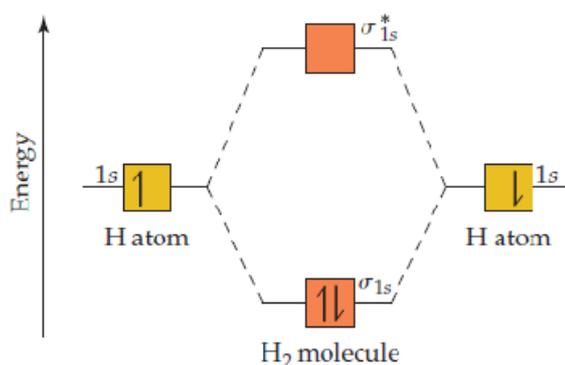
Thus MO configuration of H_2 may be presented as below:



Since there are only two bonding electrons hence

The bond order = $\frac{1}{2}(2-0) = 1$.

It means there is a single bond in hydrogen molecule. The dissociation energy of H_2 molecule has been found to be 458 kJ mol^{-1} and bond length is 0.74 \AA .



2. Hydrogen molecule ion (H_2^+)

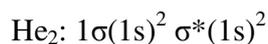
There is one electron in H_2^+ ion which occupies $\sigma(1s)$ MO.

Thus its MO configuration is $H_2^+ : \sigma(1s)^1$, and bond order is $\frac{1}{2} (1-0) = \frac{1}{2}$.

Since the bond order is less than that of H_2 molecule hence H_2^+ must be less stable than H_2 . It is supported bond dissociation energy (269 kJ mol^{-1}) and bond length (1.04 \AA).

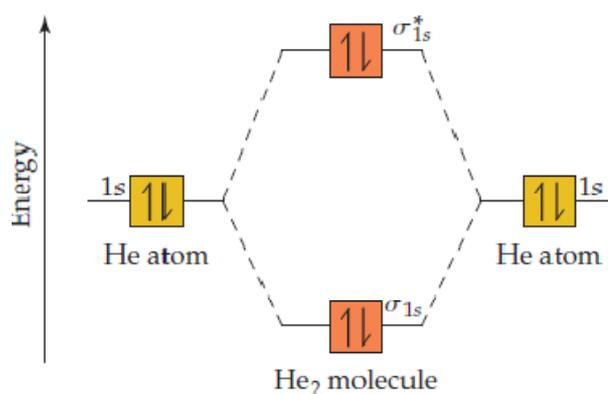
3. Helium molecule (He_2)

The electronic configuration of helium is $1s^2$. Thus there are four electrons are present in He_2 molecule which are distributed in $\sigma(1s)$ $\sigma^*(1s)$ MOs as



$$\text{Bond order} = \frac{1}{2} (2-2) = 0$$

Because in this case bond order is zero therefore He_2 molecule does not exist.

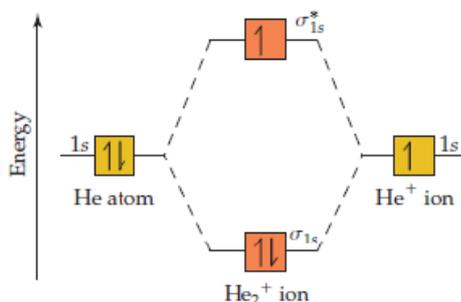


4. Helium molecule ion (He_2^+)

The electronic configuration of Helium is $1s^2$. When He_2^+ is formed we have three electrons to distribute in $\sigma(1s)$ and $\sigma^*(1s)$ MOs. Since $\sigma(1s)$ MO has lower energy than $\sigma^*(1s)$ MO configuration of He_2^+ is as follows: $He_2^+: \sigma(1s)^2 \sigma^*(1s)^1$.

$$\text{The bond order} = \frac{1}{2} (2-1) = \frac{1}{2}$$

It means that He_2^+ is less stable than that of H_2 molecule. Similarly we can explain the formation of HeH molecule (or H_2^- ion) which also has three electrons.



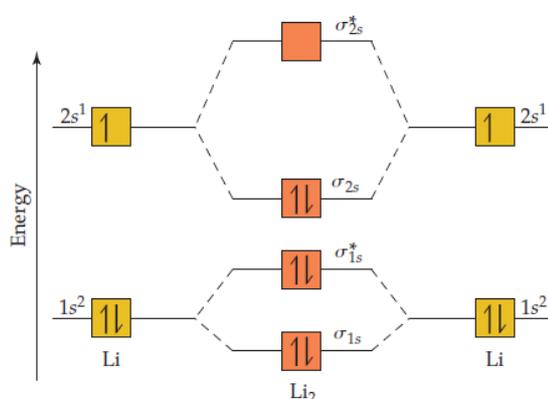
5. Lithium molecule (Li_2)

The electronic configuration of lithium is $1s^2 2s^1$. Thus in Li_2 molecule there is six electrons are available to fill in molecular orbitals. Out of 6 electrons, four electrons belong to K shell and only two electrons are to be distributed in MOs. Thus MO configuration of Li_2 is as:



$$\text{Bond order} = \frac{1}{2}(2-0) = 1$$

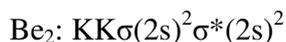
It means Li_2 molecule exists and there is single bond (Li-Li) in lithium molecule. The bond energy of Li_2 molecule is low (105 kJ mol^{-1}) and its bond length is large (2.67 \AA).



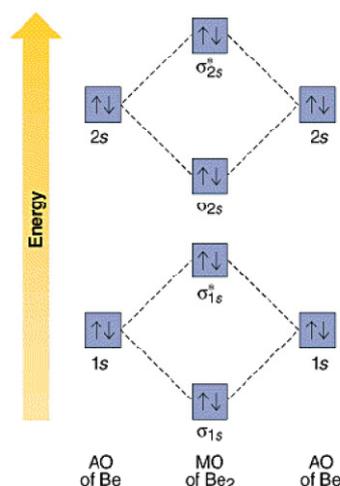
Now the question is why the bond energy of Li_2 is quite lower than that of H_2 or the bond length of Li_2 is quite larger than that of H_2 . The reason is that in the case of Li_2 molecule 2s AOs overlap which is less effective than the overlapping of 1s-1s AOs. At the same time due to the presence of inner 1s orbitals $\sigma(2s)$ MO is shielded by these orbitals. Hence the attraction between the nuclei and the electron in $\sigma(2s)$ MO is less.

6. Beryllium molecule (Be_2)

The electronic configuration of Beryllium is $1s^2, 2s^2$. Therefore there are eight electrons are available to fill in MOs for Be_2 molecule, out of which four electron belong to K-shells and four electrons are distributed in $\sigma(2s)$ and $\sigma^*(2s)$ MOs. Thus the MO configuration of Be_2 is



$$\text{The bond order} = \frac{1}{2} (2-2) = 0$$



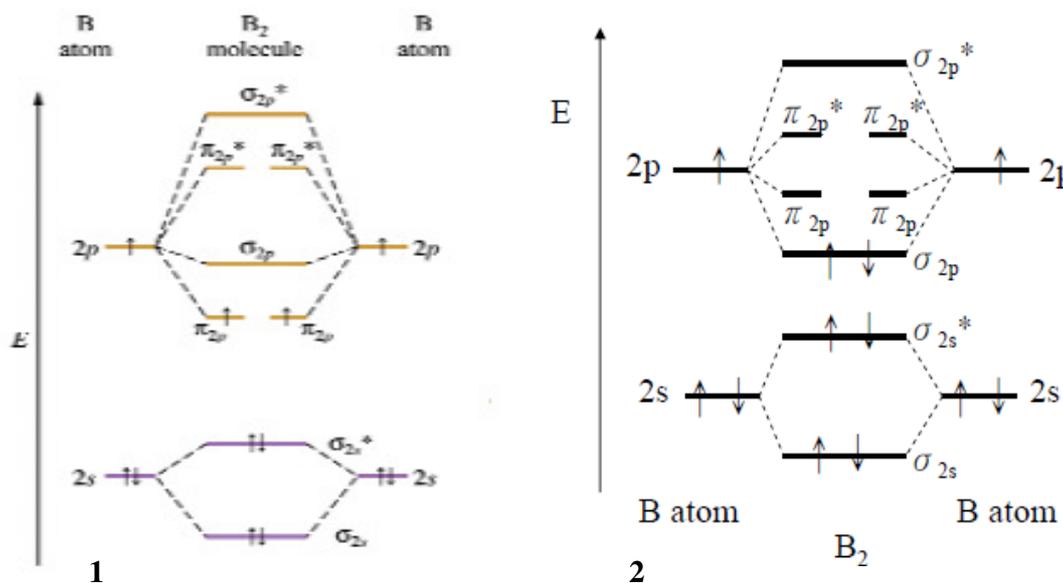
Because in this case bond order is zero therefore Be₂ molecule does not exist.

7. Boron Molecule

The electronic configuration of boron is 1s², 2s², 2p¹, It means there are ten electrons in B₂ molecule available for filling up MOs, out of which four electrons belong to K-shells and six electrons are distributed as $\sigma(2s)^2$, $\sigma^*(2s)^2$, $\pi(2p_x)^1 = \pi(2p_y)^1$ MOs. Thus the MO configuration of B₂ is,

$$B_2 = KK \sigma(2s)^2, \sigma^*(2s)^2, \pi(2p_x)^1 = \pi(2p_y)^1$$

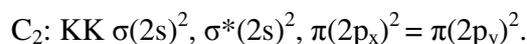
$$\text{Bond order} = \frac{1}{2}(4-2) = 1$$



Since there are two unpaired electrons [$\pi(2p_x)^1 = \pi(2p_y)^1$] in B_2 molecule hence it is paramagnetic in nature as expected. It is interesting to note that if we distribute the electrons in different MOs according to figure 2 then MO configuration becomes $KK \sigma(2s)^2, \sigma^*(2s)^2, \sigma(2p_z)^2$. Since in this case there is no unpaired electron hence the B_2 molecule should be diamagnetic but it is not so. Therefore we can say that mixing of orbitals (2s and 2p) takes place, where the difference in energy level between 2s and 2p is smaller (e.g. $Li_2, Be_2, B_2, C_2, N_2$).

8. Carbon molecule (C_2)

The electric configuration of carbon is $1s^2, 2s^2, 2p^2$. Thus there are twelve electrons in C_2 molecule available to fill up MOs, which are distributed in different MOs as follows:

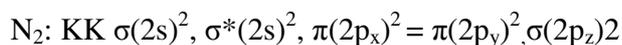


$$\text{Bond order} = \frac{1}{2}(6-2) = 2$$

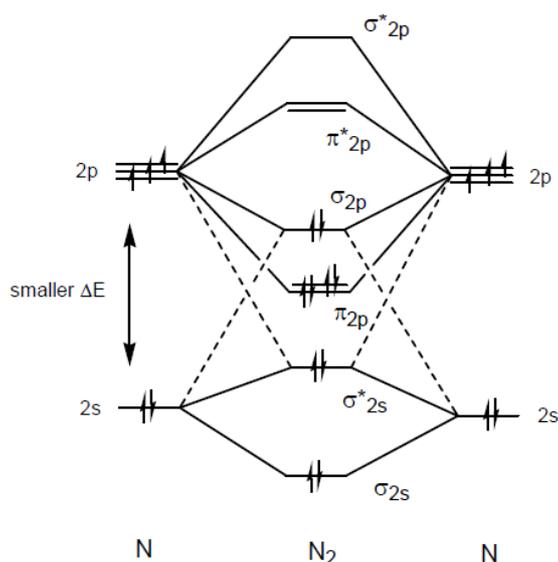
Since there is no unpaired electron in C_2 molecule hence it is diamagnetic in nature as expected. Its bond energy and bond length have been found to be 627.9 kJmol^{-1} and 1.31 \AA respectively. It is to be noted that the diamagnetic character of C_2 molecule cannot be explained according to energy level diagram,

9. Nitrogen molecule

The electronic configuration of nitrogen is $1s^2 2s^2 2p^3$. Thus there are fourteen electrons in N_2 molecule which are distributed different MOs as follows.



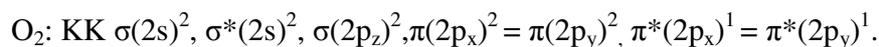
$$\text{Bond order} = \frac{1}{2}(8-2) = 3$$



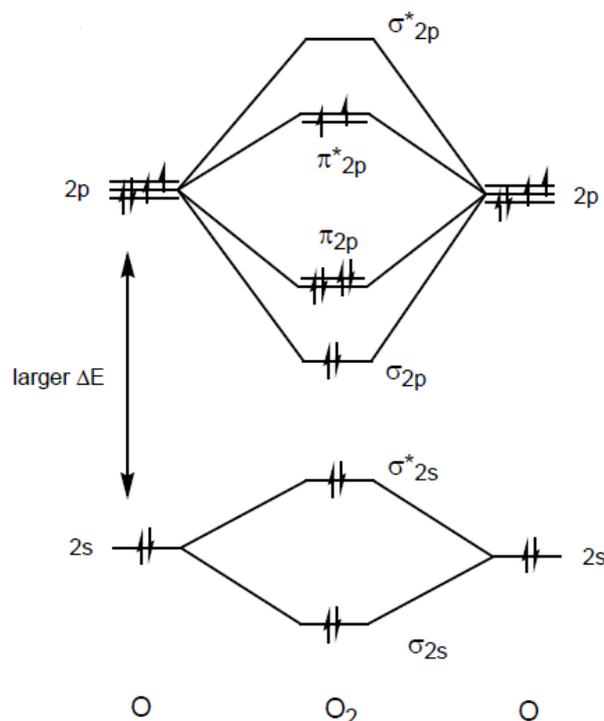
Thus nitrogen contains a triple bond. It is diamagnetic in nature as expected. Because in this case there are four bonding orbitals and only one antibonding orbital, therefore it should be highly stable molecule. Its bond dissociation energy and bond length have been found to be $945.6 \text{ kJ mol}^{-1}$ and 1.10 \AA respectively.

10. Oxygen molecule (O_2)

The electronic configuration of oxygen is $1s^2 2s^2 2p^4$. Thus oxygen molecule has 16 electrons out of which 12 electrons are distributed in different MOs as follows



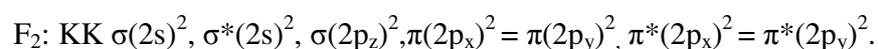
$$\text{Bond order} = \frac{1}{2}(8-4) = 2$$



Thus oxygen molecule contains a double bond. It is paramagnetic due to the presence of two unpaired electrons. Since there are four antibonding electrons it is less stable (or more reactive) than nitrogen. Its bond energy is $494.6 \text{ kJ mol}^{-1}$ and bond length is 1.21 \AA .

11. Fluorine Molecule (F_2)

The electronic configuration of fluorine is $1s^2, 2s^2, 2p^5$. Thus fluorine molecule has 18 electrons out of which 14 electrons are distributed in different MOs as follows



$$\text{Bond order} = \frac{1}{2}(8-6) = 1$$

Thus a fluorine molecule contains a single bond it is diamagnetic in nature as expected. Since there are four bonding orbitals and three antibonding orbitals hence F_2 molecule is more reactive and hence F_2 molecule is more reactive than O_2 molecule. Its bond dissociation energy is 155kJmol^{-1} and bond length is 1.42\AA .

12. Neon molecule (Ne_2)

The electronic configuration of neon is $1s^2, 2s^2 2p^6$. Thus a neon molecule has 20 electrons out of which 16 electrons are distributed in different MOs as follows.

$$Ne_2: KK \sigma(2s)^2, \sigma^*(2s)^2, \sigma(2p_z)^2, \pi(2p_x)^2 = \pi(2p_y)^2, \pi^*(2p_x)^2 = \pi^*(2p_y)^2, \sigma^*(2p_z)^2$$

$$\text{Bond order} = \frac{1}{2}(8-8) = 0$$

Since bond order in neon molecule is zero. Hence molecule does not exist.

3.11 Molecular orbital diagram of higher period ($n > 2$ valence orbitals) molecule

The (S_2) molecule like O_2 molecule is paramagnetic and its molecular configuration is as follows.

$$S_2: KK LL \sigma(3s)^2, \sigma^*(3s)^2, (3p_z)^2, \pi(3p_x)^2 = \pi(3p_y)^2, \pi^*(3p_x)^1 = \pi^*(3p_y)^1,$$

As described earlier KKLL means that the inner electrons are essentially localized on their respective nuclei. In other words these electrons are non-bonding electrons.

Halogen Molecules (Cl_2 , Br_2 and I_2):

The general molecular configuration of halogen molecules are as follows.

$$X_2: \sigma(s)^2, \sigma^*(s)^2, \sigma(p_z)^2, \pi(p_x)^2 = \pi(p_y)^2, \pi^*(p_x)^2 = \pi^*(p_y)^2,$$

As discussed above the bond order is $\frac{1}{2}(8-6) = 1$ for halogen molecule (i.e. Cl_2 , Br_2 and I_2)

The bond length and bond energies of these molecules are given below.

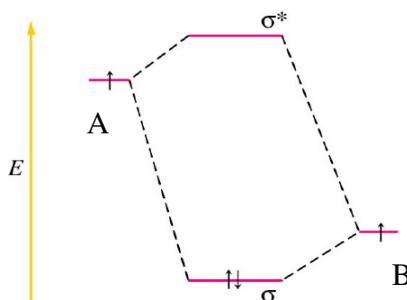
	F_2	Cl_2	Br_2	I_2
Bond length (\AA)	1.417	1.998	2.281	2.666
Bond energy (kJ mol^{-1})	155	239	190	148

The bond length increases from F_2 to I_2 but there is irregularity in bond energy. Actually bond energy of F_2 is exceptionally low. The molecular configuration $\pi(p_x)^2 = \pi(p_y)^2, \pi^*(p_x)^2 = \pi^*(p_y)^2$

is equivalent to four p (π) lone pairs. Repulsion of electron in $2p(\pi)$ orbitals will be large in the case of F_2 therefore its bond energy is anomalously low.

3.12 MO Configuration of Hetero Nuclear Diatomic Molecules

In heteronuclear diatomic molecules the electronegativity of two atoms is different. Therefore the molecular orbital diagram will not be symmetrical like homonuclear diatomic molecules. But the methods of distribution of electron are same. In heteronuclear diatomic molecules the electrons in MO spend more time near (or closer) the more electronegative atom where as the electrons in antibonding MO spend more time near (or closer) the less electronegative atom. The formation of ψ_b and ψ^* (bonding and antibonding MOs) from two AOs having different energies is shown in the following figure.



Since the two atoms A and B belong to different elements hence they have different electronegativities. Let B be more electronegative than A therefore energy level of B is shown lower in the molecular orbital diagram while energy level of A is shown in higher in the molecular orbital diagram. This is the reason that BMOs receive more contribution from atomic orbitals of atom B and hence will be closer to this atom. On the other hand ABMOs will be closer to A. A molecular orbital diagram for such molecule is shown in above figure.

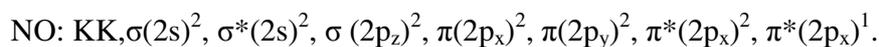
The basic conditions to combine the different atomic orbitals of hetero nuclear diatomic molecules are the same as for homo-nuclear diatomic molecule or ion such as:

- i) Only atomic orbitals of almost same energy level can combine effectively to form molecular orbitals.
- ii) There should be maximum overlap of the atomic orbitals.
- iii) The atomic orbitals must have same symmetry.

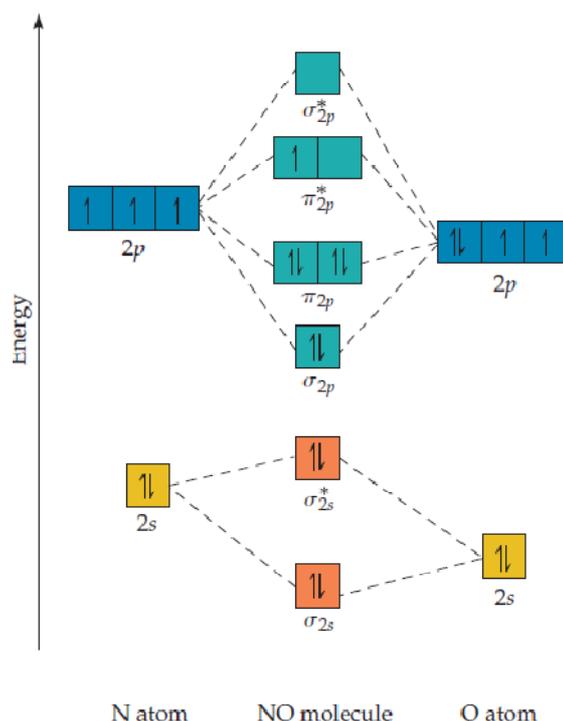
Now we describe molecular orbital diagrams of some hetero nuclear diatomic molecules/ions.

1. Nitricoxide molecule (NO)

The electronic configuration of nitrogen and oxygen atoms is $1s^2, 2s^2, 2p_3$ and $1s^2, 2s^2, 2p^4$ respectively. As in the above case only 11 electrons are to be adjusted in different MOs. These electrons are distributed as



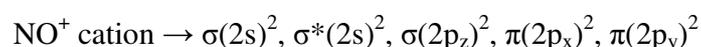
$$\text{B.O.} = \frac{1}{2}(8-3) = 2.5$$

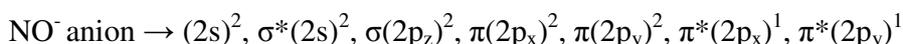
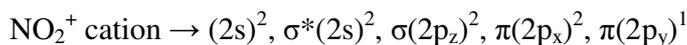


This shows that in NO molecule there are one σ and two π bonds less the antibonding effect of one unpaired electron [$\pi^*(2p_x)$]. Due to the presence of one unpaired electron NO molecule is paramagnetic.

If we compare the stability of NO molecule with N_2 and O_2 molecules, we find that in NO molecules there is one electron extra in antibonding orbitals as compared to N_2 molecule therefore NO molecule is less stable (bond energy $667.8 \text{ kJ mol}^{-1}$) than N_2 molecule (bond energy $945.9 \text{ kJ mol}^{-1}$). Similarly we can prove that NO molecule is more stable than O_2 molecule (bond energy $494.6 \text{ kJ mol}^{-1}$).

The molecular configuration of NO^+ (nitrosyl or nitrosonium cation), NO_2^+ and NO^- ions as follows,

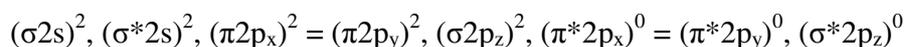




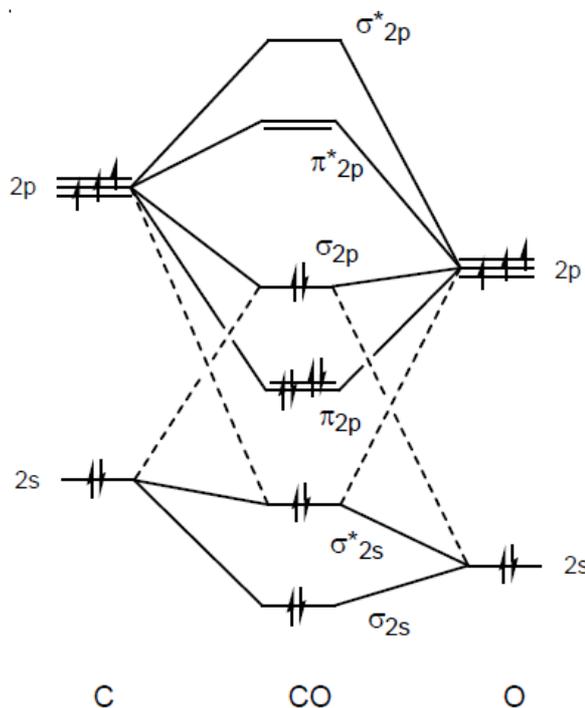
Evidently the bond order (B.O) for NO^+ , NO_2^+ , NO^- is 3, 2.5 and 2 respectively. Since B.O. is decreasing as $\text{NO}^+ > \text{NO}_2^+ > \text{NO}^-$ hence bond energy decreases possess unpaired electrons hence it is diamagnetic while NO_2^+ and NO^- ions are paramagnetic due to the presence of unpaired electrons.

2. Carbon monoxide molecule (CO)

The electronic configuration of carbon and oxygen atoms is $1s^2, 2s^2, 2p^2$ and $1s^2, 2s^2, 2p^4$ respectively. In CO molecule the electrons of the K-shells do not take part in the formation of M.Os. Thus four electrons ($2s^2, 2p^2$) and six electrons ($2s^2, 2p^4$) i.e., ten electrons are involved in the formation of M.Os. These electrons are distributed in different M.Os. as follows.



Thus its bond order is equal to $\frac{1}{2}(8-2) = 3$ showing that carbon and oxygen atoms in CO molecule are linked together by one σ and two π -bonds.



3. Carbon dioxide molecule (CO₂)

Although CO_2 is a linear molecule but it differs from CH_2 , due to the difference between oxygen and hydrogen atoms. For simplicity $2s$ -orbitals of oxygen atoms are considered as non-bonding.

Therefore following four molecular orbitals (bonding and antibonding) are generated from the overlap of $2p_x$ orbital of C-atom and $2p_x$ orbital of oxygen atom (O_A) and from the overlap of $2p_x$ orbital of C- atom and $2p_x$ orbital of oxygen atom (O_B). These molecular orbitals may be written as:

$$\sigma(2s) = [2s(C) + \lambda_1\{(2p_{yA}(O) + 2p_{yB}(O))\}]$$

$$\sigma^*(2s) = [2s(C) - \gamma_1\{(2p_{yA}(O) + 2p_{yB}(O))\}]$$

$$\sigma(2p_x) = [2p_x(C) - \lambda_2\{(2p_{xA}(O) + 2p_{xB}(O))\}]$$

$$\sigma^*(2p_x) = [2p_x(C) - \gamma_2\{(2p_{xA}(O) - 2p_{yB}(O))\}]$$

Since molecular axis is x-axis hence $2p_y$, and $2p_z$ orbitals from π -bonds. In this case six π -molecular are generated which are perpendicular to x-axis. Two each of them are bonding, non-bonding and antibonding. These may be written as:

$$\pi(2p_y) = [2p_y(C) + \delta_1\{2p_{yA}(O) + 2p_{yB}(O)\}]$$

$$\pi(2p_z) = [2p_z(C) + \delta_2\{2p_{zA}(O) + 2p_{zB}(O)\}]$$

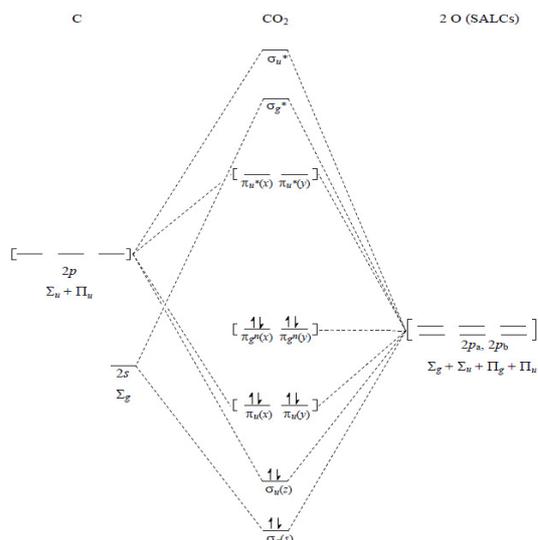
$$\pi_y^{nb} \propto 2p_{yA}(O) - 2p_{yB}(O)$$

$$\pi_z^{nb} \propto 2p_{zA}(O) - 2p_{zB}(O)$$

$$\pi^*(2p_y) = [2p_y(C) - \delta_3\{2p_{yA}(O) - 2p_{yB}(O)\}]$$

$$\pi^*(2p_z) = [2p_z(C) - \delta_4\{2p_{zA}(O) + 2p_{zB}(O)\}]$$

The energy level diagram for CO_2 may be given as follows:

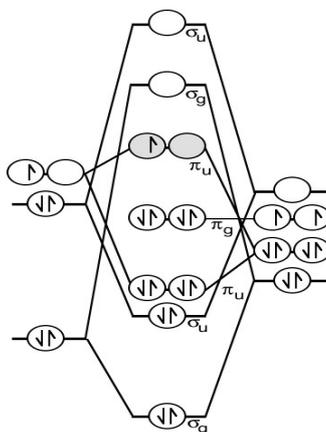


There are 16 valence electrons to be found in these MOs. Out of these, eight electrons are filled in four non-bonding MOs [$2s_A, 2s_B, \pi^{nb}(2p_y)$ and $\pi^{nb}(2p_z)$] and eight electrons are filled in four

bonding MOs [$\sigma(2s)$, $\sigma(2p_y)$ and $\pi(2p_y)$ and $\pi(2p_z)$]. Thus in CO_2 molecule there are two σ bonds and two π -bonds, or there are two double bonds in CO_2 molecule ($\text{O}=\text{C}=\text{O}$). It is also noted that the filled orbitals are more stable when the molecule is linear therefore it is concluded that CO_2 molecule is a linear molecule.

4. *Molecular orbital diagram of NO_2*

There are 17 valence electrons to be filled in these MOs out of these eight electrons are filled in four non bonding MOs [$2s_A$, $2s_B$, $\pi^{\text{nb}}(2p_y)$ and $\pi^{\text{nb}}(2p_z)$] and nine electrons are filled in four bonding MOs [$\sigma(2s)^2$, $\sigma(2p_x)^2$, $\pi(2p_y)^2$, $\pi(2p_z)^2$] and one antibonding MOs $\pi^*1(2p_z)$ thus in NO_2 molecule there are two σ (sigma) bond and two π (pi) or three are two double bond in NO_2 ($\text{O}=\text{N}=\text{O}$). The molecular orbital diagram is similar to that of CO_2 molecule, an unpaired electron is present in π_z^* antibonding MOs.



3.13 Similarity between Valence bond theory (VBT) and Molecular orbital theory (MOT)

- i) Both the theories are the interpretation of covalent bond.
- ii) According to both the theories the AO's of the two atoms must overlap to form a covalent bond. The AO's overlapping each other must have the same symmetry and must be of the same energy.
- iii) According to both theories the electronic charge residue in the region between the atomic nuclei.
- iv) Both the theories postulate that a covalent bond possesses directional properties.

3.14 Differences between MOT and VBT

MOT	VBT
i) MO's are formed by LCAO approximation method. The AO's involved in the formation of these MO's are from valence shell of two atoms	i) Two AO's give an interatomic orbital obtained by the combination of the space functions of two unpaired electrons, one being in each of the two AO's
ii) AO's of the resulting molecule lose their individual identity.	ii) The resulting molecule consists of atoms which although interacting, retain a large measure of their individual character.
iii) MO's are poly-centric	iii) AO's are mono-centric.

3.15 Summary of the Unit:

There are two main ways to explain how the electrons of a molecule are involved in bonding. Which are, Localized bond approach also called VBT and Molecular orbital approach (also known as MO theory) which involves the assignment of electrons to molecular orbitals which are, in general, delocalized over the whole molecule. In some instances, such as in the description of bonding in diatomic molecules, the two approaches give essentially identical results. The valence bond approach is the approach with which you will be most familiar - it is conceptually simpler and is widely used in organic chemistry, but it fails to adequately explain the bonding in certain classes of molecules, including aromatic compounds. The MO approach is generally harder to implement but better explains the bonding in those molecules where the valence bond approach fails, and is generally more consistent with the results of spectroscopic measurements.

3.16 Key Words:

Molecular orbital; Sigma bond; Pi bond; Bonding molecular orbital; Anti bonding Molecular orbital; Energy level diagram; Degenerate orbitals; Bond order.

3.17 References for further study

- 1) An Introduction to Molecular Orbitals by Y. Jean, F. Volaton, J. Burdett. *Oxford University Press, USA, 1993.*
- 2) Text book of Inorganic chemistry, by Amitt Arora, *Discovery Publishing House, 2005.*
- 3) Advanced Inorganic chemistry by F. Albert Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann; *Wiley-Interscience; 6th Ed. 1999.*

- 4) Concise Inorganic Chemistry by J. D. Lee, *John Wiley & Sons*, 5th Ed. **2008**.
- 5) Inorganic Chemistry by Petter Atkins, Fraser Armstrong, Jonathan Rourke, Tina Overton, Mark Welle; *Oxford University Press* 5th Ed. **2011**.

3.18 question for self understanding

- 1) Discuss the basic principle or molecular orbital theory.
- 2) Write a note on Salient Features of Molecular Orbital Theory.
- 3) Explain in detail about linear combination of atomic orbitals.
- 4) Draw the energy level diagram for Molecular Orbitals.
- 5) What is bond order?
- 6) Draw the Molecular orbital configuration of following homonuclear diatomic molecules, calculate the bond order and predict their magnetic property.
 1. Hydrogen Molecule (H_2)
 2. Hydrogen molecule ion (H_2^+)
 3. Helium molecule (He_2)
 4. Helium molecule ion (He_2^+)
 5. Lithium molecule (Li_2)
 6. Beryllium molecule (Be_2)
 7. Boron Molecule
 8. Carbon molecule (C_2)
 9. Nitrogen molecule
 10. Oxygen molecule (O_2)
 11. Fluorine Molecule (F_2)
 12. Neon molecule (Ne_2)
- 7) Draw the Molecular Orbital Configuration of following Hetero Nuclear Diatomic Molecules, calculate their bond order and predict the magnetic property.
 1. Nitricoxide molecule (NO)
 2. Carbon monoxide molecule (CO)
 3. Carbon dioxide molecule (CO_2)
 4. Molecular orbital diagram of NO_2
- 8) What are the similarities between MOT and VBT?
- 9) What are the Differences between MOT and VBT?

Unit -4**Structure**

- 4.0 Objectives of the unit
- 4.1 Introduction
- 4.2 Electron deficient compounds
- 4.3 Nomenclature of Boranes
- 4.4 Preparation of boranes
- 4.5 Structure of diboranes
- 4.6 Nature of bonding in Hydrogen Bridge: Structure of diborane
- 4.7 Molecular Orbital Treatment of 3Centres-2Electrons(3c-2e) Bond formation in B_2H_6
- 4.8 Types of bonds in higher boranes
- 4.9 Structure and Bonding in Some Higher Boranes
 - I) Tetraborane-10 (B_4H_{10})
 - II) Pentaborane-9 (B_5H_9)
 - III) Pentaborane-II (B_5H_{11})
 - IV) Hexaborane-10 (B_6H_{10})
 - V) Decaborane-14 ($B_{10}H_{14}$)
- 4.10 Trimethylaluminium
- 4.11 Methyl lithium
- 4.12 Summary of the unit
- 4.13 Key words
- 4.14 References for further study
- 4.15 questions for self under standing

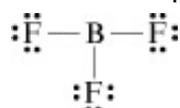
4.0 Objectives of the unit

After studying this unit you are able to

- ❖ Explain nature of electrons deficient compounds
- ❖ Identify the different types of bond formed in electron deficient compounds
- ❖ Write the structure of different hydroborane molecule
- ❖ Differentiate between 2c-2e and 3c-2e bonds
- ❖ Write the dimeric structure of $\text{Al}(\text{Me})_3$
- ❖ Write the structure of Li_4Me_4

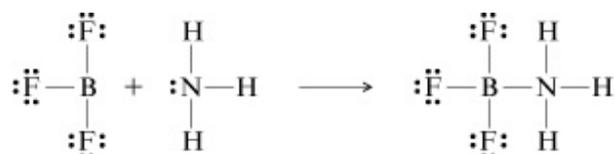
4.1 Introduction

Elements like H, Be, and B, often have fewer than eight electrons in their Lewis structures. Hydrogen has a single valence electron in a 1s orbital and therefore accommodates only two electrons when it forms covalent bonds. Hence it could form only one chemical bond to another atom and does not accommodate lone pairs of electrons. Similarly Beryllium has two valence electrons and boron has three valence electrons, but they often accommodate four or six electrons respectively, in Lewis structures. For example, in a compound BF_3



Each fluorine has a complete octet configuration (i.e, six nonbonding electrons plus two bonding electrons), but boron has only six electrons (six bonding electrons form 3B-F bands and no lone pairs on boron atom). Changing a fluorine lone pair to a bonding pair would alleviate the electron deficiency, but the high electron affinity of fluorine atoms means restrict share its nonbonding electrons with boron.

Therefore BF_3 is a highly reactive compound and it reacts readily with compounds having lone pair electron like NH_3 . In this reaction, the lone pair electrons of N form a new covalent bond with boron in BF_3 compound. So in the new covalent compound, both N and B have full octets.



4.2 Electron deficient compounds

The compounds in which the number of usable orbitals is greater than the number of electrons to use all the orbitals are known as electron deficient compounds.

Or

The molecule in which there are not enough electrons to form two electron bonds between the atoms are called electron deficient molecules.

Example: $(\text{BH}_3)_2$; $[\text{Be}(\text{CH}_3)_2]_n$; $[\text{Al}(\text{CH}_3)_3]_3$ etc. are electron deficient molecules since they do not contain enough electrons to form the two-electron bonds between the atom.

Elements of group IIIA form more electron deficient compounds than any of other group elements in a periodic table. This is because the atoms of IIIA group have the tendency to form 4-covalent but have only three valence electrons (ns^2p^1). However this does not lead to the property of electron deficiency in all types of compounds.

Example trivalent halides such as AlCl_3 are not electron deficient compounds.

The structure and bonding in electron deficient molecules are studied usually by taking Boranes as examples. Boranes are compounds composed solely of boron and hydrogen (and sometimes a cation) and may be neutral or anionic.

Several hydrides of boron have recognized so far and they are commonly having analogy with the hydrocarbons. These hydrides can be represented by general formulae B_nH_{n+4} and B_nH_{n+6} . The former are more stable than the later.

4.3 Nomenclature of Boranes

According to IUPAC system of nomenclature, the number of boron atoms in the borane molecule is indicated by a Greek numerical prefix eg. di for 2 boron; tri for 3, tetra for 4, penta for 5, hexa for 6, etc...., followed by the number which indicates the number of hydrogen atoms. For example, B_6H_{10} is called hexaborane-10. Here hexa indicates the number of boron atoms and 10 indicates the number of hydrogen atoms.

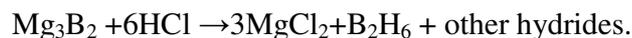
Boranes fall into 5 structure categories, out of which 3 are most important and they are

a) *closo* - B_nH_n b) *nido* - B_nH_{n+4} and c) *arachno* - B_nH_{n+6}

For closed structure prefix *closo* is used, for non-closed structure prefix *nido* is used.

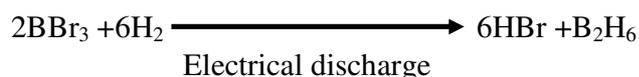
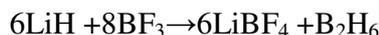
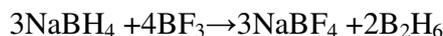
4.4 Preparation of boranes

Stock and his coworker prepared a mixture of boron hydrides (B_2H_6 , B_4H_{10} , B_5H_9 , $\text{B}_{10}\text{H}_{14}$ etc...) by the reaction of magnesium boride with moderately concentrated hydrochloric acid as follows.

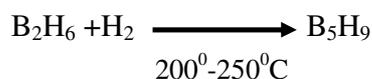


The different boranes obtained are separated by distillation method.

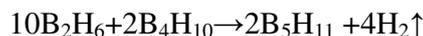
i) Diborane may also prepared by the following reactions:



- ii) When diborane is decomposed in a silent electric discharge in the presence of an inert gas, it gives mixture of B_4H_{10} (40%) B_5H_9 (20%) B_5H_{11} (30%), B_9H_{15} and other in small quantity.
- iii) Pentaborane-9 may prepared by circulating a mixture of diborane and hydrogen through a glass tube at $200^\circ\text{-}250^\circ\text{C}$.



While pentaborane-11 may be prepared by heating a mixture of diborane and tetraborane-

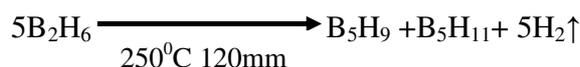
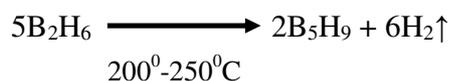
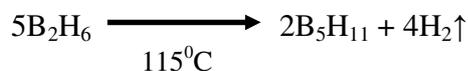


iv) *By interconversion of boranes:*

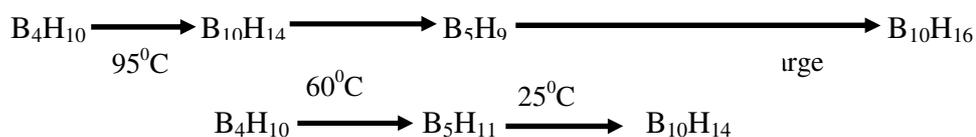
Different boranes may also be obtained by heating different boranes at specific temperature.

For example;

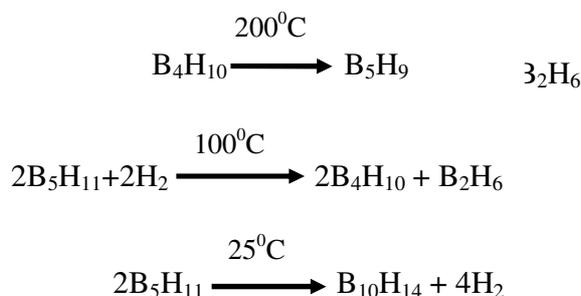
a) B_2H_6 on heating at different temperatures gives higher boranes as shown below



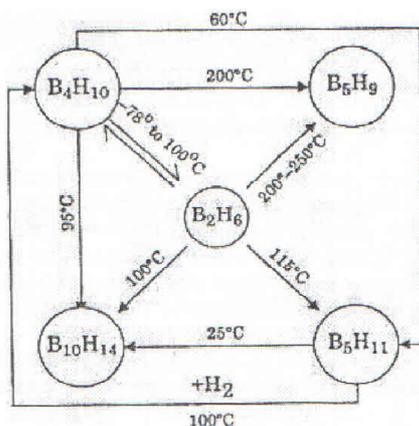
b) B_4H_{10} may be converted in to higher borane as shown below



c) B_5H_{11} on heating ,



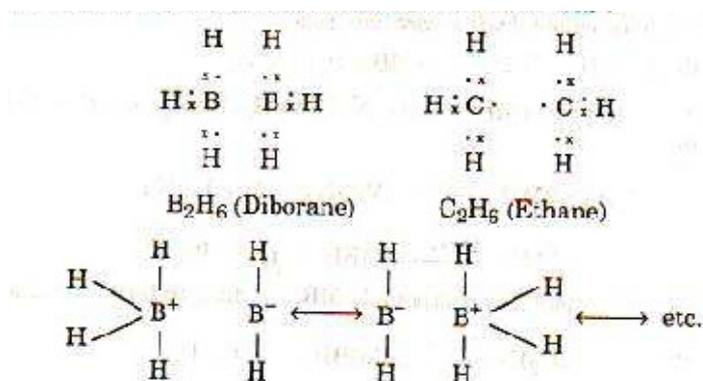
These conversions are shown in the following figure



4.5 Structure of diboranes

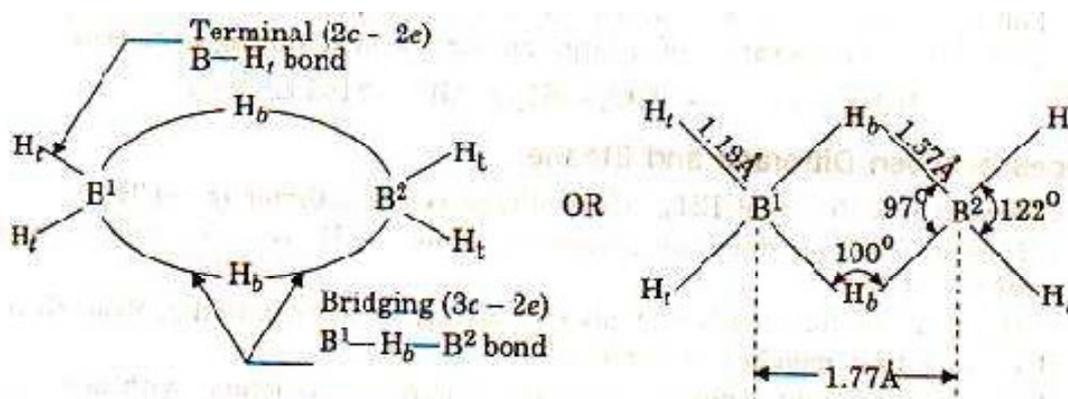
The structure of the diborane is of great interest. The diborane is an electron deficient compound i.e. there are not enough valency electrons to form the expected number of covalent bonds. The following structures were proposed for diboranes.

The ethane like structure of diborane and the ionic form



These structures have lack of experimental support, hence treated as incorrect one. $B_2H_4^-$ anion is isoelectronic with C_2H_4 but these two are not isostructural, because $B_2H_4^-$ anion has a cloud of electron density above and below the B-H plane as in C_2H_4 . The neutral B_2H_6 molecule could then be formally produced by embedding a proton in the electronic cloud above and below the plane of $B_2H_4^{2-}$ ion. Although this structure was not accepted but this bonding model is currently accepted as the three centre-two electron $3c-2e$ bond.

Electron diffraction and spectral studies supports the hydrogen bridge structure in which one hydrogen atom forms a bridge between two atoms, while the terminal hydrogen atoms form normal covalent bonds with boron atoms. This structure may be represented in Fig. 2



In this structure four hydrogen atoms (two each on the left and right hand side) are known as terminal hydrogen (H_t) and two other hydrogen atoms are known as bridging hydrogens (H_b). The two boron atoms and four terminal hydrogen atoms lie on the same plane while two bridging hydrogen atoms lie on a plane perpendicular to this plane. Different parameters are as given below:

The bond lengths between B- H_t , B- H_b and B-B are 1.19 Å, 1.37 Å and 1.77 Å respectively.

B- H_b is longer than B- H_t due to electron deficiency. Bond angles H_t-B-H_t , B- H_b -B and H_b-B-H_b are 122° , 100° and 97° respectively

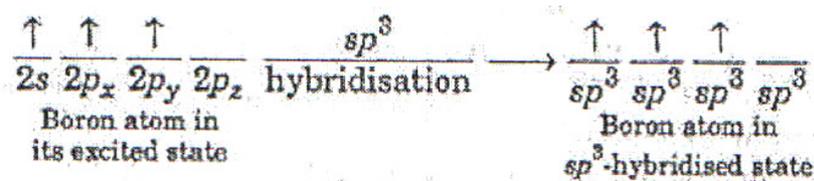
The bridge structure of diborane is supported by the following facts;

- Electron diffraction measurement confirms that four terminal hydrogen atoms are coplanar and two bridge hydrogen atoms occupy the plane above and below the plane.
- Vibrational spectral (Raman and infrared) studies show two intense bands at 2101 cm^{-1} and 2523 cm^{-1} B-H bonds. This indicates that all the B-H bonds are not identical.

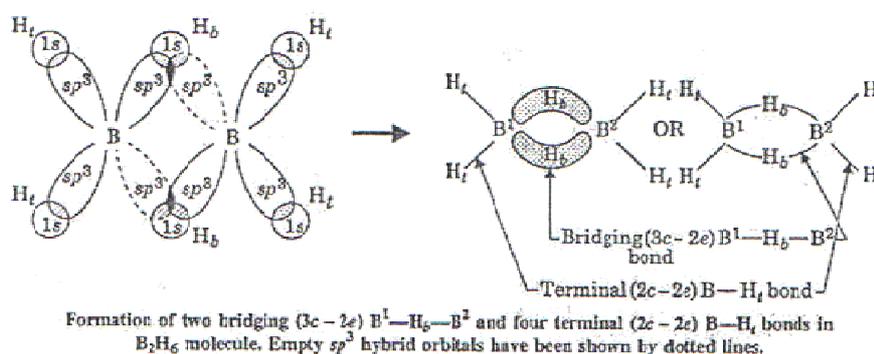
- iii) Nuclear magnetic resonance studies show three main regions of absorption which are due to boron atoms, terminal hydrogen atoms and bridge hydrogen atoms. These studies again support the presence of bridging structure.
- iv) The specific heat of diborane is found to be 54.4 kJ while for ethane is 12.5 kJ. This indicates that there is hindrance of rotation in diborane molecule that is due to bridge structure.
- v) Diborane on methylation gives $B_2H_2(CH_3)_4$ indicating that four hydrogen atoms are of different nature than the rest of two hydrogen atoms, i.e, bridge hydrogen atoms.

4.6 Nature of bonding in Hydrogen Bridge: Structure of diborane

The hydrogen bridge formation is now well established. The orbital theory explains its formation, in which boron atoms show sp^3 hybridization.

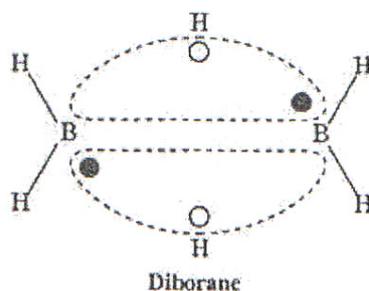


Because three electrons are available hence out of four hybrid orbitals, one sp^3 hybrid orbital is empty. The two sp^3 hybrid orbitals of one borane atom overlap with two s-orbital of two hydrogen atoms forms two sp^3 -s B-H bonds which are referred as terminal hydrogen atoms in the diborane. The third hydrogen atom form bond with one sp^3 hybrid orbital of the first boron atom and one sp^3 hybrid orbital of the second boron atom which is empty hybrid orbital, such type of overlapping cause of banana type bond as shown in below figure.



The above idea gives new concept of the three centre-bond formation, in which the three nuclei are bonded by two electrons hence known as 3c-2e while terminal hydrogen atoms form usual bond 2c-2e ie, two centre-two electron bond.

Therefore diborane may also be represented as shown in the bellow figure.



In this figure dark circular spot represents an electron originally on boron atom and empty spot represents an electron originally on hydrogen atom. Hence each loop links two boron atoms and one hydrogen atom.

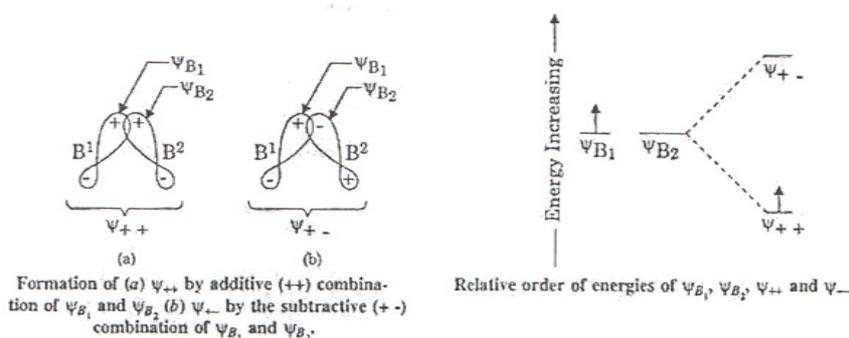
4.7 Molecular Orbital Treatment of 3Centres-2Electrons(3c-2e) Bond formation in B_2H_6

In molecular orbital theory (MOT) 3c-2e bond is called 3-centre molecular orbital. In B_2H_6 both boron atoms exhibit sp^3 -hybridization hence there are four sp^3 -hybrid orbitals available for bonding. Out of four sp^3 -hybrid orbitals one is empty. Two half filled sp^3 -hybrid orbitals overlap with s orbitals of two hydrogen atoms to form usual covalent bonds.

Let wave function of the singly filled sp^3 -orbital B_1 atom and that of the empty sp^3 -hybrid orbital of B_3 atom be represented as Ψ_{B1} and Ψ_{B2} respectively. Similarly singly filled 1s-orbital of bridging hydrogen atom is represented as Ψ_H . Now when Ψ_{B1} , Ψ_{B2} and Ψ_H combine to each other, three molecular orbitals (M.Os) are obtained which are bonding molecular orbital (B.M.Os) denoted by Ψ^b and three antibonding molecular orbital (A.B.M.Os) denoted by Ψ^* and non-bonding molecular orbital denoted by Ψ^n .

The formation of three M.Os takes place as follows.

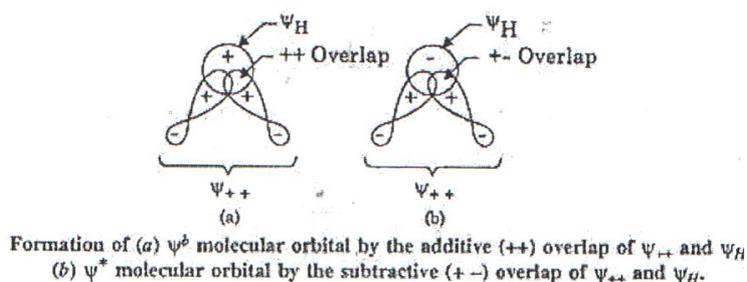
i) First of all Ψ_{B1} (singly filled) and Ψ_{B2} (empty) make additive (+ +) and subtractive (+ -) combination as a result of that we have two M.Os whose wave functions are Ψ_{++} and Ψ_{+-} respectively. This combination is shown in fig. 5.the energy of Ψ_{++} is lower than that of Ψ_{B1} and Ψ_{B2} , and energy of Ψ_{+-} is higher than energy of Ψ_{B1} and Ψ_{B2} .therefore the single electron residing initially Ψ_{B1} A.O. Now occupies Ψ_{++} M.O.



Mathematically Ψ_{++} and Ψ_{+-} are related with Ψ_{B_1} and Ψ_{B_2} as follows:

$$\Psi_{++} = \frac{1}{\sqrt{2}}(\Psi_{B_1} + \Psi_{B_2}) \text{ and } \Psi_{+-} = \frac{1}{\sqrt{2}}(\Psi_{B_1} - \Psi_{B_2})$$

ii) In second step Ψ_{++} M.O. makes additive and subtractive overlap with Ψ_H to give 3-centre bonding M.O. (ψ^b) and 3-centre antibonding Ψ^* respectively as shown below:

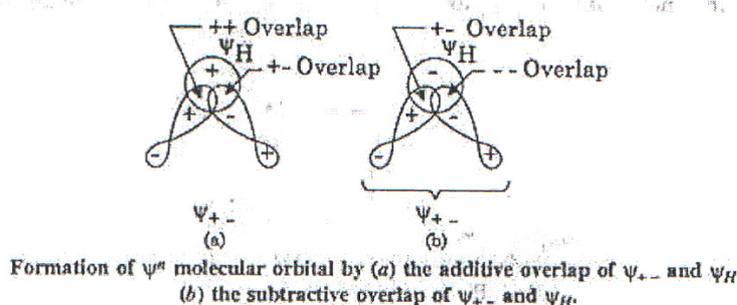


It is important to note that these Ψ^b are 3-centre molecular orbitals, because these are formed by the combination of 2-centre M.O. Ψ_{++} and one atomic orbital of hydrogen Ψ_H .

Mathematically these Ψ^b may be represented as:

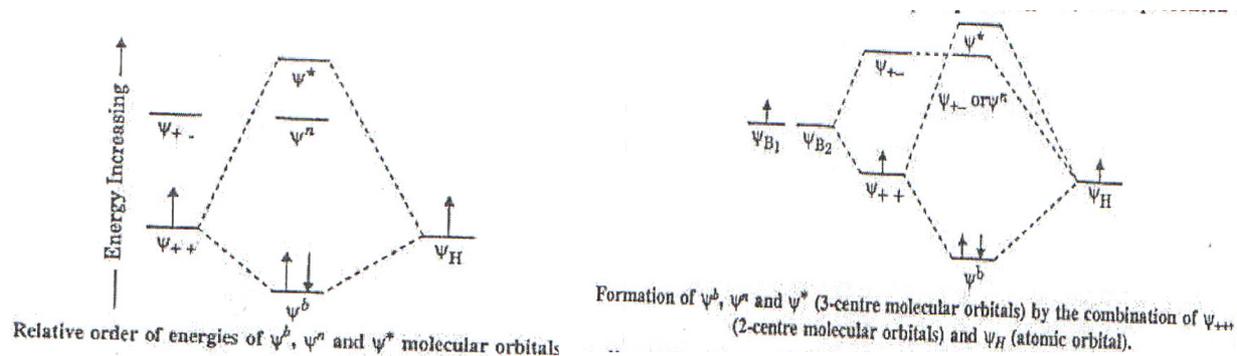
$$\psi^b = \frac{1}{2}(\Psi_{B_1} + \Psi_{B_2}) + \frac{1}{\sqrt{2}}\Psi_H, \quad \Psi^* = \frac{1}{2}(\Psi_{B_1} + \Psi_{B_2}) - \frac{1}{\sqrt{2}}\Psi_H$$

iii) In the third step Ψ_{+-} M.O. makes additive and subtractive overlap with Ψ_H as shown



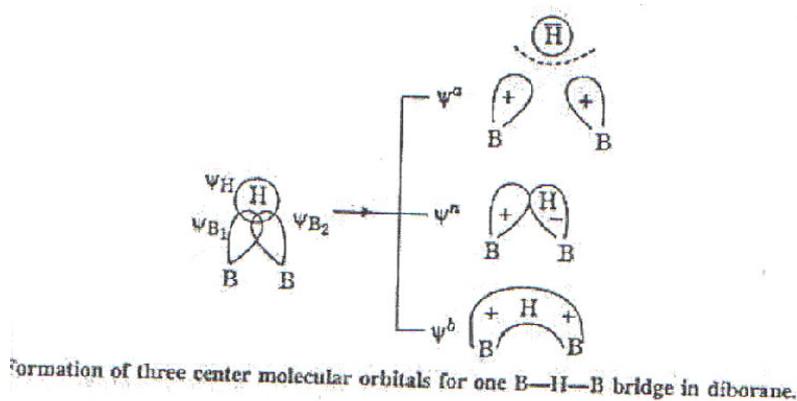
It is clear from the figure that in both additive and subtractive combination ++ overlap is cancelled by +- overlap and +- overlap is cancelled by - overlap respectively. In other words Ψ_{+} M.O. cannot combine with Ψ_H or it gives non-bonding molecular orbital (Ψ^n).

On the basis of above discussion may conclude that Ψ_{++} , Ψ_{+-} and Ψ_H gives rise to three 3-centred molecular orbitals namely Ψ^b , Ψ^* and Ψ^n . the order of their energy level is $\Psi^b < \Psi^n < \Psi^*$ and shown in the following figure. Since the energy level of Ψ^b is the lowest hence both the electrons (one from Ψ_{++} M.O and one from Ψ_H A.O) are present in Ψ^b M.O.



(Linear combination of Ψ_{B1} , Ψ_{B2} and Ψ_H may be represented as shown in write side figure)

The diagrammatic possibilities of overlap along with sketches of the different molecular orbitals (bonding, non bonding and antibonding) are given in the following figure.



4.8 Types of bonds in higher boranes

Higher boranes may contain few or all of the following types of bonds.

- Terminal (2c-2e) B-H bonds: this is a normal covalent bond formed by overlapping of singly filled sp^3 -hybrid orbital of boron atom and singly filled is-orbital of hydrogen atom.
- Direct (2c-2e) B-B bonds: this is a normal covalent bond formed y overlapping of singly filled sp^3 -hybrid orbitals of two boron atoms.

- iii) Bridging or Open (3c-2e) B-H-B bond: this type of bond is formed by overlapping of two sp^3 -hybrid orbitals of boron atoms (one singly filled and other empty) and 1s-orbital of hydrogen atom.
- iv) Triply bridge or closed (3c-2e) B-B-B bond: this type of bond is formed by overlapping of three sp^3 -hybrid orbitals of three boron atoms. Out of these one sp^3 -hybrid orbital is empty. Thus each boron atom contribute $2/3$ electrons for the formation of this bond. This type of bond may be represented as below.

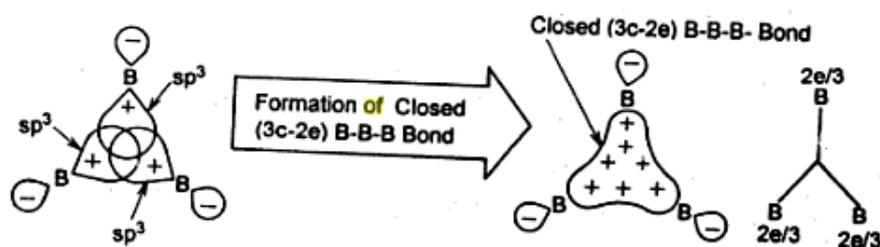


Fig. 16.7. Formation of closed (3c-2e) B-B-B bond.

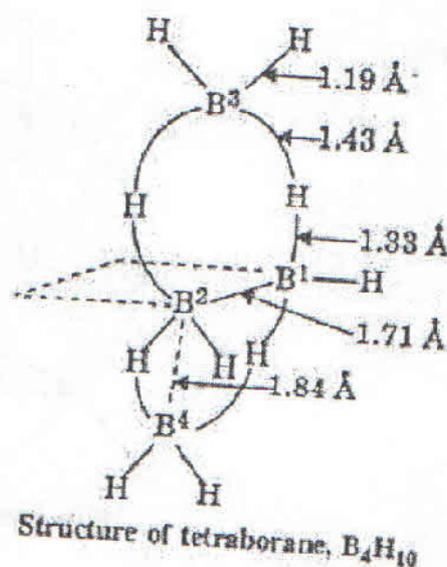
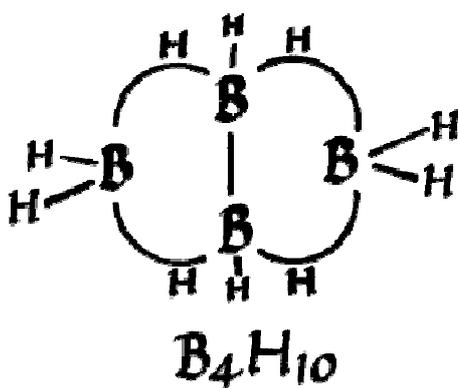
4.9 Structure and Bonding in Some Higher Boranes

The structure and bonding of some common boranes are given here,

VI) Tetraborane-10 (B_4H_{10})

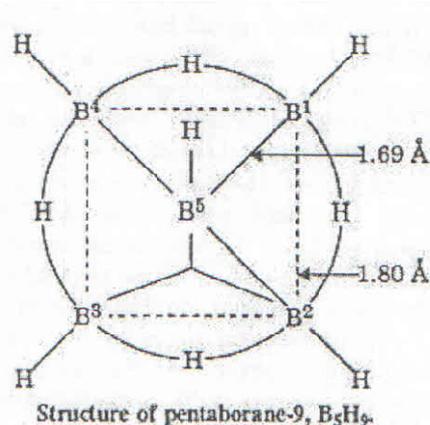
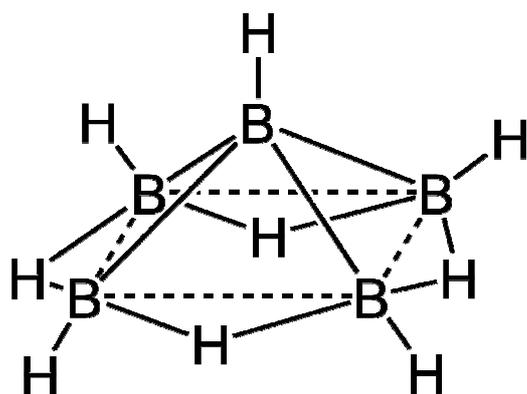
In this molecule four B-atoms form slightly distorted octahedral geometry. There are

- Four bridging (3c-2e) B-H-B bonds viz B^1-H-B^3 , B^3-H-B^2 , B^2-H-B^4 and B^4-H-B^1 ;
- One direct (2c-2e) B-B bond (B^1-B^2) and
- Six terminal (2c-2e) B-H bonds viz B^1-H , B^2-H , B^3-H , B^3-H , B^4-H and B^4-H bonds.

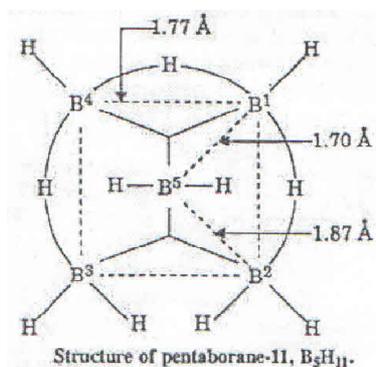


VII) Pentaborane-9 (B_5H_9)

In this molecule five B-atoms are situated at five corners of an asymmetrical square pyramidal. Four B-atom (B^1 , B^2 , B^3 and B^4) are at the base and fifth B-atom (B^5) is at the apex of the pyramid. All these B-atoms form five terminal (2c-2e) B-H bonds. The apex B-atoms are bonded to each other by four four bridging (3c-2e) B-H-B bonds. The apex B-atoms are bonded to two B-atoms (B^1 and B^4) by two (2c-2e) B-B bonds. There is one closed (3c-2e) B-B-B bond also viz. B^5 - B^3 - B^2 bond. Thus this molecule possesses all the four types of bonds discussed above.

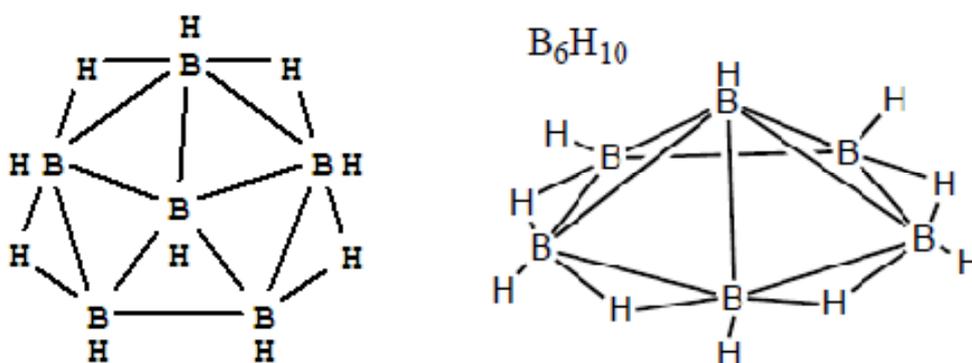
VIII) Pentaborane-II (B_5H_{11})

In this molecule five B-atoms are situated at five corners of an asymmetric square pyramidal. Four B-atoms (B_1 , B_2 , B_3 and B_4) are at the base and fifth B-atom (B_5) is at the apex of the pyramid, which forms two closed (3c-2e) B-B-B bonds, viz B_1 - B_4 - B_5 and B_2 - B_3 - B_5 . Two basal B-atoms (B_2 , B_3) and apical B-atom (B_5) each are linked with two H-atoms by two terminal B-H bonds while the remaining B_1 and B_4 atoms are linked with one H-atom by one terminal B-H bonds while the remaining B_1 and B_4 atoms are linked with one H-atom by one terminal B-H bond. Thus there are eight terminal (2c-2e) B-H bonds in this molecule. Except it there are three bridging (3c-2e) B-H-B bonds viz B_1 -H- B_4 , B_4 -H- B_3 and B_1 -H- B_2 bond

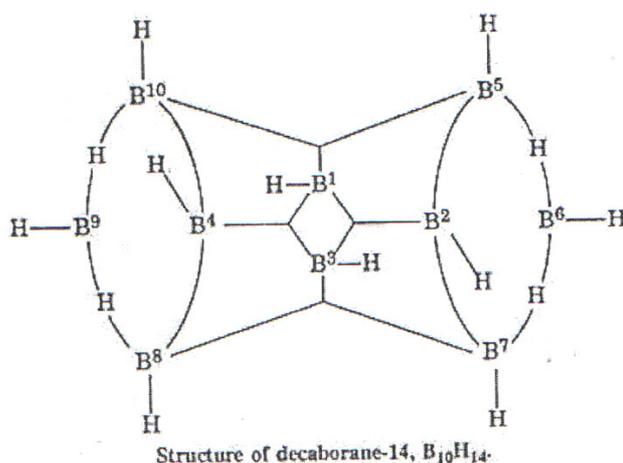


IX) Heaxaborane-10 (B_6H_{10})

In this molecule six B-atoms are situated at the corners of a pentagonal pyramid. Five B-atoms are the base of the pyramid and sixth B-atom (B_6) is at the apex. The basal and apical B-atoms each are linked with six H-atoms by six terminal (2c-2e) B-H bonds. There are four bridging (3c-2e) B-H-B bonds viz B_1 -H- B_2 , B_2 -H- B_4 , and B_3 -H- B_4 . Except it there are two (2c-2e) B-B bonds viz B_1 - B_5 and B_3 - B_5 and two closed (3c-2e) B-B-B bonds viz B_1 - B_2 - B_6 and B_4 - B_5 - B_6 bonds also present in the molecule.

X) Decaborane-14 ($B_{10}H_{14}$)

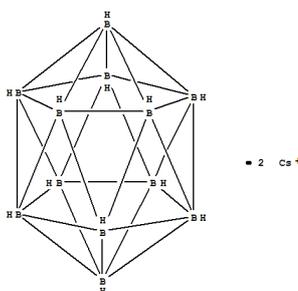
As revealed by X-ray analysis, in $B_{10}H_{14}$ molecule the B-atoms are arranged in two pentagonal pyramids with an edge common to both the pentagonal pyramids. This molecule consist four bridging (3d-2e) B-H-B bonds (viz B_5 -H- B_6 , B_6 -H- B_7 , B_8 -H- B_9 and B_9 -H- B_{10}) in the open face. There are ten terminals (2c-2e) B-Hbond. In addition to these there are four (2c-2e) B-B bonds (viz B_2 - B_5 , B_2 - B_7 , B_4 - B_8 and B_4 - B_9) and four closed (3c-2e) B-B-B bonds viz B_1 - B_2 - B_3 , B_1 - B_3 - B_4 , B_1 - B_5 - B_{10} and B_3 - B_7 - B_8 bonds).



Number and types of bond in B_2H_6 , B_4H_{10} , B_5H_9 , B_5H_{11} , B_6H_{10} and $B_{10}H_{14}$ are summarized in the below table

Borane Molecule	Terminal (2c-2e) B-H bonds	Direct (2c-2e) B-B bonds	Bridging (3c-3e) B-H-B bonds	Closed (3c-2e) B-B-B bonds
Diborane, $B_2H_6(12)$	4 (4 x 2 = 8)	-	2 (2 x 2 = 4)	-
Tetrahydrane-10 $B_4H_{10}(22)$	6 (6 x 2 = 12)	1 (1 x 2 = 2)	4 (4 x 2 = 8)	-
Pentaborane-9 $B_5H_9(24)$	5 (5 x 2 = 10)	2 (2 x 2 = 4)	4 (4 x 2 = 8)	1 (1 x 2 = 2)
Pentaborane -11 $B_5H_{11}(26)$	8 (8 x 2 = 16)	-	3 (3 x 2 = 6)	2 (2 x 2 = 4)
Hexaborane-10 $B_6H_{10}(28)$	6 (6 x 2 = 12)	2 (2 x 2 = 4)	4 (4 x 2 = 8)	2 (2 x 2 = 4)
Decaborane-14 $B_{10}H_{14}(44)$	10 (10 x 2 = 20)	4 (4 x 2 = 8)	4 (4 x 2 = 8)	4 (4 x 2 = 8)

The structure of dodecaborane anion $[B_{12}H_{12}]^{2-}$ is regular icosahedrons of atoms in which there are twenty faces of equilateral triangle. In this structure all twelve boron atoms form icosahedrons structure and attached with twelve hydrogen atom to form terminal B-H bonds. This ion consists of 2c-2e B-B and 3c-2e B-B-B bonds. An icosahedral frame work of B-atoms is important in boron chemistry. Because several boranes may be considered as fragments of a B_{12} icosahedron (or of the $B_{12}H_{12}^{2-}$ ion) in which extra hydrogen atoms are used to sew up the unused valencies around the edge of the fragment.



For example the structure of decaborane -14 $[B_{10}H_{14}]$ may be considered similar to $B_{12}H_{12}^{2-}$ frame work from which B_1 and B_6 have been removed and four B-H-B bonds are formed such as B_2 -H- B_3 , B_2 -H- B_{11} , B_4 -H- B_5 and B_5 -H- B_{10} . Similarly the structure of hexaborane-10, pentaborane-11, octaborane-12 and nonaborane-15 are related to icosahedrons structure of $[B_{12}H_{12}]^{2-}$. It is experimentally proved that icosahedron structure of $[B_{12}H_{12}]^{2-}$ was merely the upper limit of a series of regular deltahedra $[B_nH_n]^{2-}$ where $n = 6$ to 12. Except this B_4C_{14} (i.e, $n = 4$) also exists. It has tetrahedral structure in which all the four corners are occupied by four boron atoms which form four B-Cl bonds and each boron bonded with three boron atoms.

If all the vertices of the deltahedron are occupied as in the $[B_nH_n]^{2-}$ series, the structure is called a closo (in Greek closed) structure. The number of vertices in the deltahedron will be less than the number of bonding pairs in the frame work. This approach is called Wade's rule or polyhedral skeletal electron pair theory, accordingly the number of frame work electrons is equal to $2n+2$. For example in the case of $[B_{12}H_{12}]^{2-}$ each boron atom has one of its three valence electron bonded with one hydrogen atom to form B-H bond, remaining two electrons are used up to form frame work, giving total $2n$ electrons from boron atoms. two extra electrons as obtained from two negative charge. It is important to note that neutral B_nH_n species are not known. Thus $[B_{12}H_{12}]^{2-}$ ion requires 26 electrons to fill up the bonding molecular orbitals and correspond to $[n+1, n = 12]$ electrons pairs expected for an isohedron. If we remove one boron atom from a vertex of a closo structure a nest or cup-like structure is obtained. Such structures are known as nido [latin = nest] structure to satisfy the valencies of the corresponding boron atoms extra hydrogen atoms are added. Therefore the nido structures obey the frame work electron formula $2n + 4$.

For example, in the case of B_5H_9 , there are five B-H bonds which contributes two electrons each and four extra hydrogen atoms will contribute four electrons for a total of 14 ($2n + 4, n = 5$). These four H-atoms form bridges across the open edges of the nest. This corresponds to 7 ($n + 2$) electron pairs and the geometry of the molecule will be derived from an octahedron ($n - 1$ vertices). Thus we can explain the square pyramid nido structure is derived from the closed octahedron. If we remove two vertex boron atoms then we get arachno (greek spider's web) structure. Accordingly arachno structure obey electronic formula $2n + 6$ (or $n + 3$ electron pairs). Therefore pentaborane-11 has arachno structure. The hypo (Greek -net) series of boranes with electronic formula $2n + 8$ has been suggested to closo nido and arachno series. If any borane is

such that which construct units consisting of more than one of the above type, that is called conjuncto (Latin = joined subunits).

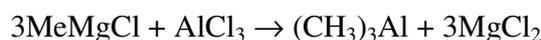
4.10 Trimethylaluminium

Trimethylaluminium is an organoaluminium compound and which can be prepared by following methods.

i) Reaction between methyl iodide and metallic aluminium followed by reduction with magnesium metal.

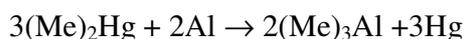


ii) It can be prepared by reaction of aluminium chloride with methylmagnesium chloride (Grignard reagent).



The above reaction actually gives a mixture of MeAlCl_2 , Me_2AlCl , Me_3Al .

iii) It can be prepared by the reaction of aluminium with dimethylmercury compound

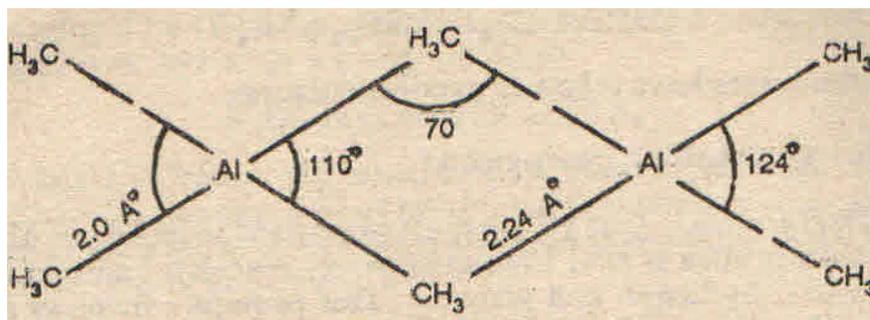


Properties

It is electron-deficient and behaves as Lewis acids. It is a reactive liquid, inflammable in air and explosively sensitive to water.

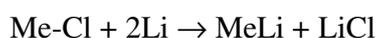
Structure

Trimethylaluminium exists as dimeric form with bridge structure. In the dimer structure, two of the six methyl groups perform a bridging role between the two aluminium atoms and form two three-centre, two-electron (3c-2e) bonds and these methyl groups are called bridging methyl groups. The remaining methyl groups form four two-centre, two-electron (2c-2e) bonds, two bonds each on aluminium atoms and they are called terminal methyl groups. The total energy of the four terminal (2c-2e) Al-C and two bridging (3c-2e) bonds of the trimethylaluminium dimer is 19 k cal/mole more stable than that of six terminal (2c-2e) Al-C bonds of two monomeric molecules of AlMe_3 . Each Al-C-Al bridge bond is 9.5 k cal/mole stronger than its terminal Al-C bonds. This energy is sufficient to keep the dimeric form at normal temperature but not enough to prevent cleavage of the dimer by Lewis bases like ethers or triethylamines, in which trimethylaluminium dissociates into monomer. The bond angles and bond distances of various bonds in trimethylaluminium dimer molecule is shown in the below figure.



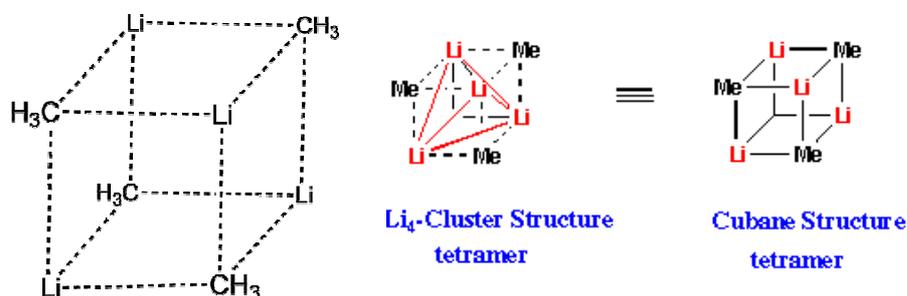
4.11 Methyl lithium

Methyl lithium is an organolithium compound. It can be easily synthesized by the reaction of lithium metal and methyl chloride. This method is still widely employed for the direct synthesis of methyl and other organolithium compounds.



Organolithium reagents get aggregated on long standing, with lithium co-ordinating to more than one carbon atom and carbon co-ordinating to more than one lithium atom.

Because the lithium atom in CH_3Li has three vacant orbitals, it is prone to stabilize up to three high-energy electron pairs in addition to the electrons of the C-Li bond. This results in the formation of a tetrameric complex. In 1964 Weiss and Lucken deduced that the structure of methyl-lithium exists as a tetramer in which 4 lithium atoms form a tetrahedron with each face capped by a methyl group which bonds simultaneously to three Li atoms. The tetrameric cluster consists of a distorted cubane, with carbon and lithium atoms at alternate corners. The Li-Li distances are 2.68 Å, almost identical with the Li-Li bond in gaseous dilithium. The C-Li distances are 2.31 Å. Carbon is bonded to three hydrogen atoms and three Li atoms as shown in the below figure.



4.12 Summary of the unit

Molecules containing less than two valence electrons per bond are referred to as electron deficient. The simplest such molecule is the trigonal trihydrogen cation (H_3^+). The bonding in

this molecule is interpreted in terms of a symmetric three-center ($3c$) bonding molecular orbital containing the two valence electrons. Addition of another electron to an asymmetric MO leads to a breakdown of the trigonal symmetry. In this unit we learn about the structure of diborane and interpret it in terms of two ($3c-2e$) molecular orbitals, each formed by combination of one sp^3 hybrid orbital from each B atom with the $1s$ AO on a bridging H atom. The analogous structure of trimethylaluminium dimer $(Al(CH_3)_3)_2$ is also described. Other electron deficient structure that is discussed include $Li_4(CH_3)_4$.

4.13 Key words

Boranes; electron deficient compounds; $2c-2e$ bond; $3c-3e$ bond; banana shape bond.

4.14 References for further study

- 1) Advanced Inorganic Chemistry, Vol.- I, by Gurdeep raj, *Krishna Prakashan Media (p) Ltd.* 32nd Ed. **2011**.
- 2) Text book of Inorganic chemistry, by Amitt Arora, *Discovery Publishing House*, **2005**.
- 3) Advanced Inorganic chemistry by F. Albert Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann; *Wiley-Interscience*; 6th Ed. **1999**.
- 4) Concise Inorganic Chemistry by J. D. Lee, *John Wiley & Sons*, 5th Ed. **2008**.
- 5) Inorganic Chemistry by Petter Atkins, Fraser Armstrong, Jonathan Rourke, Tina Overton, Mark Welle; *Oxford University Press* 5th Ed. **2011**.

4.15 questions for self under standing

- 1) What are electron deficient compounds? Give three examples
- 2) Write a note on nomenclature of boranes
- 3) Give five methods for different diboranes
- 4) Discuss structure of diborane
- 5) Discuss nature of bonding in Hydrogen Bridge in diborane
- 6) Write a note on molecular orbital treatment of 3-centred-2electron ($3C-2e$) bond formation.
- 7) Discuss types of bonds in higher boranes
- 8) Discuss in brief the following higher boranes
 - a) Tetraborane-10 (B_4H_{10})
 - b) Pentaborane-9 (B_5H_9)
 - c) Pentaborane-II (B_5H_{11})
 - d) Hexaborane-10 (B_6H_{10})

- e) Decaborane-14 ($B_{10}H_{14}$)
- 9) Give three methods for synthesis of Trimethylaluminium and discuss its structure in details
- 10) Write a note on structure of methyl lithium

Unit- 5**Structure**

- 5.0 Objectives of the unit
- 5.1 Introduction
- 5.2 Ionic bond or electrovalent bond
- 5.3 Conditions for the formation of ionic compound
- 5.4 Properties of ionic compounds
- 5.5 Inert pair effect
- 5.6 Lattice Energy
- 5.7 Theoretical calculation of lattice energy
- 5.8 Applications of lattice energy
- 5.9 Relation between lattice energy and solubility of ionic solids
- 5.10 Experimental determination of lattice energy of an ionic solid- Born-Haber cycle
- 5.11 Applications of Born-Haber Cycle
- 5.12 Kapustinskii's equation
- 5.13 The use of Kapustinskii's equation
- 5.14 Summary of the unit
- 5.15 Key words
- 5.16 References for further study
- 5.17 Questions for self study

5.0 Objectives of the Unit

After studying this unit you will be able to

- ❖ Explain the formation of ionic bond
- ❖ Identify properties of ionic compounds
- ❖ Explain the Inert pair effect in formation of ionic compound
- ❖ Construct the Born-Haber cycle
- ❖ Evaluate the lattice energy of ionic compounds.
- ❖ Recognize the significance of Kapustinskii's equations

5.1 Introduction

According to the law of nature, the most stable state of a system is one which having minimum energy. Two or more atoms combines together to form a molecule because molecules possess less energy compare to the total energy of the individual atoms present in the molecule. Dalton attributed that the chemical combination is nothing but interaction between individual atoms. However this statement did not provide any indication about the manner in which the atoms attached themselves each other in a molecule. Franckland from his observation suggested that each element was characterized by a saturation capacity or valency and it is defined as the number of atoms of hydrogen with which one atom of a given element could combine. Kekule, extend this view and pointed out that valency is a fundamental and invariable property of an element. However the existence of compounds, such as PCl_3 and PCl_5 ; similarly FeCl_2 and FeCl_3 , made it clear that valency of an element is not fixed. Rapid developments came when J.J.Thomson discovered the electron in 1897. He suggested that the chemical properties of the elements were somehow dependent on their electronic configuration. Inspired from J.J.Thomson discovery, Kossel investigated that the some elements, immediately following noble gases have tendency to lose one or more electron to form positively charged ions with noble gas electron configuration. Such elements are called electro-positive elements. Some elements, immediately preceding noble gases have tendency to gain one or more electrons to form negatively charged ions with noble gas configuration. Such elements are called electro-negative elements. When electro positive and electronegative elements are brought together, one or more electrons are transferred from electro-positive elements to electro-negative elements so that resulting charged ions has a stable configuration of the nearest noble gases. And the oppositely charged ions are held together by strong electrostatic force of attraction between them and resulting molecules are

called ionic compounds or electrovalent compounds. In this unit we will learn more about formation, nature and properties of electrovalent bond.

5.2 Ionic bond or electrovalent bond

A chemical bond is only some short of inter-atomic, inter-molecular, or inter-ionic attraction which holds the two constituents together. *When atoms with large electronegativity differences are brought together, electrons are transferred from low electronegativity (electro-positive) atoms to those of high electronegativity (electro-negative) atoms resulting in formation of opposite charged ions and there is a strong electrostatic force of attraction between oppositely charged ions. This electrostatic force binds the oppositely charged ions together is called electrovalent or ionic bond.*

Ionic bond can also defined as “A chemical bond formed due to the electrostatic attraction between stable ions formed by the complete transfer of electrons from one atom to another” it is important to remember that the electron lost or gain to form a ions between two atoms is always from the outermost shell.

An ion is an atom or group of atoms which is charged due to the loss or gain of one or more electrons. The atom which loses electron, it will contract (i.e., reduced in size), gets positive charge and called cation. On the other hand atom which gains electron will expand (i.e., increase in size), gets negative charge and called anion. For example in formation of sodium chloride molecule, an electron is transferred from sodium atom to chlorine atom. The resulting Na⁺ and Cl⁻ ions possessing configurations of neon and argon respectively combine to form an electrovalent compound as shown below



Formation of ionic bond with other elements is shown in fig. 1.

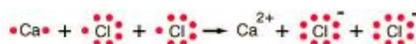


Fig. 1: Formation of ionic compounds

The anions formed in ionic compounds always achieve an inert gas configuration, whereas the cations formed may achieve any of the following configurations

- Inert gas configuration (ns^2 or ns^2p^6)

- b) Pseudo-inert gas configuration ($ns^2p^6d^{10}$)
 c) Inert pair configuration [i.e., 18 + 2 electrons configuration] ($(n-1)s^2p^6d^{10}ns^2$)
 d) $ns^2p^6d^x$ configuration where the sum of $(2 + 6 + x)$ should be nine to seventeen

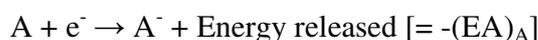
5.3 Conditions for the formation of ionic compound

The formation of ionic compound C^+A^- is occur through the following steps,

i) Atom C give up an electron by absorbing energy equal to its ionization energy or ionization potential $(IP)_C$ and is converted in to cation C^+ . Thus,



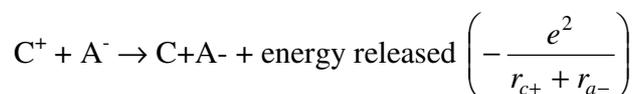
ii) In the second step the atom A picks up the electron released from C and converted in to anion A^- by releasing energy equal to its electron affinity. i.e.,



iii) In the final step cation C^+ and anion A^- combine together due to the electrostatic force of attraction and form a stable ionic crystal C^+A^- . Heat of formation of C^+A^- compound is equal to,

$-\frac{e^2}{r_{c^+} + r_{a^-}}$ is released. Here 'e' is the charges on C^+ and A^- , and r_{c^+} and r_{a^-} are the ionic radii of

C^+ and A^- respectively. Thus,



Thus the overall energy change, E_{ionic} in the formation of the ionic crystal C^+A^- is given by,

$$E_{\text{ionic}} = (IP)_C - (EA)_A - \left(-\frac{e^2}{r_{c^+} + r_{a^-}} \right)$$

The bonded ions C^+ and A^- are more stable than the free atoms C and A, therefore E_{ionic} is

negative. Hence the value of $\left(-\frac{e^2}{r_{c^+} + r_{a^-}} \right)$ is always higher then $[(IP)_C - (EA)_A]$ i.e.,

$$\left(-\frac{e^2}{r_{c^+} + r_{a^-}} \right) \gg [(IP)_C - (EA)_A]$$

Therefore for the formation of a stable ionic compound C^+A^- (or ionic bond) the following conditions must be satisfied by C and A.

a) Atom C should have high tendency to lose electron. i.e., $(IP)_C$ should be low. Hence C should have electro-positive elements such as an alkali metal or alkaline earth metal.

b) Atom A should have high tendency to accept electron. i.e., $(EA)_A$ should be high. Hence atom A should be electro-negative elements such as halogens or elements of group VI A group elements.

5.4 properties of ionic compounds

Some of the properties of ionic compounds are mentioned below:

a) Ionic compounds are soluble in polar solvents with high permittivities (dielectric constants).

The energy of interaction of two oppositely charged ions is shown below

$$E = \frac{q^+ q^-}{4\pi r \epsilon_0}$$

where q^+ and q^- are the charges, r is the distance of separation and ϵ_0 is the permittivity of the medium. For example, the permittivity of water is $7.25 \times 10^{-10} \text{ C}^2 \text{ m}^{-1} \text{ J}^{-1}$ giving relative permittivity of $82\epsilon_0$ for water and that of liquid ammonia, equal to $2.2 \times 10^{-10} \text{ C}^2 \text{ m}^{-1} \text{ J}^{-1}$ corresponding to relative permittivity of $25\epsilon_0$. Since the permittivity of water is more, the attraction between ions gets dissolved in water. But, the attractions between the solvent molecules and the ions are not strong enough to overcome the attractions holding the crystal together in organic solvents and hence, ionic compounds are insoluble in organic solvents.

b) Ionic compounds exhibit a very low conductance in solid state while they conduct quite well in molten state. This conductivity is due to the presence of ions that are free to move under the influence of an electric field. In the solid, the ions are bound strongly in the lattice and are not free to migrate and carry electrical current.

c) Ionic compounds generally have high melting points since ionic bonds usually are quite strong to break and the ionic bonds are omnidirectional. The high melting point of NaCl results from the strong electrostatic attractions between the Na^+ and Cl^- ions, and from the lattice structure.

d) Ionic compounds usually are hard but brittle.

5.5 Inert pair effect

Many transition and non-transition metals show variable electrovalency. This is due to the presence of the unstable configuration of the core in them. The residue obtained after all the valence electrons are removed from the atom is called core or kernel. The core obtained from normal element is stable because it has 2 or 8 electrons (inert-gas configuration). The core

obtained from the transition metal is unstable therefore one or more electrons can be removed from such configuration. Hence it is possible to get ions with variable oxidation states.

Heavier elements of groups IIIB, IVB, VB and VIB form two types of compounds, one corresponding to group valency and another corresponding to group valency minus two. The group valency compounds are less stable while the group valency minus two compounds is more stable as we move down the group. i.e., the lower valency compounds are more stable than group valency compounds for the heaviest member in the each group. In case of many heavier p-block elements exhibit normal group oxidation state called G and in addition to that they also exhibit lower oxidation state equal to (G-2). The group oxidation state G is obtained when all the ns and np electrons from ns²np^x configuration of p-block elements are lost, while the lower oxidation state equal to G-2 is obtained when only np-electrons are lost and ns –electron pair remains inert i.e., not lost due to extra stability. Such pair of ns-electrons is called inert pair. Hence, *the inertness of s subshell electrons towards the bond formation is called inert pair effect or it can be said as the inactiveness of electrons present in outermost shell (i.e. ns²) to get unpaired and involve in bond formation is called inert pair effect.*

or

Inert pair effect may be defined as inertness of inner ns sub-shell towards chemical reaction.

For example; Thallium (Ti = 81) [1s², 2s², 2p⁶, 3s², 3p⁶, 4s², 3d¹⁰, 4p⁶, 5s², 4d¹⁰, 5p⁶, 6s², 4f¹⁴, 5d¹⁰, 6p¹] (the group is IIIB hence group valency is 3) forms both the trivalent ion and monovalent ion. It is observed that monovalent thallium compounds are more stable than those of the trivalent thallium compounds.

Similarly, Tin (Sn = 50) [1s², 2s², 2p⁶, 3s², 3p⁶, 4s², 3d¹⁰, 4p⁶, 5s², 4d¹⁰, 5p²] and Lead (Pb = 82) [1s², 2s², 2p⁶, 3s², 3p⁶, 4s², 3d¹⁰, 4p⁶, 5s², 4d¹⁰, 5p⁶, 6s², 4f¹⁴, 5d¹⁰, 6p²] (both are IVB group compounds hence group valency is 4) both form the expected tetravalent ions and divalent ions, Sn²⁺ ion is less stable than Sn⁴⁺ ion, whereas Pb²⁺ is more stable than Pb⁴⁺. This is because inert pair effect is more marked in the heavier elements, i.e., Pb. This explains why stannous oxide and stannous chloride are reducing agents, whereas leadoxide (public oxide) and leadtetrachloride are oxidizing agents. Moreover lead terabromide and leadteraiodide do not exist but the corresponding compounds of tin can be obtained.

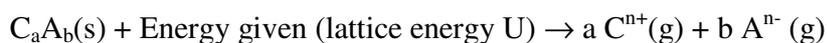
5.6 Lattice Energy

Each ion pair C^+A^- resulting from free atom C and A has a strong residual electric field, hence it will attract other ions pair and thus a large number of such ion pairs will arrange themselves in the most stable way within ionic crystal and cluster will formed and is called crystal lattice. In this process energy will be released. Thus the strength of attractive forces that operate between oppositely charged ions in the crystal is measured by a property called 'lattice energy. Hence *the decrease in energy that takes place in the process of bringing the ions from an infinite distance to their equilibrium position in the stable lattice is called lattice energy and is denoted by U.*

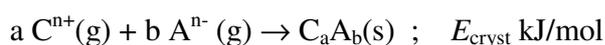
In other words the lattice energy of an ionic crystal C^+A^- may be defined as *the energy released when the correct number of gaseous cations C^+ and anions A^- are brought together from an infinite distance to form one gram mole of the solid crystal.*

$a C^{n+}(g) + b A^{n-}(g) \rightarrow C_aA_b(s) + \text{Energy released (lattice energy } U)$ in the case U is negative.

The lattice energy, U, is also the amount of energy required for complete separation of ions in one mole of a compound. i.e.,



In this case U is positive and could be expressed in terms of kJ/mol. This quantity cannot be directly determined by experimentally, but it can be determined using Hess Law in the form of Born-Haber cycle. It can also be calculated from the electrostatic consideration of its crystal structure. For the reverse process, i.e., in the first case the energy released is called as the energy of crystallization, E_{cryst} . In other words, $U = -E_{\text{cryst}}$.



The values of lattice energies (kJ/mol) for some ionic solids are shown in Table 1.

Table 1. Lattice energies of compounds of alkali and alkaline earth metal ions

Solid	U, kJ/mol	Solid	U, kJ/mol	Solid	U, kJ/mol	Solid	U, kJ/mol
LiF	1036	LiCl	853	LiBr	807	LiI	757
NaF	923	NaCl	786	NaBr	747	NaI	704
KF	821	KCl	715	KBr	682	KI	649
MgF ₂	2957	MgCl ₂	2526	MgBr ₂	2440	MgI ₂	2327

The lattice energy of a crystal depends on following factors, they are

- i) Type of crystal structures,
- ii) Charge on the ions and size of the ions.

The melting points of ionic solids are directly related to their lattice energies.

5.7 Theoretical calculation of lattice energy

The theoretical treatment of the ionic lattice energy was proposed by Born and Lande. The derivation for lattice energy, known as Born-Lande equation is as follows:

The lattice energy of an ionic crystal is determined by coulombic interaction between all ions. (i.e., attractive forces between the oppositely charged ions and repulsive forces results from the interpenetration of outermost electron clouds while close packing).

Consider the formation an ionic pair, C^+A^- wherein the ions are separated by a distance, r .

When the ions are approaches each other, at initial the attractive forces acting between them is directly proportional to the product of the charges carried by the cation and anion and inversely proportional to the distance of their separation. Thus the electrostatic energy of attraction is obtained from Coulomb's law shown below:

$$E = \frac{q^+ q^-}{4\pi r \epsilon_0} \text{----- (1)}$$

The energy is negative and becomes increases as the distance of separation between ions decreases. The variation of potential energy with distance of separation between a cation and an anion for an ionic compound like NaCl is shown in Fig.2.

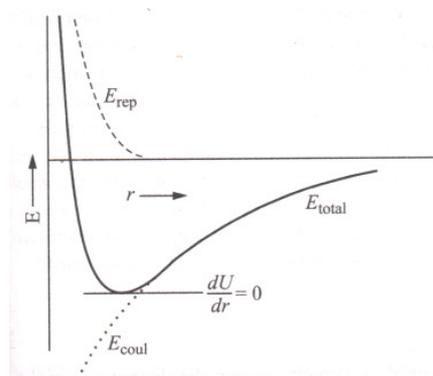


Figure 2: Energy curves for an ion pair

Since, it is common to express Z^+ and Z^- as multiples of the electronic charge, $e = 1.6 \times 10^{-19}$ coulomb, the equation (1) is rewritten as

$$E = -\frac{q^+ q^- e^2}{4\pi r \epsilon_0} \text{-----} (2)$$

In an ionic crystal the force on any one ion will be determined not only by the oppositely charged ions which are directly surrounding it but also by the other ions (both positive and negative) at greater distance. Thus in ionic crystal not only two separate ions are to be considered but the whole crystal must be considered. Thus there will be more interactions than the simple one in an ion pair. The positive ions experience both attraction and repulsion from ions of opposite charge and ions of the same charge.

For example, let us consider the NaCl crystal, r be the distance between Na^+ and Cl^- ions. The nearest neighbors of Na^+ are 6 Cl^- ions at a distance $\sqrt{1}r$, 12 Na^+ ions at a distance $\sqrt{2}r$, 8 Cl^- at $\sqrt{3}r$, 6 Na^+ at $\sqrt{4}r$, 24 Na^+ at $\sqrt{5}r$, and so on. Thus, the energy due to one ion is

$$E = -\frac{q^+ q^- e^2}{4\pi \epsilon_0 r} \left[\frac{6}{\sqrt{1}} + \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} + \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} + \text{-----} \right] \text{-----} (3)$$

where z^+ and z^- are the charges of the ions ($=1$ for NaCl); e is the charge of an electron ($= 1.6022 \times 10^{-19}$ C); $4\pi \epsilon_0 = 1.11265 \times 10^{-10}$ C²/(J m) and the series shown in the bracket is called the Madelung constant, M . The above discussion is valid only for the sodium chloride (rock salt) structure type. This is a geometrical factor, depending on the arrangement of ions in the solid. The Madelung constant depends on the structure type, and its values for some structural types are given in Table 2.

Table 2. Madelung constants for some common crystal lattices

Solid	M	Anions : Cations	Type
NaCl	1.747558	6 : 6	Rock salt
CsCl	1.76267	8 : 8	CsCl type
CaF ₂	2.51939	8 : 4	Fluorite
TiO ₂	2.408	6 : 3	Rutile

Al ₂ O ₃	4.1719	6 : 4	Corundum
ZnS	1.63806	4: 4	Zinc blende
ZnS	1.64132	4: 4	Wurtzite

As evident from the above Table, the value of A is evaluated only by the geometry of the lattice and is independent of ionic charge and radius.

Considering the Madelung constant, the energy of a pair of ions in the crystal is given by

$$E = \frac{-Aq^+q^-e^2}{4\pi\epsilon_0 r} \text{----- (4)}$$

We know that unless there is repulsion energy to balance the attractive coulombic energy, no stable lattice can form. The repulsive energy is negligible at large distances but increases very rapidly as the ions approach each other closely. Born suggested that this repulsive energy could be expressed as follows:

$$E_R = \frac{B}{r^n} \text{----- (5)}$$

where B is a constant and n is the Born exponent. This n is the number related to the electronic configurations of the ions involved. The values of n for inert gases and some common ionic solids are recorded in Table 3.

Table 3. Born exponent values for some ions and compounds

Element/ion	N	Ionic solid	N
He	5	LiF	5.9
Ne	7	LiCl	8.0
Ar, Cu ⁺	9	LiBr	8.7
Kr, Ag ⁺	10	NaCl	9.1
Xe, Au ⁺	12	NaBr	9.5

The total energy for a mole of the crystal lattice containing an Avogadro's number, N of ions is

$$U = E_C + E_R = -\frac{ANq^+q^-e^2}{4\pi\epsilon_0 r} + \frac{NB}{r^n} \text{----- (6)}$$

At the minimum in the curve,

$$\frac{dU}{dr} = 0 \text{----- (7)}$$

This corresponds to the equilibrium situation. Therefore,

$$\frac{dU}{dr} = 0 = - \frac{ANq^+q^-e^2}{4\pi\epsilon_0 r} - \frac{nNB}{r^n} \text{----- (8)}$$

Since, the energy at the minimum is fixed, we can denote U_0 and r_0 to refer this energy and the equilibrium distance. From equation 8, we get

$$B = - \frac{ANq^+q^-e^2r^{n-1}}{4\pi\epsilon_0 r} \text{----- (9)}$$

$$U_0 = \frac{ANq^+q^-e^2}{4\pi\epsilon_0 r_0} \left[1 - \frac{1}{n} \right] \text{----- (10)}$$

Equation 10 is known as the Born-Landé equation for the lattice energy of an ionic compound. Using this equation and the following data, the lattice energy of NaCl is calculated.

For NaCl: $A=1.74756$; $N=6.022 \times 10^{23}$ ions per mole (Avogadro's number), $q^+=+1$ for Na^+ ; $q^-=-1$ for Cl^- ; $r_0=r_{\text{Na}^+}+r_{\text{Cl}^-}=2.814 \times 10^{-10}$ m ; $\epsilon_0=8.854188 \times 10^{-19}$ C

$$N = n_{\text{Na}^+} + n_{\text{Cl}^-} / 2 = [7+9]/2 = 8 ; \pi = 3.14159$$

By substituting these values in equation 10, we get $U_0 = -755$ kJ/mol which is close to the experimental value of about -770 kJ/mol.

In the absence of knowledge of crystal structure, the appropriate Madulung constant, a reasonable estimation of the lattice energy can be obtained from the equation suggested by Kapustinskii as shown below:

$$U_0 = [120,200 \gamma q^+ q^- / (r_c + r_a)] [1 - (34.5 / (r_c + r_a))] \text{----- (11)}$$

where γ is the number of ions per molecule of the compound (for example, 2 for NaCl, 3 for CaCl_2 and 5 for Al_2O_3), r_c and r_a are the radii of the cation and anion in pm, and q^+ and q^- are

their charges. For NaCl, $\gamma = 2$ and $r_c + r_a = 281$ pm. Substituting these values in equation 11, we get a lattice energy of -750 kJ/mol which is about 98% of the experimental value.

Born-Landé equation is modified for improving the repulsion. This is known as Born-Mayer equation and the same is shown below:

$$U_0 = \frac{ANq^+q^-e^2}{4\pi\epsilon_0r_0} [1 - (0.345/r_0)] \text{ ----- (11)}$$

where $r_0 = r_c + r_a$.

5.8 Applications of lattice energy

With the help of the lattice energy it is possible to estimate electron affinities, proton affinities and heats of formation. More applications are listed below.

- 1) In the discussion of the special properties of fluorine in relation to other halogens.
- 2) In the account of stabilities of metal hydrides, polyhalides and peroxides and superoxides.
- 3) In the derivation of crystal field stabilisation energies.
- 4) In the discussion of characterisation of high oxidation states of metals as fluorides and of their low oxidation states as iodides.

5.9 Relation between lattice energy and solubility of ionic solids

The magnitude of lattice energy of an ionic solid gives an idea about its solubility in different solvents. For a solid to dissolve in a solvent the strong forces of attraction between its ions (lattice energy) must be overcome by the ion-solvent interactions. The salvation of ions is referred to in terms of solvation which is always negative i.e., in the process of solvation energy is released. The amount of solvation energy depends on the nature of the solvent. In case of non-polar (covalent) solvents, the solvation energy is small and hence is not sufficient to overcome the lattice energy of the solid. Consequently the solid does not dissolve in non-polar solvent. The solvation energy increases if the solvent has high dipole moment/ or high polarity. As a general rule for a solid to be able to dissolve in a particular solvent its solvation energy must be greater than its lattice energy so that the latter may be overcome by the former.

5.10 Experimental determination of lattice energy of an ionic solid- Born-Haber cycle

The lattice energy of an ionic solid MX can be determined by a process known as Born-Haber cycle proposed by Born-Haber in 1919. The various steps involved in this process is shown graphically as a cycle known as Born-Haber cycle. This method is based on the assumption that

the formation of one mole of crystalline MX can occur either by the direct combination of M(s) and $\frac{1}{2}X_2(g)$ or by an alternative process which consists of five steps.

1) *Direct combination of M(s) and $\frac{1}{2}X_2(g)$*

It is a single step reaction and energy equal to the heat of formation of MX ($\Delta H_{\text{for}}MX$) is released in it. This is the exothermic process. The release of energy has been shown by putting negative sign before it.

2) *An alternative process*

This process consist of the following five steps

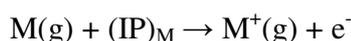
i) Sublimation of M(s) to M(g) . In this step one mole of solid M absorbs energy equal to its sublimation energy, $(\Delta H_{\text{sub}})_M$ and sublimated to gaseous state. This process is an endothermic process. The absorption of energy is indicated by putting +ve sign before $(\Delta H_{\text{sub}})_M$



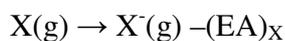
ii) Dissociation of $\frac{1}{2}X_2(g)$ to X(g). In this step half a mole of $X_2(g)$ absorbs energy equal to the dissociation energy (ΔH_{diss}) of $X_2(g)$. This process is also an endothermic process. The absorption of energy is indicated by putting +ve sign before (ΔH_{diss})



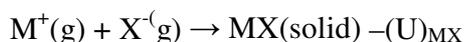
iii) Ionization of M(g) to $M^+(g)$. Each M(g) atom absorbs energy equal to its ionization energy or ionization potential $(IP)_M$ and loses its outer most electron to form $M^+(g)$. It is also an endothermic process. The absorption of energy is indicated by putting +ve sign before $(IP)_M$



iv) Conversion of X(g) into $X^-(g)$. X(g) atom adds the electron given out by M(g) in above step to form $X^-(g)$. In this process energy is released and is equal to electron affinity $(EA)_X$ of X(g). It is an exothermic process and the energy released is indicated by putting -ve sign before $(EA)_X$



v) Combination of $M^+(g)$ and $X^-(g)$ to form MX (solid). This is the final step in which $M^+(g)$ and $X^-(g)$ formed in above process combine together to form one mole of MX (solid). In this process energy is released and is equal to the lattice energy $(U)_{MX}$. It is an exothermic process and the energy released is indicated by putting -ve sign before $-(U)_{MX}$.



Diagrammatically the formation of one gram molecule of solid MX by the direct combination of M(s) and 1/2 X₂(g) and by an alternative process consisting of five steps mentioned above is shown by below diagram and is the Born-Haber cycle for the formation of an ionic compound from the reaction of an alkali metal (Li, Na, K, Rb and Cs) with a gaseous halogen (F₂, Cl₂). The Born-Haber thermochemical cycle is named after the two German physical chemists, Max Born and Fritz Haber, who first used it in 1919. Born-Haber cycle for the formation of MX_(s) is shown in Fig.3.

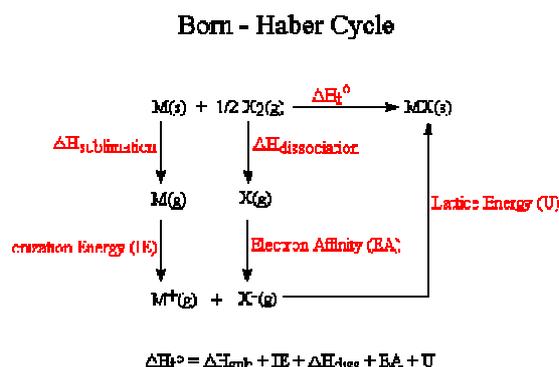


Figure 3: The Born-Haber cycle for the formation of MX (s) compound

The enthalpy change in the formation of an ionic lattice from the gaseous isolated sodium and chloride ions is about -788 kJ/mole. That enthalpy change, which corresponds to the reaction, Na⁺(g) + Cl⁻(g) → NaCl (s), is called the lattice energy of the ionic crystal. Although the lattice energy is not directly measurable, there are various ways to estimate it from theoretical considerations and some experimental values. For all ionic crystals, the lattice energy is negative. It is ultimately the lattice energy of an ionic crystal which is responsible for the formation and stability of ionic crystal structures. The Born-Haber cycle for the formation of NaCl and MgF₂ crystals is given in Fig.4.

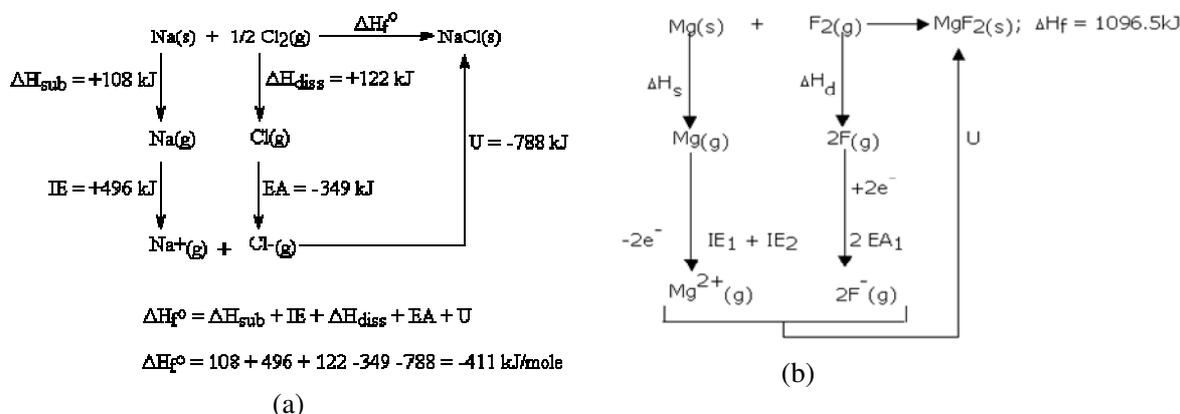
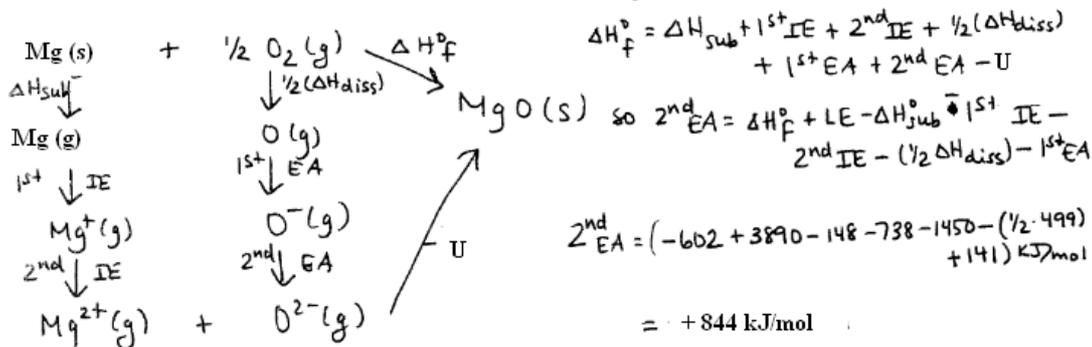


Figure 4: The Born-Haber cycle for the formation of (a) NaCl and (b) MgF₂

Given the following information for magnesium, oxygen, and magnesium oxide calculate the second electron gain enthalpy for oxygen {i.e. for $O^-(g) + e^- \rightarrow O^{2-}(g)$ }.

for Mg (s), $\Delta H_{sub} = +148$ kJ/mol
 1st ionization energy for Mg = +738 kJ/mol
 2nd ionization energy for Mg = +1450 kJ/mol

bond dissociation energy for $O_2 = +499$ kJ/mol
 1st electron gain enthalpy for O = -141 kJ/mol
 for MgO (s), lattice energy = +3890 kJ/mol
 for MgO (s), enthalpy of formation = -602 kJ/mol



5.11 Applications of Born-Haber Cycle

- The heat of formation or enthalpy of formation of an ionic compound can be calculated with accuracy using the Born-Landé equation and the B-H cycle.
- The lattice energy of an ionic crystal can be calculated to a greater accuracy
- Consideration of the terms in a B-H cycle helps to rationalize the existence and non existence of certain compounds. For example, consider the hypothetical compound, $NaCl_2$. If all the terms are evaluated using the B-H cycle, it is observed that the increased energy necessary for 2nd ionisation energy of Na is more than that which is realized by the increased lattice energy. It is possible to calculate the heat of formation, ΔH_f by assuming that the internuclear distance in $NaCl_2$ is the same as in $NaCl$ and that it would crystallize in the fluorite structure with a Madelung constant (A) of 2.52. The lattice energy, $U_0 = -2180$ kJ/mol. The summation of all the terms (in kJ/mol) in B-H cycle is as follows:

$U_0 = -2180; \Delta H_{ANa} = +108; \Delta H_{IE1} = +496; \Delta H_{IE2} = +4562; 2 \Delta H_{EA} = -698.$

By adding all the above values, we get, $\Delta H_f = -276$ kJ/mol.

From the above data, it is evident that $NaCl_2$ does not exist. The extra stability of the lattice is insufficient to compensate for the large 2nd IE.

5.12 Kapustinskii's equation

Although the Born-Landé equation provides a convenient to evaluate the lattice energy of several crystals, it has limitations in f following cases.

- i) The crystal structure must be known so that the appropriate Madelung constant can be chosen.
- ii) Crystal in which some ions are not spherical (for examples, NO_3^- is planar, SO_4^{2-} is tetrahedral, etc....) so that distance between ion centers may be different directions.

Therefore another method is required to calculate lattice energy of a crystal. Kapustinskii found that if the Madelung constant for a given structure is divided by the number of ions in one formula unit (n) the resulting values are almost constant and he suggested the most successful approach to calculate the lattice energies for a wide range of crystal using equation

$$U(\text{kJ/mole}) = \frac{120,200mZ_cZ_a}{r_c + r_a} \left(1 - \frac{34.5}{r_c + r_a} \right)$$

and this equation is called Kapustinskii's equation.

In the above equation, r_c and r_a are the radii of the cation and anion in pm, Z_a and Z_c are their charges and m is the number of ions in the formula for the compound. It is important to note that Madelung constant does not appear in the Kapustinskii's equation and only the ionic radii (distance between ion centers) and not individual radii is taken in to account. Moreover it is not necessary to know the crystal structure for the crystal in order to use the Kapustinskii's equation. This equation works very well for the substances that are ionic (example LiF, NaCl, KI... etc) and gives highly reliable calculated values for crystal where bonding is completely ionic. The difference between the lattice energy calculated using Kapustinskii's equation and that of thermochemical data is very large for crystals such as AgI. In this kind of crystals the charges on the ions are distributed over relatively large volume and Van der Waals forces becomes more important. Hence Kapustinskii's equation is based on purely electrostatic model and does not give good agreement when ions are highly polarizable and the crystal is somewhat covalent.

5.13 The use of Kapustinskii's equation

Kapustinskii's equation is more useful because for many crystals it is possible to determine a value of the lattice energy from thermodynamics data or the Born-Landé equation. Then it is possible to calculate the ionic radii $r_a + r_c$ using Kapustinskii's equation. When the radius of the one ion is known, carrying out the calculations for a series of compounds that contains that ion enables to determine the radii of the counter ions.

For example, if radius of Na^+ ion is known from the measurement or calculations, it is possible to determine the radii of F^- , Cl^- and Br^- if the lattice energies of NaF, NaCl and NaBr are known.

In fact radius could be determined even for polar ions such as NO_3^- , CO_3^{2-} ions if the lattice energies of NaNO_3 and Na_2CO_3 are known. *The ionic radii determined using this approach and based on the thermodynamic data are called thermodynamic radii.*

5.14 Summary of the unit

Ionic bonds form when a metal reacts with a non-metal. Metals form positive ions by losing one or more electrons and non-metals form negative ions by gaining those electrons. The number of positive charges must equal the number of negative charges so that the compound has no charge overall. Ionic bonds are the *electrostatic* forces of attraction between oppositely charged ions. The oppositely charged ions are arranged in a regular way to form giant ionic *lattices*. Ionic *compounds* often form crystals as a result. The amount of energy required to separate a mole of the solid (s) into a gas (g) of its ions is called lattice energy denoted by symbol U . It separates the ions in a salt so that there is no interaction between the positive and negative ions. After the separation, the ions must be in a gaseous state and the lattice energies are always positive. The same amount of energy is released when the ions are condensed from a gaseous state to a solid state. The released energy is called energy of crystallization (E_{cryst}). Since energy is released, the sign is negative. Lattice energy is a useful quantity to judge the chemical properties of the ionic solid (salt), and it can be calculated by applying the law of conservation of energy, in a manner similar to the Hess's law. The process of calculation of lattice energy is called the Born-Haber cycle.

5.15 Keywords

Electrovalent bond; Inert pair effect; Lattice Energy; Born-Haber cycle; Kapustinskii's equations.

5.16 References for further study

1. Inorganic Chemistry, J. E. Huheey, E.A. Keiter and R. L. Keiter, O. K. Medhi, *Pearson Education*, 4th Ed., **2009**.
2. Concepts and Models of Inorganic Chemistry, B. E. Douglas, D. H. McDaniel and J. J. Alexander; *John Wiley & Sons, Inc., New York*, **1983**.
3. Inorganic Chemistry, James E House, *Academic Press*, **2008**.
4. Concise Inorganic Chemistry by J. D. Lee, *John Wiley & Sons*, 5th Ed. **2008**.

5.17 Questions for self study

- 1) Relate the tendency of atoms to gain or lose electron to the type of bonds they form.

- 2) What is Electrovalent bond? Give five examples.
- 3) What are essential difference between an electrovalent bond and a covalent bond? Give two examples.
- 4) What elements are most likely to form ionic compounds?
- 5) Briefly discuss the conditions required for formation of ionic compounds.
- 6) What are the properties of ionic compounds?
- 7) What is meant by inert pair effect?
- 8) What is Lattice Energy?
- 9) How theoretically calculate lattice energy of ionic compound?
- 10) Discuss relationship between lattice energy and solubility of ionic compounds.
- 11) Explain in detail of experimental determination of lattice energy of an ionic solid-using Born-Haber cycle
- 12) Write a note on application of Born-Haber cycle
- 13) Explain Kapustinskii's equation.
- 14) Discuss the advantage of Kapustinskii's equation

Unit-6**Structure**

- 6.0 Objectives of the unit
- 6.1 Introduction
- 6.2 Size effects
- 6.3 Factors affecting the radii of ions
- 6.4 Radius Ratio
- 6.5 Calculation of radius ratio
- 6.6 Crystal lattice or unit cell
- 6.7 Packing Efficiency or Close packing
- 6.8 Summary of the unit
- 6.9 Key words
- 6.10 References for further study
- 6.11 Questions for self study

6.0 Objectives of the unit

After studying this unit you are able to

- ❖ Explain the ionic radii and atomic radii
- ❖ Explain the effect of ionic radii on formation of ionic compound
- ❖ Identify the factors affecting the radii of an ion
- ❖ Explain the effect of radius ratio on close packing of ions
- ❖ Calculate the radius ratio of different ions
- ❖ Explain the crystal lattice

6.1 Introduction

The size of an ion is dependent on how the outer orbitals shield the charge from the nucleus. For s- and p-block ions, ionic radii increase with atomic number as we move vertically in the group. In case of isoelectronic series of cations, radii decrease with increasing charges, (for example Na^+ , Mg^{2+} , Al^{3+} and Si^{4+}). Similarly radius of cation decrease with increasing oxidation state for d-block elements (for example, V^{2+} , V^{3+} , V^{4+} , V^{5+}). The relative size of the ions forming a crystal lattice has a great influence on what type of lattice forms it is necessary for ions having opposite charges to touch each other in order to maintain net attraction and the arrangement of ions in the crystal to be stable one. Otherwise, the ions of the same charges only touch each other consequently repulsion will cause this arrangement to be unstable. If the two ions are about equal size, it may be possible that six or more ions of the opposite charge will surround a given ion. In such cases both positive and negative ions are touch each other and arrangement of ions are more stable. If the negative ions are large enough so that six of them can not surround a given positive ion, it may be possible for atleast four of the anions to touch the positive ion. It is apparent that all the anions to touch the positive ion and lead to a stable arrangement. In other words if cation is too small, then only the negative ions are touch each other it gives rise to repulsion that will cause the arrangement to be unstable. In this unit we will study ore about effect of size and nature of ions on the crystal lattice.

6.2 Size effects

Ionic radius is the measurement of the distance between the nucleus of an ion and the outermost edge of the electron cloud. This radius is most accurately measured by halving the distance between two bonded ions. Ionic radius is influenced by its charge, and can be either larger or

smaller than the radius of its corresponding neutral atom. In general, the ions of metals will have smaller radii than the neutral atom of the same metal, and the ions of non-metals have larger radii than the neutral atom of the same metal. Ionic radius differs from atomic radius in that it is the ion's radius being measured rather than the atom. The ionic radii of some ions are shown below in the Table 1.

Table 1. Ionic radii of some common ions

Ion	Ionic radius, pm	Ion	Ionic radius, pm	Ion	Ionic radius, pm	Ion	Ionic radius, pm
F ⁻	136	Li ⁺	60	Sr ²⁺	110	Al ³⁺	50
Cl ⁻	181	Na ⁺	98	Ba ²⁺	129	Sc ³⁺	81
Br ⁻	195	K ⁺	133	Mn ²⁺	80	Ti ³⁺	69
I ⁻	216	Cs ⁺	169	Fe ²⁺	75	V ³⁺	66
O ²⁻	145	Be ²⁺	30	Co ²⁺	72	Cr ³⁺	64
S ²⁻	190	Mg ²⁺	65	Ni ²⁺	70	Mn ³⁺	62
H ⁻	208	Ca ²⁺	94	Zn ²⁺	74	Fe ³⁺	62

It is evident from the above Table that there is a great difference between the sizes of some ions. For example, the ionic radius of Li⁺ is 60 pm while that of Cs⁺ is 169 pm. When these ions from compounds of the type, LiCl and CsCl with Cl⁻ of ionic radius 181 pm, it is easy to understand that the geometrical arrangement of ions in the crystals would be different though they contain equal number of cations and anions. When spherical objects are stacked to obtain a 3-dimensional array (crystal lattice) the relative sizes of the spheres determine the type of possible arrangement. It is the electrostatic force that operates between cations and anions lead to stability of any ionic structure.

6.3 Factors affecting the radii of ions

- i) Ionic radius of cations (charge being constant) decreases steadily along the period:
La³⁺(117 pm) > Nd³⁺(112 pm) > Gd³⁺(108 pm) > Ho³⁺(104 pm) > Lu³⁺(100 pm)
- ii) With increase in ionic charge, the cations size decreases across the main group metals: for example, Na⁺(116 pm) > Mg²⁺(86 pm) > Al³⁺(67.5 pm)

- iii) For the same cation, the ionic size decreases with increase in oxidation state: for example, Fe^{2+} (92 pm) > Fe^{3+} (78 pm) > Fe^{4+} (72 pm).
- iv) For transition metals, the multiplicity of the spin state affects the approach of the anion towards the cation: for example, HS Fe^{2+} (92 pm) > LS Fe^{2+} (75 pm); HS Fe^{3+} (78 pm) > LS Fe^{3+} (69 pm).
- v) For both cations and anions, the crystal radius increases with increase in coordination number. As the coordination number increases, the repulsions among the coordinating counter ions become greater. In lower coordination number, the counter ions compress the central cation and reduce its crystal radius. For example K^+ CN: 4 (113 pm) < 6 (116 pm) < 8 (132 pm) < 12 (153 pm).
- vi) Ionic size increases down the group for both cations and anions: for example, Li^+ (90 pm) < Na^+ (116 pm) < K^+ (152 pm) < Rb^+ (166 pm) < Cs^+ (180 pm)
 F^- (119 pm) < Cl^- (167 pm) < Br^- (182 pm) < I^- (206 pm)

6.4 Radius Ratio

In an ionic structure each cation tends to surround itself with anions. The number that can be grouped around it will depend on the relative size of the cations and anions. The number of anions that can fit around a cation is called the coordination number (CN). This number increases as the radius ratio increases. The number of anions that can 'fit' around a cation is related to the relative size difference between the ions, and this size difference can be described using the radius ratio, which is given by $r_{\text{cation}}/r_{\text{anion}}$.

When this number is small, then only a few anions can fit around a cation. When this number is large, then more anions can fit around a cation.

The structure of ionic compound is directly depends on the relative size s of the positive and negative ions and their relative coordination numbers. A simple geometric calculation provides how many ions of a given size can be in contact with a smaller ion thus it is possible to predict the coordination number from relative sizes of the ions. For example; suppose the coordination number is three in an ionic compound MX, then three X^- ions are in contact with one M^+ ion and this gives the ratio (radius M^+ /radius X^-) = 0.155. this is the lower limit for a coordination number of 3. If the radius ratio is less than 0.155 then the positive ion is not contact with the negative ions and it rattles in the hole, hence the resulting structure is unstable. If the radius ratio is more than 0.155 then it is possible to fit three X^- ions round each M^+ ion. The radius ratio is

increase as the the difference in size of the two ions increases and at some point (when the ratio exceeds 0.225) it becomes possible to fit four ions around one (i.e., CN = 4). Similarly coordination numbers of 6 and 8 are common and the appropriate limiting radius ratio can be calculated by simple geometry.

6.5 Calculation of radius ratio

Consider the arrangement of ions in which six anions surround a cation as shown below. In this arrangement, the six anions have their centers at the corners of an octahedron with the cation at the center. There are four anions whose centers are in the same plane as the center of the cation in addition to one anion above and below the plane.

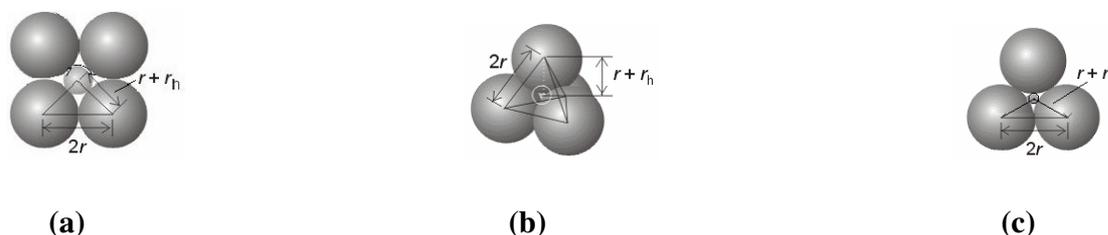


Fig. 10. Small cation with coordination 6(a), 4(b) and 3(c).

Simple geometry allows us to fix the diagonal of the square as $2r_+ + 2r_-$. The angle formed by the diagonal in the corner must be 45° , so we get

$$[2r_+ / (2r_+ + 2r_-)] = \cos 45^\circ = 0.707$$

$$\text{ie } r_+ = 0.707r_+ + 0.707r_-$$

$$\text{ie } 0.293 r_- = 0.707 r_+$$

$$\text{ie } r_+ / r_- = 0.293 / 0.707$$

$$\text{ie } r_+ / r_- = 0.414$$

This is called the limiting ratio since a cation will be stable in an octahedral hole only if it is at least large enough to keep the anions from touching, that is to say $r_+ / r_- > 0.414$.

Generally, the smaller cations will preferentially fit into tetrahedral holes in the lattice. Similarly, it is possible to calculate the lower limit for tetrahedral coordination is $r_+ / r_- = 0.225$. In other words, for radius ratios ranging from 0.225 to 0.414, tetrahedral sites will be preferred while

octahedral sites will be preferred when r_+/r_- is greater than 0.414. Similarly it is possible to find the ratio when the cation can coordinate to eight anions (0.732) or twelve anions (1.0). Typical radius ratio values are given in Table 2.

Table 2. Radius ratios for arrangements of rigid spheres

Coordination number of M	Arrangement of X	Radius ratios		Crystal structure corresponding to cation C.N.
		$\rho = r_M/r_X$	$\rho' = r_X/r_M$	
3	Triangular	0.150–0.225	4.44–5.67	
4	Tetrahedral	0.225–0.414	2.42–4.44	Antifluorite, ZnS
4	Planar	0.414–0.732	1.37–2.42	
6	Octahedral	0.414–0.732	1.37–2.42	NaCl, TiO ₂ , CdCl ₂
8	Cubic	0.732–1.00	1.00–1.37	CsCl, CaF ₂

The use of radius ratios to rationalize structures and to predict coordination numbers is illustrated below:

a) Consider NaCl lattice in which $r_{\text{Na}^+}/r_{\text{Cl}^-} = 116\text{pm}/167\text{pm} = 0.69$. So, Na^+ ions prefer octahedral holes in a closest packed lattice of chloride ions with a coordination number of 6.

b) Let us consider CsCl lattice. The radius ratio ($r_{\text{Cs}^+}/r_{\text{Cl}^-} = 181\text{pm}/167\text{pm} = 1.08$) is found to be 1.08. So, the coordination number of cations (and anions) would be 8.

c) Let us consider the compounds containing different numbers of cations and anions (SrF_2 , SnO_2 , K_2O etc). In these compounds, it is ideal to perform two calculations. For example, consider SrF_2

$$r_{\text{Sr}^{2+}}/r_{\text{F}^-} = 132\text{pm}/119\text{pm} = 1.11 \quad \text{maximum CN of Sr}^{2+} = 8$$

$$r_{\text{F}^-}/r_{\text{Sr}^{2+}} = 119\text{pm}/132\text{pm} = 0.90 \quad \text{maximum CN of F}^- = 8$$

As per the crystal lattice, there must be twice as many F^- ions as Sr^{2+} ions, so the CN of the Sr^{2+} ion must be twice as large that of F^- . Coordination numbers of 8 (Sr^{2+}) and 4 (F^-) are possible with the maximum allowable coordination numbers and with the stoichiometry of the crystal, SrF_2 crystallizes in the fluorite lattice.

d) For example, consider SnO_2

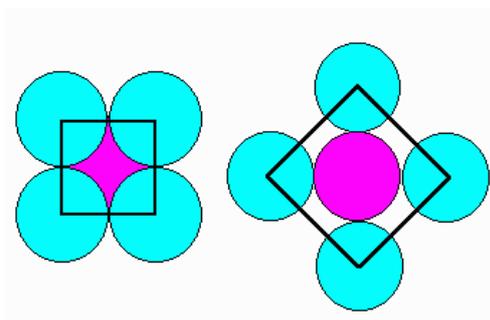
$$r_{\text{Sn}^{2+}}/r_{\text{O}^{2-}} = 83\text{pm}/126\text{pm} = 0.66 \quad \text{maximum CN of Sn}^{4+} = 6$$

$$r_{\text{O}^{2-}}/r_{\text{Sn}^{2+}} = 126\text{pm}/83\text{pm} = 1.52 \quad \text{maximum CN of O}^{2-} = 6$$

Considering the stoichiometry of the compound, the only feasible arrangement is with CN of oxide is 3, CN of $\text{Sn}^{4+}=6$; tin dioxide assumes the TiO_2 structure.

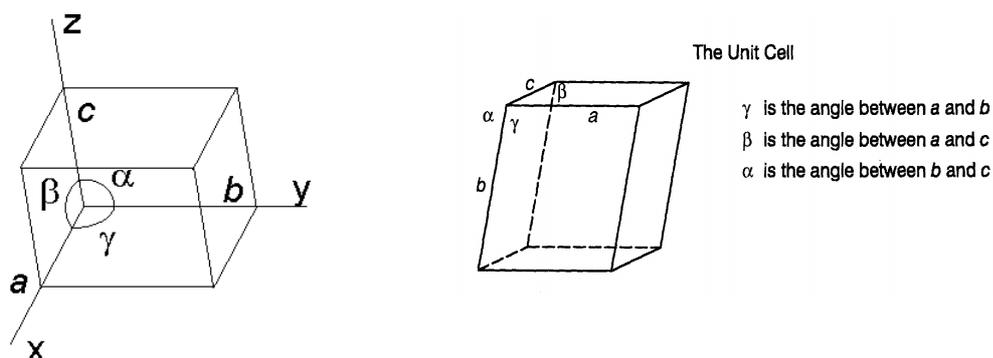
6.6 Crystal lattice or unit cell

The reason for crystals form is the attraction between the atoms (ions). Because atoms (ions) attract one another it is often favorable to have many neighbors. Also because the atoms attract one another, there is a tendency to squeeze out as much empty space as possible and the empty spaces between the atoms are interstitial sites.



Crystal lattice is the periodic and systematic arrangement of atoms that are found in crystals. The crystal lattice can be considered as the points of intersection between straight lines in a three-dimensional network. The physical properties of crystals like cleavage, electronic band structure and optical transparency are predominantly governed by the crystal lattice. A unit cell is the smallest component of the crystal lattice and describes the arrangement of atoms in a crystal. The unit cell is characterized by its lattice parameters which consist of the length of the cell edges and the angles between them.

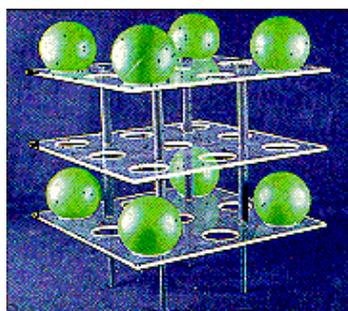
In a crystal the atoms are arranged in a regular repeating pattern. The smallest repeating unit is called the unit cell. Each unit cell is defined in terms of *lattice points*, which is the points in space about which the particles are free to vibrate in a crystal. The entire crystal structure can be reconstructed from knowledge of the unit cell. The unit cell is characterized by three lengths and three angles. The quantities a and b are the lengths of the sides of the base of the cell and γ is the angle between these two sides. The quantity c is the height of the unit cell. The angles α and β are the angles between the base and the vertical sides of the unit cell.



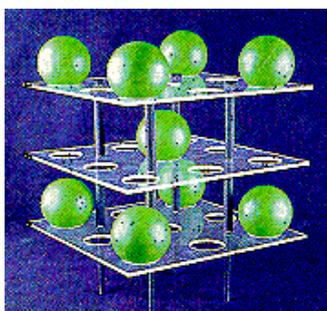
The volume of the unit cell is readily calculated from knowledge of $a, b, c, \alpha, \beta,$ and γ .

The unit cells are classified into seven crystal systems namely

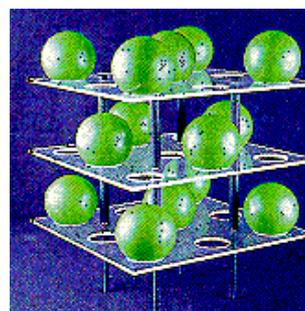
- I) Cubic unit cell- there are three types of cubic unit cells which are simple cubic, body-centered cubic and face-centered cubic unit cell.
 - a) Simple cubic lattices- is the simplest unit cell and has 8 particles centered at the eight corners of the cubic cell.
 - b) Body-centered cubic - there are eight particles on the eight corners of the unit cell (like in cubic-centered cell). In addition, there is a ninth particle in the center of the cubic unit cell.
 - c) Face-centered cubic unit cell- its structure has an additional structural particle at the center of each face.),



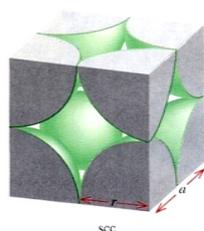
Simple cubic



Body-centered cubic

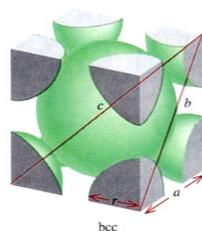


Face-centered cubic



$$a = 2r$$

Fig. 9: The relationship between the edge length (a) and radius (r) of atoms in the simple cubic cell, body-centered cubic cell and face-centered cubic cell.



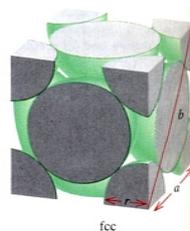
$$b^2 = a^2 + a^2$$

$$c^2 = a^2 + b^2$$

$$= 3a^2$$

$$c = \sqrt{3}a = 4r$$

$$a = \frac{4r}{\sqrt{3}}$$



$$b = 4r$$

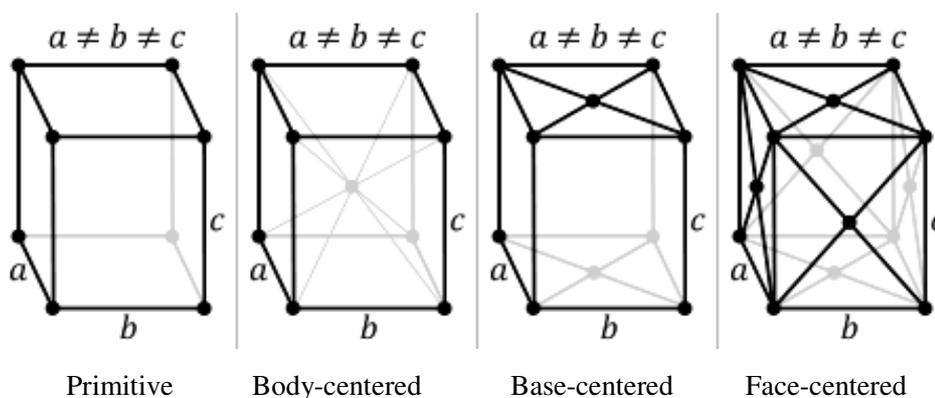
$$b^2 = a^2 + a^2$$

$$16r^2 = 2a^2$$

$$a = \sqrt{8}r$$

II) Orthorhombic- The Orthorhombic lattice has four types of unit cells.

- The primitive cell (P) has fractional lattice points at each corner for a total of one lattice point per cell.
- The base centered unit cell (C) has fractional lattice points at the cell corners and in the face-centered location of the basal planes for a total of two lattice points per cell.
- The face-centered unit cell (F) has partial lattice points at the cell corners and at the center of each face for a total of four lattice points per cell, and
- The body-centered orthorhombic cell (I) has partial lattice points at the cell corners and a lattice point in the body center of the cell for a total of two lattice points per cell.

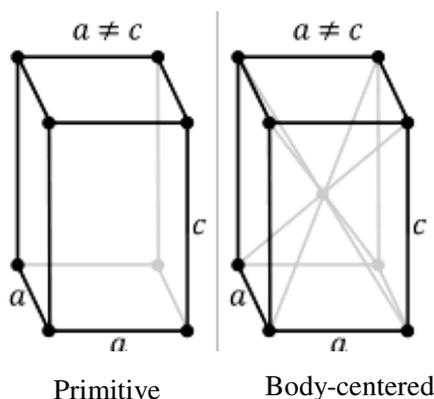


For each of these cells: a , b , c , have distinct values and $\alpha = \beta = \gamma = 90^\circ$

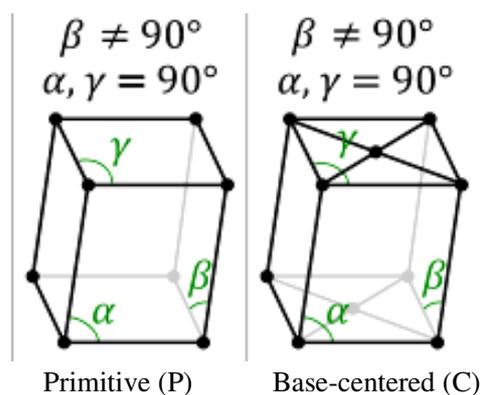
III) Tetragonal- Tetragonal unit cell is result from stretching a cubic unit cell along one of its lattice axis, therefore the cube becomes a rectangular prism with a square base. There are two types of tetragonal unit cell,

- The simple tetragonal- which can be obtained from stretching the simple-cubic unit cell and
- The centered tetragonal- which can be obtained from stretching either the face-centered or the body-centered cubic unit cell.

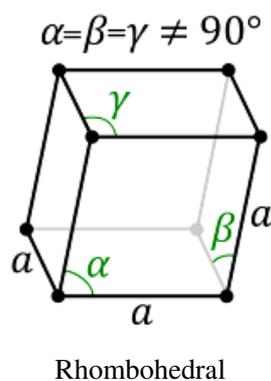
It is important to note that stretching of face-centered cubic would result in face-centered tetragonal, but face-centered tetragonal is equal to body-centered tetragonal.



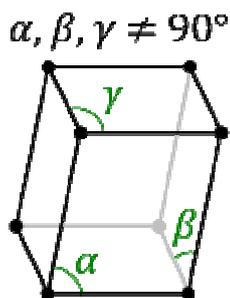
IV) Monoclinic unit cell- The monoclinic unit cell is described by vectors of unequal length, (as in the orthorhombic unit cell). Both form a rectangular prism with a parallelogram as their base. Therefore two pairs of vectors are perpendicular, while the third one makes an angle other than 90° . There are two monoclinic unit cells exist, they are the primitive monoclinic and the centered monoclinic lattices with a rectangular and rhombic lattice, respectively.



V) Rhombohedral unit cell- A Rhombohedral system is described by three non equal length vectors and also no two of which are orthogonal. The rhombohedral system can be explained as the cubic system stretched along a body diagonal. i.e., $a = b = c$; and $\alpha = \beta = \gamma \neq 90^\circ$. There is only one rhombohedral type of unit cell.

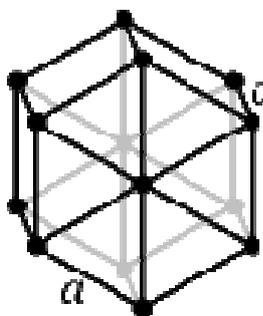


- VI) Triclinic unit cell - Trigon unit cell and Rhombohedral unit cell system are often confused with each other. The triclinic unit cell system is described by vectors of unequal length, as in the Rhombohedral unit cell system. In addition none of these three vectors are orthogonal to another. The triclinic unit cell is the least symmetric among all other unit cell system.



Triclinic

- VII) Hexagonal unit cell- The hexagonal closest-packed structure is consists of a hexagonal unit cell, which has a diamond shaped or hexagonal base with sides of equal length ($a = b$). The base is perpendicular to the longest side (length c) of the unit cell. An atom is centered on each corner of the unit cell and an atom is also centered inside the unit cell.

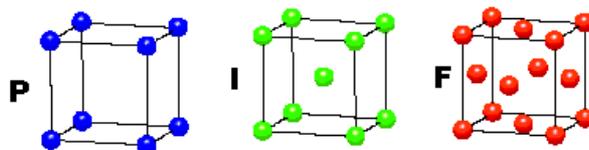


Hexagonal

In 1848, Auguste Bravais demonstrated that there are in fact only 14 possible point lattices and not more. For his efforts, the term Bravais lattice is often used in place of point lattice. Different types of crystal systems are shown below:

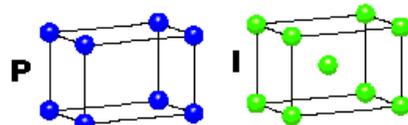
CUBIC

$a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$



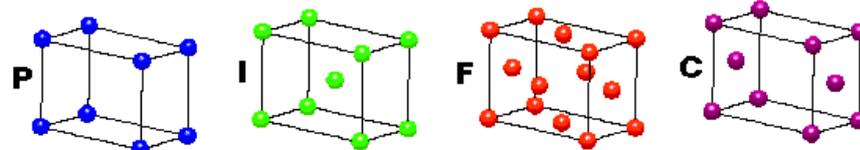
TETRAGONAL

$a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



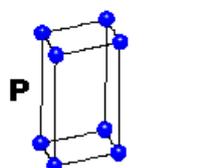
ORTHORHOMBIC

$a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



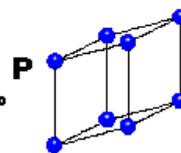
HEXAGONAL

$a = b \neq c$
 $\alpha = \beta = 90^\circ$
 $\gamma = 120^\circ$



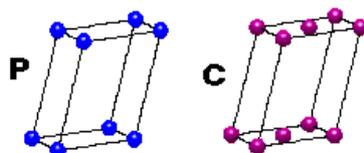
TRIGONAL

$a = b = c$
 $\alpha = \beta = \gamma \neq 90^\circ$



MONOCLINIC

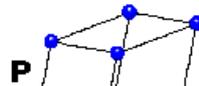
$a \neq b \neq c$
 $\alpha = \gamma = 90^\circ$
 $\beta \neq 120^\circ$



Tr
 Tr

TRICLINIC

$a \neq b \neq c$



4 Types of Unit Cell
 P = Primitive
 I = Body-Centred
 F = Face-Centred
 C = Side-Centred
 +
7 Crystal Classes
 14 Bravais Lattices

Crystal system	Axial lengths and interaxial angles	Space lattice
Cubic	Three equal axes at right angles $a = b = c, \alpha = \beta = \gamma = 90^\circ$	Simple cubic Body-centered cubic Face-centered cubic
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	Simple tetragonal Body-centered tetragonal
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Simple orthorhombic Body-centered orthorhombic Base-centered orthorhombic Face-centered orthorhombic
Rhombohedral	Three equal axes, equally inclined $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	Simple rhombohedral
Hexagonal	Two equal axes at 120° , third axis at right angles $a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	Simple hexagonal
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$	Simple monoclinic Base-centered monoclinic
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple triclinic

6.7 Packing Efficiency or Close packing

In crystals structure, atoms are considered as hard spheres and in many crystals the atoms are pack together as tightly as possible. They will achieve this by forming a *close-packed* structure. In whatever way the constituent particles (atoms, molecules or ions) are packed, there is always some free space in the form of voids. Packing efficiency is the percentage of total space filled by the particles. The packing efficiency of a crystal structure provides information about how much of the available space is being occupied by atoms. It is usually represented by a percentage or volume fraction. The packing efficiency is given by the following equation

$$\frac{(\text{number of atoms per cell}) * (\text{volume of one atom})}{\text{volume of unit cell}}$$

The two most efficient packing arrangements are the hexagonal closest-packed structure (hcp; Fig 5) and the cubic closest-packed structure (ccp; Fig 6). Consider the most efficient way of packing together equal-sized spheres and stacking close-packed atomic planes in three dimensions. For example, if plane A lies beneath plane B, there are two possible ways of placing an additional atom on top of layer B. If an additional layer was placed directly over plane A, this would give rise to the following series :

...ABABABAB....

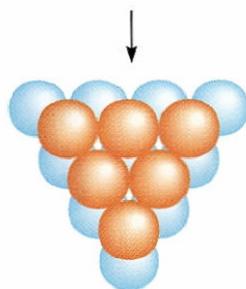


Fig. 5. Hexagonal closest-packed arrangement

This type of crystal structure is known as **hexagonal close packing (hcp)**.

In the hexagonal closest-packed structure, $a = b = 2r$ and $c = 4(2/3)^{1/2} r$, where r is the atomic radius of the atom. The sides of the unit cell are perpendicular to the base, thus $\alpha = \beta = 90^\circ$. The base has a diamond (hexagonal) shape corresponding with $\gamma = 120^\circ$.

However, if all the three planes are staggered relative to each other and that the sequence is repeated, then the following sequence arises

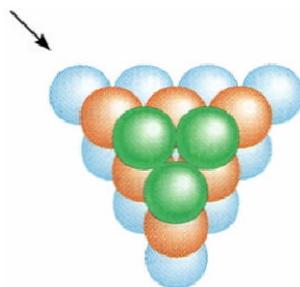


Fig. 6. Cubic close packing arrangement

ABCABCABC..., this type of crystal structure is known as cubic close packing (ccp). Both hcp and ccp are shown in Fig. 7 and Fig. 8.

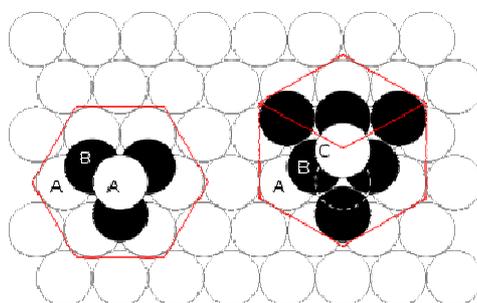


Fig. 7: Left panel-hcp packing and right panel – ccp packing

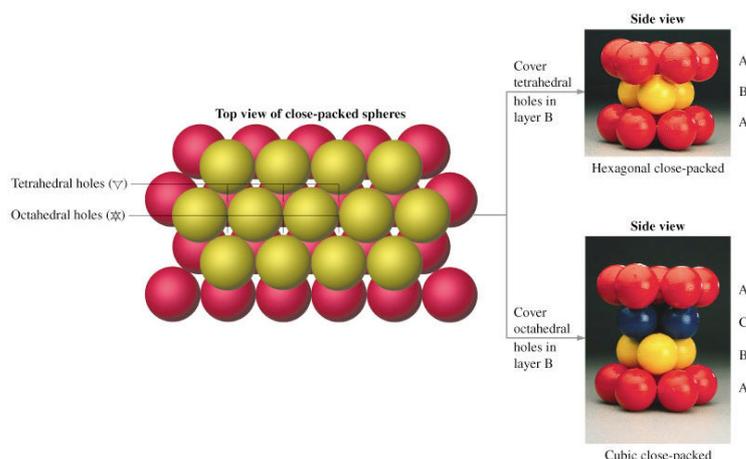


Fig. 8: Close packing of spheres in three dimensions

Ionic compounds exist in various forms like salts, oxides, hydroxides, sulphates etc...., these compounds are held together by the electrostatic force of attraction between the positive and negative ions. Actually there will be repulsion if ions of same charges are adjacent and attraction will occur when positive ions are surrounded by negative ions and vice versa. The attractive forces between the opposite charge ions is maximum when each ion is surrounded by the greatest

possible number of oppositely charged ions. The number of ions surrounded by particular ion is referred as coordination number and both positive and negative ions have the same coordination number when there are equal numbers of both positive and negative ions present in a compound, for example like in NaCl. But the coordination numbers for positive and negative ions are different numbers if both positive and negative ions present in a compound are not equal, for example like in CaCl_2 .

6.8 summary of the unit

In the ionic model, the bonding is described as the electrostatic interaction between charged spheres, whose sizes are given by the ionic radius. For determining an ionic radius, it is necessary to split up the internuclear separation into a contribution from the anion and a contribution from the cation. This is done by assuming the value of the radius of one ion, and then calculating the radii of other ions from this basis. the ionic radius of a given ion changes with coordination number: As the coordination number increases, the ions must get further away from the central ion in order to accommodate more of them, and hence the interionic separation increases, and the short ranged repulsion decreases, and the electron cloud on the central ion can expand, and hence the central ion increases in size. In an ionic structure each cation tends to surround itself with anions the number that can be grouped around it will depend on the relative size of the cations and anions. The Coordination Number (CN) is defined as the number of anions that can fit around a cation. This number increases as the radius ratio increases. The number of anions that can 'fit' around a cation is related to the relative size difference between the ions, and this size difference can be described using the radius ratio, which is given by As the size (ionic radius r) of a cation increases, more anions of a particular size can pack around it. Thus, knowing the size of the ions, we should be able to predict a priori which type of crystal packing will be observed. We can account for the relative size of both ions by using the ratio of the ionic radii $\rho = \frac{r^+}{r^-}$. Anions are often larger than cations and therefore touch each other while close packing. Small cations then fit in the holes created between anions. The structures of many metals can be described as close packed arrays of spherical atoms. There are two alternative ways to maximize the packing efficiency of equally sized spheres. Cubic Close Packing (CCP) and Hexagonal Close Packing (HCP). Cubic close packing leads to a structure with a face centered cubic unit cell. This structure represents the simplest of all structures

6.9 Key words

Ionic radii; Radius ratio; Size effect; Crystal lattice; Unit cell; Packing efficiency.

6.10 References for further study

1. Inorganic Chemistry, J. E. Huheey, E.A. Keiter and R. L. Keiter, O. K. Medhi, *Pearson Education*, 4th Ed., **2009**.
2. Concepts and Models of Inorganic Chemistry , B. E. Douglas, D. H. McDaniel and J. J. Alexander; *John Wiley & Sons, Inc., New York*, **1983**.
3. Inorganic Chemistry, James E House, *Academic Press*, **2008**.
4. Concise Inorganic Chemistry by J. D. Lee, *John Wiley & Sons*, 5th Ed. **2008**.

6.11 Questions for self understanding

- 1) Write a note on ionic radii?
- 2) What is radius ration? Explain its significance.
- 3) Write a note on factors affecting radii of an ion
- 4) What is unit cell?
- 5) Write a note on different types of crystal lattice?
- 6) What is close packing structure? Explain in brief.

Unit-7**Structure**

- 7.0 Objectives of the unit
- 7.1 Introduction
- 7.2 Structures of ionic compounds
- 7.3 Ionic compounds of the type MX
- 7.4 Structure of NaCl
- 7.5 Structure of Cesium Chloride
- 7.6 Ionic compound of the type MX₂
- 7.7 Structure of Fluorite (Calcium fluoride)
- 7.8 Structure of Rutile (Titanium oxide)
- 7.9 Structure of Cadmium iodide (CdI₂)
- 7.10 Perovskite structure
- 7.11 Summary of the unit
- 7.12 Key words
- 7.13 References for further study
- 7.14 Questions for self study

7.0 Objectives of the unit

- ❖ Explain the crystal structure of NaCl compound.
- ❖ Explain the crystal structure of CsCl structure.
- ❖ Explain the crystal structure of Fluorite.
- ❖ Explain the crystal structure of Rutile.
- ❖ Explain the crystal structure of Cadmium iodide.
- ❖ Explain Perovskite structure

7.1 Introduction

In ionic compounds, due to the attraction between opposite charges, ions of different elements are held together in rigid, symmetrical arrays. The most significant feature of ionic compounds is the arrangement adopted by the atoms and ions that make up a crystal. The spheres used to describe the ionic solids represent the cations and ions because there is an actual transfer of electrons from one type of atom to the other. A crystal of a compound is constructed from regularly repeating asymmetric units, which may either be atom, ions, or molecules. The crystal structure is obtained by associating an identical asymmetric unit with each lattice point. In a crystal structure, spheres are free to pack together as closely as geometry allows and hence adopt a close-packed structure in which there is least waste of space. In close packed structures of identical atoms each sphere has 12 neighbors and it called coordination number. This is the greatest number that geometry allows and spheres occupy all about 26 percent of available space. If direction of bonding is important then the structure is no longer close-packed the coordination number is less than 12.

7.2 Structures of ionic compounds

An ionic structure is composed of oppositely charged ions. If the larger ions are close packed, then the smaller ions may occupy either the octahedral holes or the tetrahedral holes depending on their size. Normally the type of hole occupied can be determined from radius ratio. In some compounds the relative sizes of the ions are such that the smaller ions are too large to fit in the holes, and they force the larger ion out of the contact with each other so that they are no longer close packed. Despite this, the relative position of the ions remains unchanged.

It is convenient to divide ionic compounds in to groups MX , MX_2 , MX_3 depending on the relative numbers of positive and negative ions.

7.3 Ionic compounds of the type MX

Three structural arrangements commonly found are the Zinc sulphide, sodium chloride and cesium chloride structure.

The compounds which have structures similar to those of NaCl, CsCl, zinc blende and wurtzite are indicated in Table 1 (MX type)

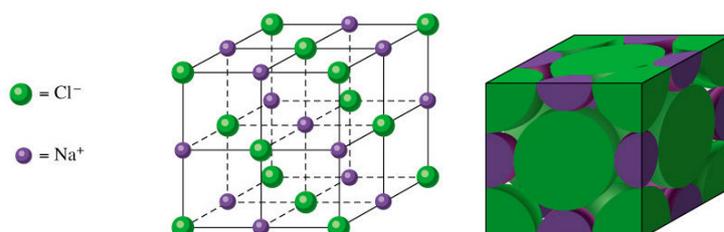
Table 1. Structures of some compounds of the type MX

Ions	Halides				Ions	Oxygen Family			
	F	Cl	Br	I		O	S	Se	Te
Li	← NaCl →				Be	W ^a	Z ^b	Z	Z
Na	← NaCl →				Mg	NaCl	NaCl	NaCl	Z
K	← NaCl →				Ca	NaCl	NaCl	NaCl	NaCl
Rb	← NaCl →				Sr	NaCl	NaCl	NaCl	NaCl
Cs	NaCl	← CsCl →			Ba	NaCl	NaCl	NaCl	NaCl
Cu	—	Z	Z	Z	Zn	W	W	W	W
Ag	NaCl	NaCl	NaCl	W	Cd	NaCl	W	W	Z
						Z	Z	Z	
						Other	Z	Z	Z

^aWurtzite. ^bZinc blende.

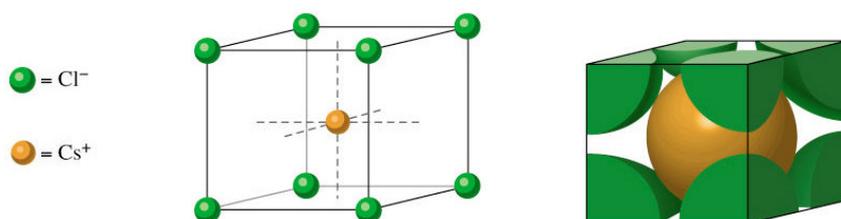
7.4

Structure of NaCl



The crystal of NaCl is a face-centered cube consistent with the radius ratio (0.52). The coordination numbers of both Na^+ and Cl^- are 6. Each Na^+ ion is surrounded by six Cl^- ions at the corners of a regular octahedron and similarly each Cl^- ion is surrounded by six Na^+ ions. In NaCl, the unit cell is formed by two interpenetrating fcc lattices. That is Cl^- is at fcc while Na^+ is at octahedral holes. This structure may be regarded as a cubic close –packed array of Cl^- ions, with Na^+ ions occupying all the octahedral holes.

7.5 Structure of Cesium Chloride



Coordination number: Cs^+ : 8; Cl^- : 8 Cl^- at primitive cubic and Cs^+ at Cubic holes

The CsCl structure has eight anions arranged on the corners of a cube around each Cs^+ . Eight cubes come together at each corner and each cube contains a Cs^+ ion, so there are eight Cs^+ ions surrounding each Cl^- . When equal number of oppositely charged ions are stacked in CsCl, the radius ratio (0.933) suggests a body-centred cubic lattice.

In a body-centred cubic arrangement, the atom at the centre of the cube is identical to those at the corners. This structure is found in metals, but in CsCl if the ions at the corners are Cl^- then there will be a Cs^+ ion at the body-centred position. So it is not strictly body-centred cubic. *The cesium chloride structure should be described as a body-centred cubic type of arrangement and not body-centred cubic.*

7.6 Ionic compound of the type MX_2

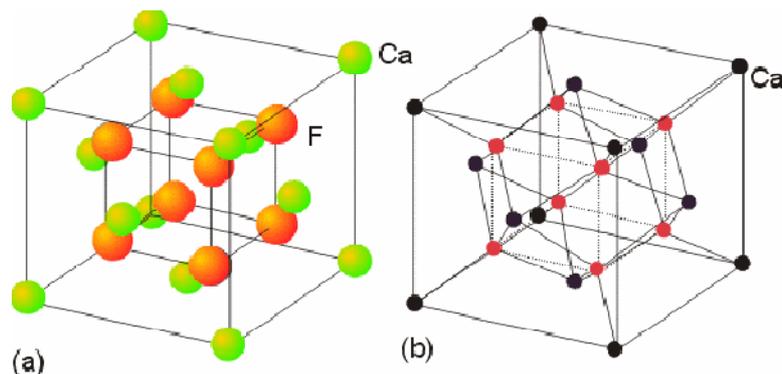
The two most common structures are fluorite CaF_2 and rutile TiO_2 and many difluorides and dioxides have one of these structures. Another fairly common structure is β -cristoblite SiO_2 . These are true ionic structures.

Table 2. Structures of some compounds of the type MX_2 and M_2X

Fluorite (CaF_2)			Rutile (TiO_2)			Antifluorite			
CaF_2	CdF_2	ZrO_2	MgF_2	NiF_2	TiO_2	Li_2O	Li_2S	Li_2Se	Li_2Te
SrF_2	HgF_2	ThO_2	MnF_2	ZnF_2	MnO_2	Na_2O	Na_2S	Na_2Se	Na_2Te
BaF_2	PbF_2	CeO_2	FeF_2	PdF_2	MoO_2	K_2O	K_2S	K_2Se	K_2Te
BaCl_2		UO_2	CoF_2		GeO_2	Rb_2O	Rb_2S		
					SnO_2				

7.7 Structure of Fluorite (Calcium fluoride)

In fluorite, each Ca^{2+} ion is surrounded by eight F^- ions, giving a body centred cubic arrangement of F^- round Ca^{2+} . Since there are twice as many F^- ion as Ca^{2+} ions, the coordination number of both ions is different and four Ca^{2+} ions are tetrahedrally arranged around each F^- ion. The coordination numbers are therefore 8 and 4, so this is called an 8:4 arrangement. The fluorite structure is found when the radius ration is 0.73.



Ca^{2+} at fcc, F^- at Td holes

Coord. #: $\text{Ca}^{2+} = 8$; $\text{F}^- = 4$

atom/ unit cell Ca: $\text{F}^- = 4$: $8 = 1:2$ CaF_2

In CaF_2 , there are twice the number of F^- ions as Ca^{2+} ions and so, the coordination number of Ca^{2+} is 8 while that of F^- is 4.

An alternative description of the structure is that the Ca^{2+} ions form a face-centred cubic arrangement. The Ca^{2+} ions are too small to touch each other, so the structure is not close packed. However, the structure is related to a close-packed arrangement since Ca^{2+} occupy the same relative positions as for a cubic close-packed structure and the F^- ions occupy all the tetrahedral holes.

7.8 Structure of Rutile (Titanium oxide)

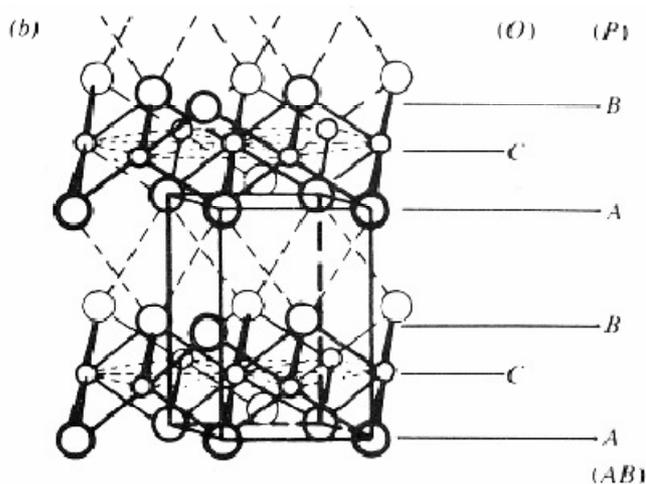
TiO_2 exists in three forms namely anatase, brookite and rutile. Generally rutile structure is commonly found in many structure in which the radius ration is between 0.41 - 0.73. This corresponds to the coordination number of 6 for one ion and coordination number of other ion must be 3, hence it is a 6:3 structure. Each Ti^{4+} in rutile structure is octahedrally surrounded by six O^{2-} ions and each O^{2-} ion has three Ti^{4+} ions round it in a plane triangular arrangement. The rutile structure is not close packed because the repeating unit (i.e., unit cell) of this structure is

not a cube. The structure is described as a considerably distorted body-centred cubic lattice of Ti^{4+} ions.

Each Ti^{4+} is surrounded octahedrally by six O^{2-} and O^{2-} ions are in positions of threefold coordination, i.e., each O^{2-} is surrounded by three Ti^{4+} ions at the corners of an equilateral triangle.

7.9 Structure of Cadmium iodide (CdI_2)

Many MX_2 compounds are not sufficiently ionic to form the perfectly regular ionic structures. Many chlorides, bromides, iodides and sulphides crystallizes into structures which are very different from those of typical ionic compounds. For example, cadmium fluoride CdF_2 forms an ionic lattice with the CdF_2 structure, in contrast cadmium iodide CdI_2 is much less ionic and does not form the fluorite structure. 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 Cd^{2+} ions with layers of I^- on either side- rather like a sandwich where a layer of Cd^{2+} in middle and I^- on either side. This is called layer structure and not a completely regular ionic structure. In CdI_2 two sheets of I^- ions are separated by Cd^{2+} with in a sandwich but between one sandwich and the next two I^- layers are in contact. There is strong electrostatic bonding between Cd^{2+} and I^- layers and there is only weak van der Waals forces holding the adjacent layers of I^- together. Hence packing of layers in the crystal structure is not regular and the solid is flaky. It can be easily cleave in to two parallel sheets.



CdI_2

Γ at hcp

Cd^{2+} at $\frac{1}{2} \text{O}_h$ sites (alternate O layer)

In cadmium iodide, the third layer of Γ is directly above the first layer, so the repeating pattern is ABABAB..... The Γ ions are regarded as an approximately hexagonal close-packed arrangement. The Cd^{2+} ions occupy half of the octahedral sites.

Many other diiodide compounds of metals (example, Ti, V, Mn, Fe, Co, Zn, Cd) are adopted this type of structure, and many hydrides (example, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Fe}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$) are also adopting this type of structure.

7.10 Perovskite structure

When the two metals differ appreciably in size the perovskite structure is formed. Calcium titanate (CaTiO_3) occurs naturally as perovskite structure. This is a cubic close-packed array of O and Ca with Ti occupying one quarter of the octahedral holes. The holes occupied are those bounded completely by O atoms thus keeping Ca and Ti as far apart as possible. BaTiO_3 is also has perovskite structure, in which Ba^{2+} ion is too large to fit into the close-packed oxide lattice without expanding it. This increases the size of the octahedral holes so that Ti can rattle in its octahedral holes. Thus causing some polarization and making the crystal strongly ferroelectric.

7.11 Summary

This unit presents a survey of ionic bonding, describes the structures of MX and MX_2 type. The relative numbers and size of the ions will determine the structure of the crystal. Radius ratio provides a useful guide to predict possible geometries and structure of an ionic compound. All the crystal with a radius ratio between 0.41 to 0.73 is expected to have the sodium chloride structure. In principle positive and negative ions should touch each other to get the ions close together and get maximum electrostatic attraction. A more favorable electrostatic attraction should be obtained by adopting a different geometric arrangement with a smaller coordination number so that ions can get together.

7.12 Key words

Fluorite; Rutile; perovskite.

7.13 References for further study

1. Inorganic Chemistry, J. E. Huheey, E.A. Keiter and R. L. Keiter, O. K. Medhi, *Pearson Education*, 4th Ed., 2009.

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2. Concepts and Models of Inorganic Chemistry , B. E. Douglas, D. H. McDaniel and J. J. Alexander; *John Wiley & Sons, Inc., New York, 1983*.
 3. Inorganic Chemistry, James E House, *Academic Press, 2008*.
 4. Concise Inorganic Chemistry by J. D. Lee, *John Wiley & Sons, 5th Ed. 2008*.

7.14 Questions for self understanding

- 1) Discuss the crystal structure of NaCl compound.
- 2) Discuss the crystal structure of CsCl structure.
- 3) Explain the difference between crystal structures of NaCl and CsCl.
- 4) Discuss the crystal structure of Fluorite.
- 5) Discuss the crystal structure of Rutile.
- 6) Discuss the crystal structure of Cadmium iodide.
- 7) CdF_2 is a perfect crystal but CdI_2 is not. Explain the reason
- 8) Write a note on Perovskite structure

Unit-8**Structure**

- 8.0 Objectives of the unit
- 8.1 Introduction
- 8.2 Covalent character in ionic compounds
- 8.3 Fajan's Rule [The degree of covalent character of ionic bond]
- 8.4 Fajans' Rules for the prediction of relative non-polar character
- 8.5 Results of polarization
- 8.6 The structure of carbonate ion
- 8.7 Melting point of ionic compounds
- 8.8 Solubility of ionic compounds
- 8.9 Solubility of Ionic Solids in Water
- 8.10 Factors affecting solubility of ionic compounds
- 8.11 Conductivity of ionic compound
- 8.12 Summary of the unit
- 8.13 Key words
- 8.13 References for further study
- 8.15 Questions for self study

8.0 Objectives of the unit

After studying this unit you are able to

- ❖ Understand the degree of covalent character of ionic bond.
- ❖ Account for the dissolution of ionic compounds

8.1 Introduction

It is reasonable to consider ions with noble gas structure as spherical shape. This is most likely true for the majority of the ions formed by elements in the main groups. There are few exceptions cases where the ions have an inert pair (example Ga^+ , In^+ , Ti^+ , Sn^{2+} , Pb^{2+} , I^+ , I^{3+}). These ions don't have centre of symmetry and the structures they form usually show some distortion.

8.2 Covalent character in ionic compounds

We have discussed about a polar covalent bond has some ionic character in the unit-2, now we will discuss how an ionic bond can acquire covalent character.

Consider aluminum chloride compound, AlCl_3 has covalent bonds between Al and Cl. This is contrary to what is expected. If AlCl_3 is an ionic compound, the Al^{3+} cation is small and has a large charge, hence this cation is willing to polarise the electron cloud of the anion. Cl^- is a large anion whose electron clouds are easily polarised. As mentioned earlier Polarisability refers to the ease of distorting the electron cloud. When Cl^- is placed next to Al^{3+} , the electron cloud of Cl^- is distorted by Al^{3+} . This distortion allows for both electron clouds to overlap. As a result of overlapping of orbital covalent bond is formed.

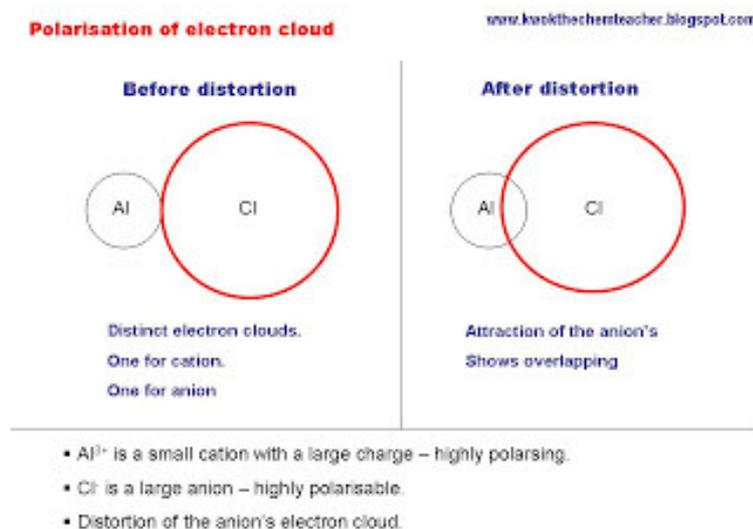


Figure 1: Formation of distorted ionic bond between ions of large size differences

An ionic bond acquires some degree of covalent character if the positive ion can attract electron density from the negative ion back into the region between the nuclei. Due to this the valence electrons will be partially shared and hence covalent character arises. The extent to which a positive ion can attract electron density from the negative ion is called polarizing power.

The polarizing power of a positive ion depends on its charge density and the size. As the positive charge on the cation increases, its attraction for the valence electrons also increases consequently ions have greater polarizing power. Hence more covalent character of the bond it forms with given negative ion.

The extent to which a positive ion can pull electrons back into the space between the nuclei depends not only on its own polarizing power but also on how easy it is to polarize the negative ion. The polarizability of a negative ion measures the ease with which its electron density can be distorted towards the positive ion. Polarizability of the negative ion increases with the charge. Large and highly charged negative ions can be polarized easily and form bonds with greater covalent character. Small and singly charged negative ions are not easy to polarize.

There is a clear trend in the polarizability of the ions of the group-VII elements. Fluoride (F^-) ions have fewer electrons and are smaller than chloride (Cl^-) ions. Fluoride ions are therefore less polarizable than the chloride ions. Therefore all fluoride compounds of alkali and alkaline earth metals have greater ionic character than corresponding chlorides.

The Iodide (I^-) ion is approximately 15% bigger than the chloride (Cl^-) ion. The iodide ion is therefore more polarizable than the chloride ion. The higher charge density of Na^+ ions distorts the electron density around the iodide ions in the NaI lattice and draws electron density into the region between the oppositely charged ions.

8.3 Fajan's Rule [The degree of covalent character of ionic bond]

When a cation approaches an anion closely, it attracts the electrons of the anion at the same time, it repels the positively charged nucleus of the anion due to which the electron density of the anion no longer remains symmetrical, but is bulged or elongated towards the cation. This is known as the polarization of the anion by the cation. The ability of the cation to polarize the anion is called the polarizing power of the cation and the tendency of the anion to get polarized is called as the polarizability of the anion.

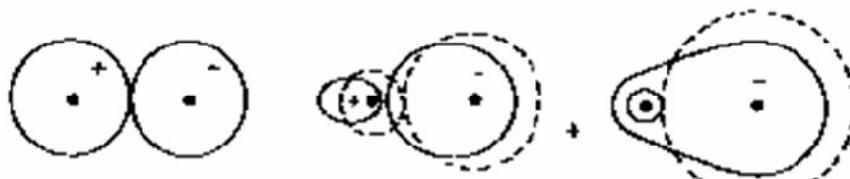


Figure 2: Polarization effects: (a) idealized ion pair with no polarization; (b) mutually polarized ion pair; (c) polarization sufficient to form covalent bond. Dashed lines represent hypothetical unpolarized ions.

8.4 Fajans' Rules for the prediction of relative nonpolar character

Electrostatic forces in a crystal are essentially isotropic (lacking in directional character) whereas polarization effects are highly anisotropic. The halides of the larger alkali metals are the most nearly ionic of any binary compounds. Kasimir Fajans introduced "nonpolar character" as a perturbation on ionic bonds. The effects of covalent vs ionic character on the physical properties of compounds can be subtle. In 1923, Fajans suggested rules to predict the degree of covalent character in ionic compounds. These are discussed below:

1) Covalent character increases with decreasing cation size or increasing cation charge. The high charge density of small and/or highly charged cations is able to exert a powerful polarizing effect which distorts the electron cloud around the anion.

For example, compare NaCl (mp 800°C) with CaCl₂ (mp 772°C; charge effect); and KI (mp 686°C) with LiI (mp 449°C; size effect).

2) Covalent character increases with an increase in anion charge or anion size. The electrons of larger, more negatively charged anions are more loosely held because they are more shielded from the nuclear charge. Thus, these anions are more easily polarized by cations.

Compare LiBr with Li₃PO₄ (charge effect); and LiF (mp 845°C) with LiI (mp 449°C; size effect).

3) Covalent character is greater for cations with a non-noble gas electron configuration (i.e., 18-electron, pseudo-noble-gas cations) than for cations with a true noble-gas configuration (8-electron cations). This effect is mostly observed in transition-metal and post-transition metal cations in which one or more d-electrons ineffectively shield the outer electrons, or the electrons of an adjacent ion, from the nuclear charge. Thus, for two ions of similar size and charge, a transition metal ion with a $(n-1)d^x ns^0$ configuration will be more polarizing and more polarizable than an alkali or alkaline earth metal with a noble gas configuration, $(n-1)s^2 (n-1)p^6 ns^0$.

Compare CuCl (mp 430°C, Cu⁺ is 3d¹⁰ 4s⁰, r = 91 pm) with NaCl (mp 800°C, Na⁺, 2s² 2p⁶, r = 116 pm) and HgCl₂ (mp 276°C, Hg²⁺ is 4f¹⁴ 3d¹⁰, r = 116 pm) with CaCl₂ (mp 782°C, Ca²⁺ is 3s² 3p⁶, r = 114 pm).

8.5 Results of polarization

Melting points and boiling points of compounds of various metals depend upon the covalency resulting from polarization. For example, compare the melting points of compounds having the same anion, but cations of different size: BeCl₂ (405°C), CaCl₂ (782°C); for cations of different charge: NaBr (747°C), MgBr₂ (700°C), AlBr₃ (97.5°C); for a constant cation, but anions of different sizes: LiF(845°C), LiCl(605°C), LiBr(550°C), LiI(449°C); and for ions having the same size and charge, the effect of electron configuration can be observed from CaCl₂ (782°C), HgCl₂(276°C).

The effect of polarization is noticed in the solubility of salts in polar solvents such as water. For instance, consider the silver halides, in which a polarizing cation and increasingly polarizable anions. AgF which is ionic, is soluble in water, but the less ionic AgCl is soluble only with the addition of NH₃. AgBr is only slightly soluble and AgI is insoluble even with the addition of NH₃. Increased covalency from F⁻ to I⁻ is expected and decreased solubility in water is noticed.

It is possible to correlate the hydration enthalpies of cations with their effective ionic radii by the expression shown below:

$$\Delta H = -69,500(Z^2/r_{\text{eff}}) \text{ kJ/mol}$$

where r_{eff} is equal to the ionic radius plus a constant, 85 pm, the radius of the oxygen atom in water. Therefore, r_{eff} is effectively the interatomic distance in the hydrate, and the Born-Landé equation can be applied.

The effect of polarization is observed in the bond lengths of silver halides. This is evident from the values shown in the Table 1. The shortening of silver halides in the direction AgF > AgCl > AgBr > AgI.

Table 1. The effect of polarization observed in the bond lengths of silver halides

Compound	R ⁺ /r ⁻	r _{exp}	Δ
AgF	248	246	-2
AgCl	296	277	-19
AgBr	311	289	-22
AgI	320	281	-39

The basis for other correlations between size, charge and chemical properties is not clear.

Thermal decomposition is the term given to splitting up a compound by heating. All the carbonates of group-II metals undergo thermal decomposition to give the metal oxide and carbon dioxide gas. All of these carbonates and the oxides that are produced are white solids. $\text{XCO}_3(\text{s}) \rightarrow \text{XO}(\text{s}) + \text{CO}_2(\text{g}) \uparrow$ 'X' represents any one of the group-II element.

The decomposition of the group-II carbonates is caused by the polarizing effect of group-II cation.

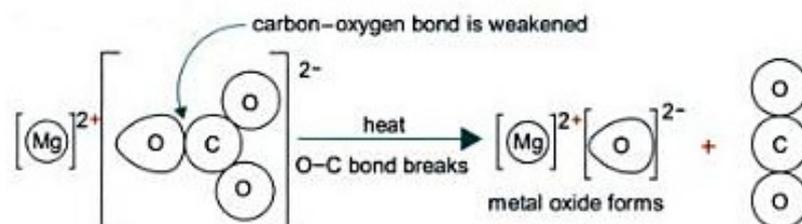
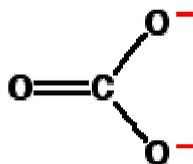


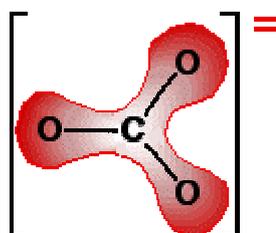
Figure 3: Decomposition of Magnesium carbonate

8.6 The structure of carbonate ion

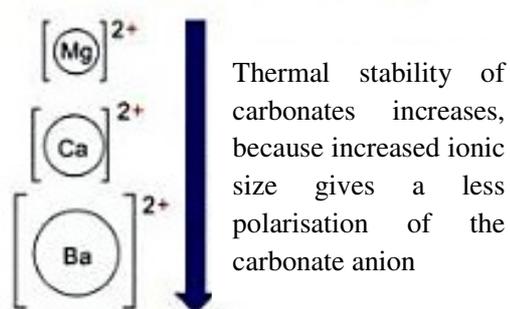
In the carbonate ion sp^2 hybridized carbon is the central atom. It has two single carbon-oxygen bonds and one carbon-oxygen double bond. Therefore it is expected that all the bonds in the carbonate ions are not equal. Each singly bonded oxygen atoms carrying a negative charge as shown in below figure.



However all the bonds in the carbonate ion are identical and the charges are spread out over the whole ion, although concentrated on the oxygen atoms i.e., charges are delocalized as shown in below figure.



When the carbonate ion is placed next to the positive ion, the positive ion attracts delocalized electrons in the carbonate ion towards itself. Hence carbonate ion becomes polarized. When the polarized ion is heated, carbondioxide breaks free to leave the metal oxide. The decomposition of carbonate ion in to carbondioxide is depends on how polarized the carbonate ion is. If it is highly polarized, the decomposition is takes place very easily. Smaller the positive ion, the higher the charge density and the greater the effect it will have on the carbonate ion. As the positive ions get bigger (ie, moving down the group) they have less effect on the polarization of carbonate ion hence decomposition is harder. Therefore the carbonates become more stable to heat as moving down the group.



The polarizing power of the metal cation decrease as the charge:size ration decreases. Therefore it is more difficult to decompose the carbonates as the group is descended. The cations of the group-I carbonates are larger than those of the group-II carbonates and their polarizing power is less. The Li^+ ion however is comparable in size with the Mg^{2+} ion and therefore lithium carbonates easily decomposed by heat. The remaining group-I metal carbonates are not decomposed by heat.

8.7 Melting point of ionic compounds

Generally ionic compounds are solids and have high melting and boiling points. This nature of ionic compounds is contrast to covalent compounds since they are gases, liquids or low melting solids. This difference is due to because of differences in bonding and structure. As we familiar, ionic compounds are made up of positive and negative ions arranged in a regular way in a lattice. The attraction between cations and anions is very strong and non-directional, hence extending equally in all directions. Melting the compounds involves breaking the lattice. Therefore it takes lot of energy to cover come this attraction in order to allow the ions to move more freely and form a liquid. So the melting point and boiling point are usually high and compounds are very hard.

The following factors are affecting the melting point of an ionic compound.

i) The charge on the ion

In general the greater the charge, the greater the electrostatic attraction between the opposite charge ions, hence the stronger the ionic bond between them and have higher melting point.

The below table compare the melting point and ion charges for sodium chloride and magnesium oxide.

Ionic compound	Melting point ($^{\circ}\text{C}$)	Cation charge	Anion charge
NaCl	801	+1	-1
MgO	2800	+2	-2

MgO has higher melting point than NaCl because 2 electrons are transferred from magnesium to oxygen to form MgO while only 1 electron is transferred from sodium to chlorine to form NaCl.

ii) Size of the ion

Smaller ions can pack closer together than larger ions so the electrostatic attraction is greater between smaller ions, hence the ionic bond between them is stronger and have higher melting point. Example, below table provides the comparison of melting point of Group IA (alkali) metal fluoride to the ionic radius of the cation.

Ionic Compound	Melting point ($^{\circ}\text{C}$)	Cation radius (ppm)
NaF	992	99
KF	857	136
RbF	775	148
CsF	683	169

As the radius of the cation increases down the group (IA) from Na^+ to Cs^+ , the melting points of the fluorides decreases.

8.8 Solubility of ionic compounds

Solubility refers to the process when a solid (the solute) becomes dispersed through a liquid (the solvent) and forms a solution. Example: solid NaCl completely disperse in water to form a NaCl solution. NaCl disperse in water quickly and completely in water but not in other liquid like oil, benzene, ether, etc... . Hence there are several factors involved in a solubility of substance in given liquid, in general solubility is determined by the degree to which the separated particles of solute are able to form bonds or attractive forces with the of solute to form bond or attractive forces with the solvent.

Consider an ionic compound being placed in water at the contact surface partial charges in the water molecules are attracted to ions of the opposite charges in the lattice which may cause them to dislodge from their position. Ions separated from the lattice in this way become surrounded by water (solvent) molecules and are said to be hydrated (solvated). When this happens the solid dissolves. Similarly many polar compounds are soluble owing to attraction between their dipoles and those in water. Sugar and ethanol are soluble in water but their solubility is not due to the attraction between dipoles since they are neutral molecule. Instead the solubility is due to their ability of forming hydrogen bonds with water.

The solubility of polar compounds is limited in larger molecules in which the polar bond is only a small part of the total structure, here the non-polar parts of the molecule unable to associate with water render it insoluble. Polar compounds will have limited solubility remaining held to each other by their dipole-dipole attractions. Non-polar substances on the other hand will be soluble owing to their ability to interact with the non-polar solvent by van der waals' forces. For example, the halogens, (non-polar molecules, $[Br_2]$) readily soluble in the non-polar solvent paraffin oil.

So it appears that solubility trends are based on the similar chemical nature of the solute and solvent as this most likely to lead to successful interactions between them. The expression “like dissolves like” often used to capture this notation.

8.9 Solubility of Ionic Solids in Water

Water is an excellent solvent for many compounds. Some dissolve in it as molecules while others, called electrolytes, dissociate and dissolve not as neutral molecules but as charged species called ions. Compounds which exist as solid ionic crystals dissolve in water as ions, and most of them are highly soluble in water.

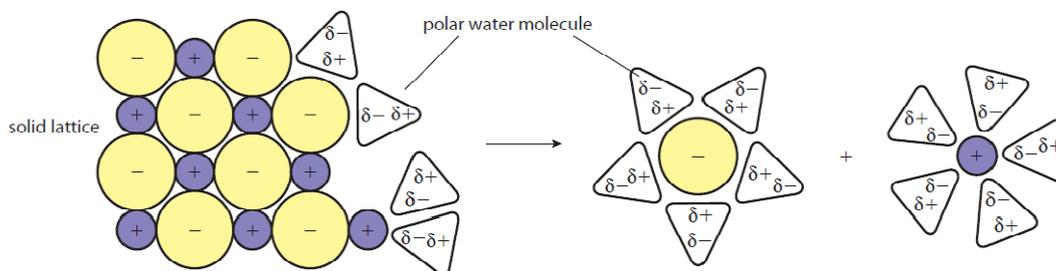


Figure 4: Solubility of ionic compound in polar solvent

The solubility of an ionic salt depends both upon its cations and its anions. Hydration of Li^+ and SO_4^{2-} is shown in Fig.5.

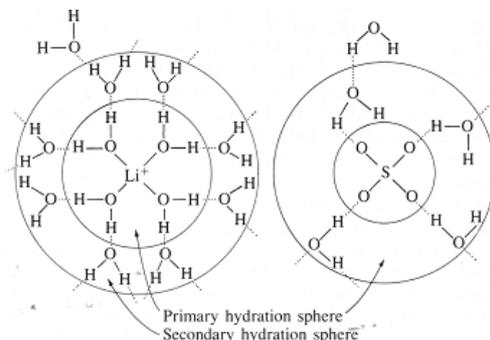


Figure 5. Hydrated Li^+ and SO_4^{2-} ions

When an ionic compound is dissolved in a solvent like water, the crystal lattice is broken apart. As the ions get separated, they get attracted to solvent molecules by ion-dipole forces. The number of water molecules surrounding an ion is known as its hydration number. The water molecules clustered around an ion constitute a shell that is referred to as the primary solvation sphere. The processes of separating the crystal lattice and solvating the ions can be represented by means of a thermochemical cycle of the Born-Haber type. For an ionic compound, $\text{MX}_{(c)}$, the cycle can be shown as follows:

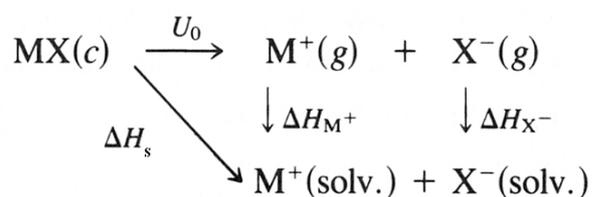


Figure 6. Formation of an ionic compound

where U_0 is the lattice energy, ΔH_{M^+} and ΔH_{X^-} are the heats of hydration of the gaseous cation and anion, respectively and ΔH_s is the heat of solution. From the above cycle, it is evident that

$$\Delta H_s = U_0 + \Delta H_{M^+} + \Delta H_{X^-}$$

The overall heat of solution may be either positive or negative depending on whether it requires more energy to separate the lattice into the gaseous ions than is released when the ions are solvated. The values of heats of hydration are given in Table 2 for some ions.

Table 2. Hydration enthalpies for ions

Ion	r _{solv.} ppm	ΔH ⁰ _{hyd} ,kJ/mol	Ion	r _{solv.} Ppm	ΔH ⁰ _{hyd} ,kJ/mol
Li ⁺	74	-520	Sr ²⁺	113	-1480
Na ⁺	102	-413	Ba ²⁺	136	-1360
K ⁺	138	-321	Al ³⁺	53	-4690
Rb ⁺	149	-300	F ⁻	133	-506
Cs ⁺	170	-277	Cl ⁻	181	-371
Mg ²⁺	72	-1920	Br ⁻	196	-337
Ca ²⁺	100	-1650	I ⁻	220	-296

It is evident from the above Table that for cations the enthalpies of hydration are dependent on the charges and sizes of the ions. For ions having the same charge, the heat of hydration decreases as the size of the ion increases since, the hydration number decreases. The heat of hydration increases significantly as the charge on the ion increases. The charge density (charge/radius) is to be considered to determine the heat of hydration of the ion. Higher hydration enthalpy for F⁻ is noticed since it is attracted to the centre of positive charge in the water molecule (which is the hydrogen atom).

The hydration enthalpy, H for an ion can be expressed as

$$H = -\left[\frac{Ze^2}{2r}\right]\left[1 - \frac{1}{\epsilon}\right]$$

where Z is the charge on the ion, r is its radius and ε is the dielectric constant of the medium.

The interactions between ions and solvent molecules are electrostatic in nature, so the dipole moment of the solvent plays a significant role. However, the structure of the solvent molecules is also important. For example, nitrobenzene is a poor solvent for ionic compounds though it has higher dipole moment (4.22 D) compared to that of water (1.85D). The high dipole moment results from the charge being separated over a long distance. Further, the molecules of nitrobenzene are too large to pack efficiently around small cations, so that the solvation number is too small to result in strong solvation.

Example: NaCl

Sodium chloride is an example where even though the dissolving energy is endothermic, the organization energy is sufficiently exothermic that the compound is soluble. So,

$$\begin{aligned}\Delta E_{\text{dissolve}} &= \Delta E_{\text{hydration}} (\text{NaCl}) + \Delta E_{\text{lattice}} (\text{NaCl}) \\ &= (-784 \text{ kJ/mol}) + (+787 \text{ kJ/mol}) = +3 \text{ kJ/mol},\end{aligned}$$

which favors insolubility. Using the ion organization energies, the organization energy evaluates to the exothermic value

$$\begin{aligned}\Delta E_{\text{org}} &= \Delta E_{\text{org}} (\text{Na}^+) + \Delta E_{\text{org}} (\text{Cl}^-) \\ &= (-1.3 \text{ kJ/mol}) + (-12 \text{ kJ/mol}) = -13 \text{ kJ/mol},\end{aligned}$$

which favors solubility. The organization energy is sufficiently exothermic that the total energy of dissolving is also exothermic,

$$\Delta E_{\text{total}} = \Delta E_{\text{dissolve}} + \Delta E_{\text{org}} = +3 \text{ kJ/mol} - 13 \text{ kJ/mol} = -10 \text{ kJ/mol}.$$

This means the solubility of sodium chloride is due to energy being more dispersed in the solution than in the solid.

Example: MgCO₃

Magnesium carbonate is an example opposite to sodium chloride: Even though the dissolving energy is exothermic, the organization energy is sufficiently endothermic that the compound is insoluble. The dissolving energy evaluates to the exothermic value which favors solubility. Using the ion organization energies, the organization energy evaluates to the exothermic value which favors solubility. Using the ion organization energies, the organization energy evaluates to the exothermic value

$$\begin{aligned}\Delta E_{\text{org}} &= \Delta E_{\text{org}} (\text{Mg}^{2+}) + \Delta E_{\text{org}} (\text{CO}_3^{2-}) \\ &= (+56 \text{ kJ/mol}) + (-25 \text{ kJ/mol}) = +31 \text{ kJ/mol}\end{aligned}$$

which favors insolubility. Because the endothermic organization energy is so large, the total energy of dissolving is also endothermic,

$$\Delta E_{\text{total}} = \Delta E_{\text{dissolve}} + \Delta E_{\text{org}} = -26 \text{ kJ/mol} + 31 \text{ kJ/mol} = +5 \text{ kJ/mol}.$$

This means that the insolubility of calcium carbonate is due to energy being less dispersed in the solution than in the solid.

8.10 Factors affecting solubility of ionic compounds*i) Solvent*

As mentioned earlier the "like dissolves like" rule is used to predict the solvent needed for solution process. In other words, to dissolve ionic compound, it is required to use a solvent that is also highly polar with a high dielectric constant. Small solvent molecules have a smaller dipole which can approach the ions closely to increase solubility.

ii) Lattice Energy (LE)

As we know it takes energy to separate ions from their crystal lattice and from hydrated ions. Smaller size of the ions increases both the lattice energy and hydration enthalpy. If the lattice enthalpy increases more than the hydration enthalpy, then heat of solution become more endothermic and vice versa.

iii) Enthalpy of hydration, $\Delta H_{\text{hydration}}$

The attraction of a dipole solvent (water) dipole to an oppositely charged ion often released as salvation (hydration) energy. This hydration energy is used to break the ionic lattice. Non-polar and weakly polar solvents do not have sufficiently strong hydration to overcome LE and to dissolve electrolytes. In a crystal hydrate, the ions are largely hydrated, and consequently the hydration energy is considerably less than that of the anhydrous solute. The hydrates, therefore, usually have lower water solubility.

iv) The enthalpy of solution, $\Delta H_{\text{solution}}$

Usually substances with a large negative heat of solution (i.e., exothermic reaction) are more soluble than substances with a smaller negative heat of solution. Compounds that have a positive heat of solution (endothermic) may also be soluble.

v) Charge

Larger the charges on ions increases LE more than the $\Delta H_{\text{hydration}}$, therefore ionic compounds with di-positive or negative charge tend to make the enthalpy of solution less negative (less soluble).

vi) Size

It turns out that the main factor increasing $\Delta H_{\text{hydration}}$ over LE is the size of the negative and positive ions.

E.g. Small anions- NO_3^- , ClO_4^- , ClO_3^- , and $\text{C}_2\text{H}_3\text{O}_2^-$ form soluble compounds. The lattice energy increase less than the hydration enthalpy of the positive ions. That means that the enthalpy of solution will become more negative.

E.g. Small cations- H^+ , Na^+ , K^+ , and NH_4^+ forms soluble compounds. The lattice energy increase less than the increase in hydration enthalpy of these small positive ions make enthalpy of solution will become more negative.

E.g. Large anions- PO_4^{3-} , S^{2-} , CO_3^{2-} , and SO_3^{2-} ions are insoluble except those that also contain alkali metals or Na^+ , K^+ , and NH_4^+ . Changes in the size of the positive ion don't make as great a percentage difference to the inter-ionic distance as they would if the negative ion was small. The hydration enthalpy of the positive ions decreases more than the lattice energy. The enthalpy of solution will become less negative.

8.11 Conductivity of ionic compound

Ionic compound conduct electricity in the melted form and in solution. The conductivity is due to the migration of ion towards the electrode under the influence of an electric potential.

For example, if electric current is passed through a solution of sodium chloride, Na^+ ions are attracted to the cathode (negatively charged electrode), where Na^+ ion gain an electron and form a sodium atom. The Cl^- ions are attracted to the anode (positive charge electrode), where they lose an electron and become chlorine atom. This process is called electrolysis. The conduction occurs by an ionic mechanism involving the migration of both positive and negative ions in opposite directions.

In the solid state, the ions are trapped in fixed places in the crystal lattice and they cannot migrate. Hence ionic compound cannot conduct electricity in solid state. However the crystal may conduct electricity to a very small extent by semiconduction if the crystal contains some defects. For example, suppose a lattice site is unoccupied, i.e., there is hole due to missing of an ion. An ion may migrate from its lattice site to the vacant site, and in so doing it makes a hole somewhere else. The new hole is filled by another ion and so on, eventually the hole migrates across the crystal and a charge is carried in the other direction. The amount of current carried by this mechanism is extremely small.

8.12 Summary of the Unit

Although ionic crystals are held together by electrostatic forces, the ions become separated when the solid dissolves. Ions are strongly attracted to the ends of polar ends of polar molecules that

have charges opposite to those of the ions. Since, the dissolution of solids is intimately related to their chemical behavior, the energy relationships for dissolving ionic solids have been discussed. Ionic bonds are very strong, therefore a lot of energy is needed to break them so ionic compounds have high melting and boiling points. They are Conductive when liquid, Ions are charged particles, but ionic compounds can only *conduct* electricity if their ions are free to move. Ionic compounds do not conduct electricity when they are solid - only when dissolved in water or melted.

8.13 Key words

Fajan's Rule; Polarization; Covalent character; Melting point; Solubility; Conductivity.

8.14 References for further study

5. Inorganic Chemistry, J. E. Huheey, E.A. Keiter and R. L. Keiter, O. K. Medhi, *Pearson Education*, 4th Ed., **2009**.
6. Concepts and Models of Inorganic Chemistry, B. E. Douglas, D. H. McDaniel and J. J. Alexander; *John Wiley & Sons, Inc., New York*, **1983**.
7. Inorganic Chemistry, James E House, *Academic Press*, **2008**.
8. Concise Inorganic Chemistry by J. D. Lee, *John Wiley & Sons*, 5th Ed. **2008**.

8.15 Questions and problems

1. Calculate the lattice energy of NaCl using Kapustinskii equation (Given $r_{-}=165$ pm and $r_{+}=115$ pm).
2. If the ionic radii of Sn^{4+} and O^{2-} are 83 ppm and 126 ppm respectively, predict the probable structure for SnO_2 .
3. Draw the Born-Haber cycle and calculate the enthalpy of formation of RbBr using the following data (in kJ mol^{-1}): ΔH_{sub} for Rb (s)=75.8; ΔH_{IE} for $\text{Rb}_{(\text{g})}$ =403; ΔH_{BE} for $\text{Br}_{2(\text{g})}$ =192; ΔH_{EA} for $\text{Br}_{2(\text{g})}$ =324; ΔH_{vap} for $\text{Br}_{2(\text{l})}$ =30.9; $\Delta H_{\text{Lattice energy}}$ for $\text{RbBr}_{(\text{s})}$ =-670.
4. How Fajan's rules are helpful in describing the gradual lowering in melting points($^{\circ}\text{C}$) for LiF (870), LiCl(612), LiBr(546) and LiI(442)? Explain.
5. Despite the crystals of KCl and CaO being isostructural, the latter has a higher lattice energy than the former. Why?
6. Hydration energy of Na^{+} is greater than that of K^{+} . Give reason.
7. Represent diagrammatically the unit cells of (i) a simple cubic lattice, (ii) a fcc lattice and (iii) a bcc lattice. Calculate the number of atoms present in each of these.

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8. If the ionic radii of Sr^{2+} and F^- are 132 pm and 199 pm respectively, predict the probable structure for SrF_2 .
 9. Although CaF_2 has the fluorite structure while MgF_2 has the rutile structure. Explain this difference.
 10. Predict the crystal type for each of the following using the radius ratio: a) K_2S b) CoF_2 c) Fe_2O_3 and d) CaCl_2
 11. Give rational explanation to the solubility rules in terms of ion sizes, lattice energy (U) ΔH_{hyd} and $\Delta H_{\text{solution}}$.
 12. Define Following
 - a) Enthalpy of solution,
 - b) Enthalpy of hydration,
 - c) Solvent-Solvent intermolecular attractions
 12. Explain the lattice energy and melting point trend.
 13. How does polarization and covalency affect lattice energy and melting points?
 14. Would you expect sodium chloride to dissolve in carbon tetrachloride, (CCl_4) explain the reason
 15. Which one of each of the following pairs will be smaller radius? Explain your reasoning in each case.
 - a) K or K^+
 - b) K^+ or Ca^{2+}
 - c) Br^- or Rb^+
 - d) Se^{2-} or Br^-

Unit - 9**Structure**

- 9.0 Objectives of the unit
- 9.1 Introduction
- 9.2 General properties of metals
- 9.3 Metals and metallic bond
 - i) The electron sea model or free electron model
 - ii) Valence bond model
 - iii) The band model/molecular orbital approach
- 9.4 Metals (conductors)
- 9.5 Insulators (Non conductors)
- 9.6 Semiconductors
 - i) n -type extrinsic semiconductor
 - ii) P-type extrinsic semiconductor
- 9.7 Summary of the unit
- 9.8 Key words
- 9.9 References for further study
- 9.10 Questions for self under standing

9.0 Objectives of the unit

After studying this unit you are able to

- ❖ Differentiate the metals and non metals.
- ❖ Identify the properties of metals
- ❖ Explain the electron sea model
- ❖ Explain the valence bond model
- ❖ Explain the band model

9.1 Introduction

The three-fourth of the known elements is metals. But much less theoretical work has been done to understand the bonding between the same or different metal atoms compared to between the metal and non-metal or non-metal and non-metal atoms. This is because metals combine with each other to form products of indefinite composition called bertholides, whereas metal with non-metal or non-metal with non-metal compounds combines with definite stoichiometry called daltonides.

The metallic bond is not ionic because ionic bond is formed between elements of different electronegativity. And it is not covalent bond because there are not sufficient numbers of valency electrons on metal to form electron pair bonds with 8 to 20 neighbouring metal atoms.

Metals are made up of positive ions packed together in one of the three following arrangement,

- i) Cubic close-packed (also called face-centred cubic).
- ii) Hexagonal close-packed.
- iii) Body-centred cubic.

The cohesive force in metals is very large and three conventional bonding types (ionic, covalent and coordinate) are unable to explain characteristic properties of the metals such as, metallic luster, high melting and boiling points, hardness, malleability, ductility, high density, thermal and electrical conductivity etc..... There may be new type of cohesive force in metals might exist and called metallic bond.

9.2 General properties of metals

All metals have following characteristic physical properties

- a) They are exceptionally good conductor of heat and electricity.

All metals are exceptionally good conductor of heat and electricity. Electric conduction is due to the movement of electrons. This is in contrast to the movement of ions in the aqueous solution

of ionic compounds. In the solid state ionic compounds are poor conductor and there is an enormous difference in the conductivity between metals and ionic compounds.

b) They have characteristic metallic luster, bright, shiny and highly reflective.

All metals except copper and gold are silvery in color. Smooth metal surface have a lustrous shiny appearance. The shininess is special and appears in all angles. This is in contrast to the shininess of few non-metals like sulphur, iodine, which appears shininess when viewed at low angles

c) They are malleable and ductile.

The most important mechanical properties of metals are malleability and ductility. This shows that there is not much resistance for deformation of the structure. i.e., a larger cohesive force holds the structure together.

d) They readily forms alloys

9.3 Metals and metallic bond

Metal are those materials which generally hard, and are characterized by high electrical and thermal conductivity, malleability, ductility, bright luster and good tensile strength. Basically 3 models have been proposed to account for the nature of bonding in metals. They are.

i) The electron sea model or free electron model

ii) Valence bond model

iv) The band model/molecular orbital approach

i) The electron sea model or free electron model

This theory is called as electron pool or gas theory of bonding in metals. This is the first theory of metallic bonding. Drude at the beginning of the 20th century made a guess about electronic structure and proposed electron theory for metals. This electron theory was further modified by Lorentz few years later, and hence this theory also known as ‘‘Drude-Lorentz theory’’ of metals. The basic assumption of this theory is that, a metal crystal consists of positive metal ions (kernel) and whose valence electrons are free to move between the ions as if they constituted electron gas. The crystal is then visualized to be held together by electrostatic forces of attraction between the positively charged ions and negatively charged ions electron gas or electron sea as shown in the Fig 1.

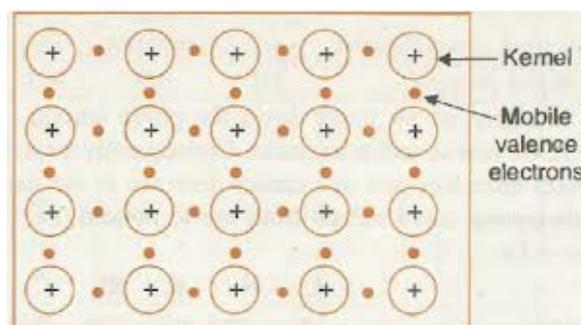


Figure 1: characterization of metallic state

Further, it is also assumed that the electrons are free to move throughout the entire crystal. *Thus the force of attraction, which binds a metal atom kernel to a number of electrons within its sphere of influence, is known as metallic bond.* The theory in its original form assumes that the classical kinetic theory of gases is applicable to the electron gas, mutual repulsion between electrons was ignored and the electrons were expected to have velocities which are temperature dependent according to a Maxwell-Boltzmann distribution law.

This free electron sea model was able to explain most of the metallic properties.

1. *High electrical conductivity* of metals is due to the presence of free mobile electrons. These electrons move readily in electric fields and hence conduct the electricity throughout the metal from one end to another.
2. *High thermal conductivity* is also because the presence of free mobile electrons. If one part of metal is heated, the electrons present in that part gain large amount of kinetic energy, and these electrons are free to move rapidly in the metal crystal from one end to another and convey the heat i.e., they conduct the heat to the other part of the crystal.
3. *Bright metallic luster* it is also explained once again due to the presence of free mobile electrons. When a light radiation impinges on the surface of the metal, the electrical component of the light waves sets the electron present on the surface into to and fro oscillations. These oscillating electrons emit radiations in the form of light. Thus when the light falls on the metal surface it appears as, light is being reflected and hence exhibits typical metallic luster.

ii) Valence bond model

The valence bond theory considers all possible interactions between the immediate neighbouring atoms in the metallic crystal. Metals do not have sufficient number of valency electron to form covalent bonds with as many as 8 or 12 nearest neighbor atoms. Consequently it is assumed that a large number of resonance structures are possible.

Consider lithium, a simple metal which has a body-centered cubic structure, with eight nearest neighbors at a slightly greater distance. A lithium atom has one electron in its outer shell, and may be shared with one of its neighbors, to form a normal two-electron bond. The atom could equally well be bounded to any of its other eight neighbors and hence different arrangements are possible, as shown in fig 2. 2a and 2b are two examples.

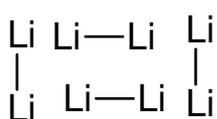


Fig .2a

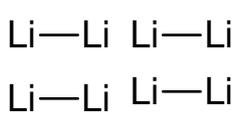


Fig. 2b

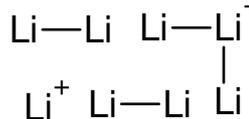


Fig .2c

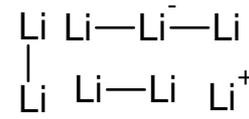


Fig .2d

Figure 2: Representations of some different bonding possibilities in lithium

On the other hand, lithium atom may form two bonds if it ionizes, and it can then form many structure similar to those in figures 2c and 2d. Hence Pauling suggested that the true structure is a mixture of all the many possible bonding forms. The more possible structures there are, the lower the energy. This means that the cohesive force which holds the structure together is large, and in metallic lithium the cohesive energy is three times greater than in Li_2 molecule. The cohesive energy increases from group 1 to 2 to 13, and this explained by the atoms being able to form an increased number of bonds, and give an even larger number of possible structures. The presence of ions could explain the electrical conduction, but the theory does not explain the conduction of heat in solids, or the luster, or the retention of metallic properties in the liquid state or in solution.

iii) The band model/molecular orbital approach

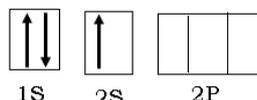
According to molecular orbital theory metallic bonding results the delocalization of the electron orbitals over all the atoms of a metal structure.

When two atomic orbitals combine, they form two molecular orbitals, a bonding molecular orbital with lower energy and a non bonding molecular orbital of higher energy compare to parent atomic orbitals. Similarly when three atomic orbitals are combines, three molecular orbitals, a bonding M.O. of lower energy, a non bonding M.O. of the same energy and a antibonding M.O. of higher energy compared to parent atomic orbitals. In general, combinations of N atomic orbitals yields N molecular orbitals of which N/2 are bonding M.Os, and remaining N/2 are anti bonding M.Os molecules. The larger the number of atomic orbitals overlaps, the

energy separation between the various M.Os will be exceedingly small and this leads to the overlap of energy band.

For example, consider the lithium atom

The electronic configuration of lithium atom is



The Li_2 molecule exists in the vapour state, and bonding occurs using the 2s atomic orbital. There are three empty 2p orbitals in the valence shell, and *the presence of empty atomic orbitals (AOs) is a prerequisite for metallic properties.* (carbon in its excited state, nitrogen, oxygen, fluorine, and neon all lack empty AOs in the valence shell and are all non metals.)

The valence shell has more AOs than electrons, so even if the electrons are all used to form normal two- electron bonds, the atom cannot attain a noble gas structure. Hence compounds of this type are considered as 'electron deficient'.

According to the molecular orbital description of a Li_2 molecule, it has six electrons, arranged in molecular orbitals (MOs) as $\sigma 1s^2, \sigma^* 1s^2 \sigma 2s^2$. Bonding occurs because the $\sigma 2s^2$ bonding MO is full and the corresponding anti bonding orbital is empty. Ignoring any other inner electrons, the 2s AOs on each of the 2 Li atoms combine to give two MOs. One bonding and one antibonding MO as shown in Fig 3a.

If three Li atoms joined to form Li_3 , three 2s AOs would combine to form 3 MOs- one bonding, one non- bonding and other one is anti bonding. The energy of a non-bonding MO is lie in between the bonding and anti bonding orbitals. The three valence electrons from 3 atoms would occupy the bonding MO (two electrons) and the non- bonding MO (one electron) as shown in Fig 3b.

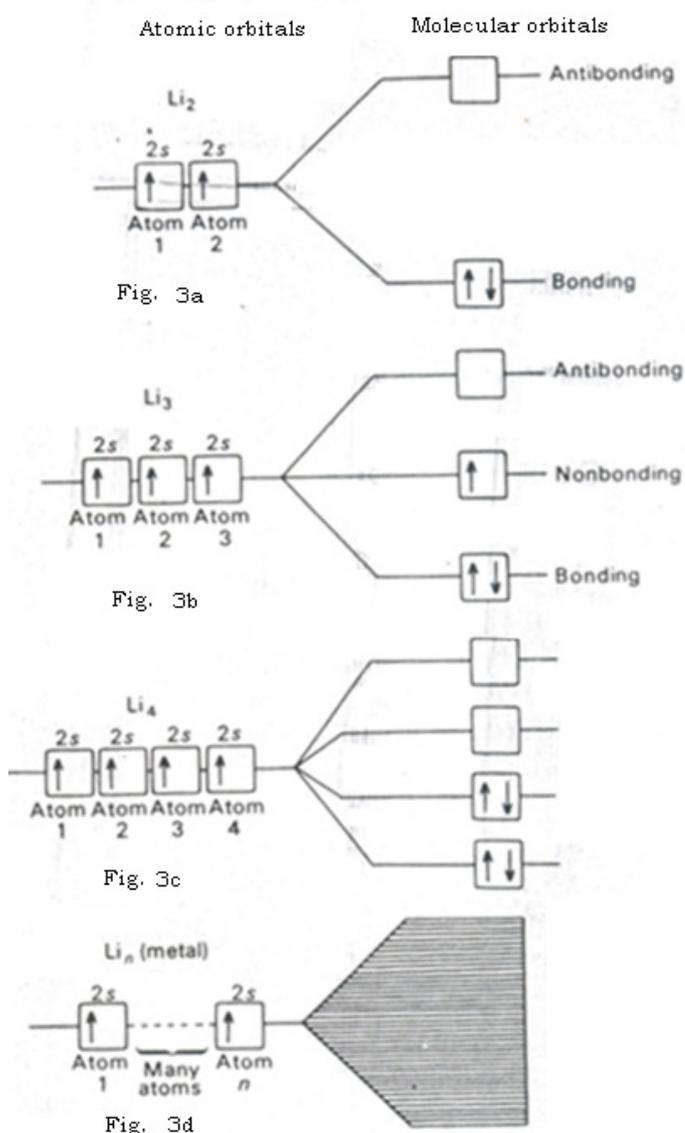
In Li_4 , the four AOs would form 4 MOs – two bonding, – and two anti bonding. The presence of two non bonding MOs between the bonding and anti bonding orbitals reduce the energy gap between the orbitals. The 4 valence electrons would occupy the two lowest energy MOs, which are both bonding orbitals, as shown in Fig.3c

As the number of electrons in the cluster increases , the spacing between the energy levels of the various orbitals decreases further , and when there are a large number of atoms, the energy levels

of the orbitals are so close together that they almost form a continuum and appear as band as shown in Fig 3d.

The number of MOs must by definition be equal to the number of constituents AOs. Since there is only one valence electron per atom in Li, and a MO can hold two electrons, means that only half of the MOs in the 2s valence bands are filled i.e., the bonding MOs. Hence it requires only a minute amount of energy to perturb an electron to an unoccupied MO.

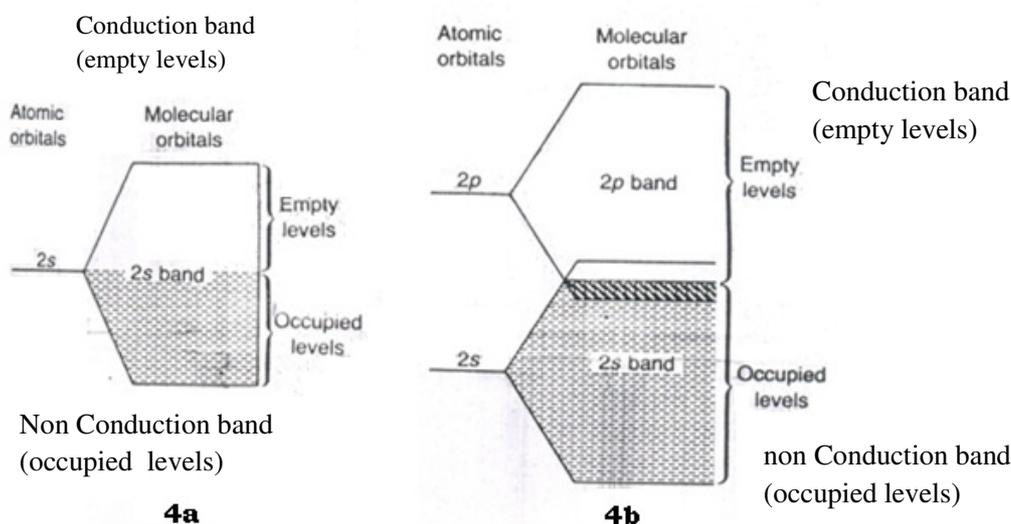
The MOs extend in three dimensions overall the atoms in the crystals, and hence electrons have a high degree of mobility. The mobile electrons account for the high thermal and electrical conduction of metals.



If one end of a piece of metal is heated, electrons at that end gain energy and move to an unoccupied MO where they can travel rapidly to any other part of the metal, which in turn becomes hot. In a similar manner, electrical conduction takes place through a minor perturbation in energy promoting an electron to unfilled level, where it can move readily. In the absence of an electric field, equal numbers of electrons will move in all directions. If a positive electrode is placed at one end, and a negative electrode at the other, then electron will move towards the anode much more readily than in the opposite direction; hence an electric current flows.

Conduction occurs because the MOs extend over the whole crystal, and because there is effectively no energy gap between the filled and unfilled MOs. The absence of an energy gap in lithium is because only half the MOs in the valence band are filled with electrons (figure 4a).

In beryllium there are two valence electrons, so the valence electrons would just fill the 2s valence band of MOs. In an isolated beryllium atom, the 2s and 2p atomic orbitals differ in energy by 160 KJ/mole. As the 2s AOs form a band of MOs similarly the 2p AOs form a 2p band of MOs. The upper part of the 2s band overlaps with the lower part of the 2p band (fig. 4b). Because of this overlap of the bands, some of the 2p band is occupied and some of the 2s band is empty. Hence it is easy to perturb electrons to an unoccupied level in the conduction band where they can move throughout the crystal. Hence beryllium behaves as a metal.



The electronic energy bands where electrons can move are called the permitted bands. These bands are also known as Brillouin zones. Two Brillouin zones are separated from each other by empty bands called forbidden zones or forbidden energy gap represented by E_g . The width of

On the basis of band theory one can explain behavior of solids as metals, insulators and semiconductors.

9.4 Metals (conductors)

Metals are those materials in which plenty of electrons are available for conduction. However, in terms of band theory, the conduction band of the metal is partially filled and contains large number of electrons. As the bands are overlapping (fig. 5a) band gap is practically nil and hence exhibit electrical and thermal conductivity.

9.5 Insulators (Non conductors)

Insulators are those materials in which the energy gap between conduction band and valence band is very large (fig 5b). Hence energy required for the promotion of an electron from the completely filled valence shell band to the empty conduction band is relatively very high and is therefore normally not available. Therefore, such materials are known as insulators.

9.6 Semiconductors

In this type of materials the electrical properties are lie in between good conductors and insulators. Further, the energy gap of semiconductor lies in between that of insulator and conductor (fig 5c) these materials in their extremely pure form they will conduct the electricity and such semiconductors are known as 'intrinsic semiconductors'. Eg: Germanium, Silicon etc. Intrinsic semiconductors have filled valence band (non conduction band) and empty conduction band. The energy gap between them so small that, even at room temperature the electrons from the filled valence band can jump to the vacant conduction band and hence exhibit low thermal conductivity. Further, as the temperature is increased, the width of the energy gap is decreased and some more electrons can jump to the conduction band. Thus exhibits increased conductivity with increase of temperature.

Sometimes substances which are normally insulators can be converted in to the semiconductors by the addition of small amount of impurities (dopants). Such materials are known as extrinsic or impurities semiconductors. Depending on the nature of dopants added to the extrinsic semiconductors it has been classified in to two types

- A. n -type extrinsic semiconductor
- B. p-type extrinsic semiconductor

i) n -type extrinsic semiconductor

These materials are obtained when an impurity atom to be added has more external electrons than the parent atoms. Eg: when penta valent atoms such as phosphorous , arsenic or antimony are added to pure silicon or germanium (both containing four electrons). In this case each phosphorous atom forms four covalent bonds with the neighboring four silicon atoms by using its four valency electrons and its fifth electron is left unused as shown in the fig.6.

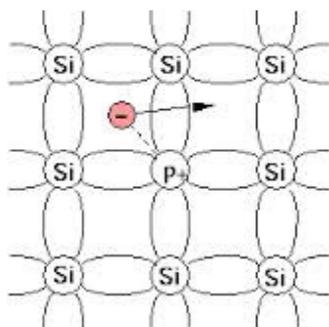


Figure 6: Doping of silicon by phosphorus

Thus the extra electron at the lattice point is occupied by phosphorous atoms compared to the lattice point occupied by silicon atoms. This extra electron is responsible for the conduction of electricity. These extra electrons occupy delocalized level which is just below the empty conduction band of silicon crystal. these extra electron can easily be excited to the empty conduction band by application of electric field or by thermal energy and thus silicon becomes semiconductor. Hence crystals of germanium are semiconductors because of the presence of extra electrons and hence behave as n-type extrinsic semiconductors.

ii) P-type extrinsic semiconductor

These materials are obtained when an impurity atom added has less external electron than the parent insulator atom. Eg: when boron or aluminum (both containing three electrons) atoms are added to pure tetravalent silicon or germanium. So, when silicon is doped with aluminum, aluminum forms three covalent bonds with silicon there by leaving one bond with silicon containing only one electron (from silicon). Thus in this bond, in the lattice there is an electron deficiency which creates a positive hole in the valency band of silicon as shown in the fig.7.

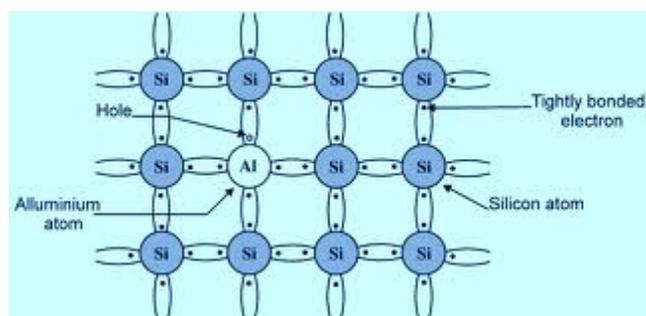


Figure 7: doping of silicon by aluminium

Positive holes are the places where electrons are missing. These holes occupy the level (called acceptor impurity level) which present close to the filled valency band of silicon crystal. The conductivity in these type of materials is due to movement of holes from one atom to another through the crystal and these type of conductivity is known as p-type conductivity and materials are known as the p-type extrinsic semiconductors.

9.7 Summary of the unit

Metals are made up of positive ions packed together. Negatively charged electrons hold the ions together. The number of positive and negative charges are exactly balanced. The strength of the metallic bonding is related to the number of valence electrons. The cohesive energy increases at first on crossing the transition series Sc-Ti-V as the number of unpaired d electrons increases. The cohesive energies are much larger than the weak van der Waals forces which hold discrete covalent molecules together in solid state. There are two rules about the cohesive energy and structure of metals: they are i) the bonding energy of a metal depends on the average number of unpaired electrons available for bonding on each atom. ii) the crystal structure adopted by the metal depends on the number of s and p orbitals on each atom that are involved with bonding.

9.8 Key words

Metals; Electron sea model; Valence bond model; The band model; Conductors; Insulators; Semiconductors; n-type; P-type.

9.9 References for further study

1. Concise inorganic chemistry – J D Lee, 5th Edition, ELBS - 1996.
2. Inorganic chemistry- principles of structure and applications. Huhey Keither and Keither 4th Edition, Pearson education - 2006
3. Inorganic chemistry – Sharpe, 3rd Low price Edition - 2005.
4. Principles of inorganic chemistry – Puri, Sharma, Khalia, -2008

5. Solid state chemistry and its applications – A R west, John Wiley and sons - 1998.

9.10 Questions for self understanding

- 1) List the physical properties of metals
- 2) What are the three common crystal structures adopted by metals?
- 3) Describe the various theories of metallic bond
- 4) Discuss the energy band theory in detail
- 5) Explain the electrical conductivity of metals and semi-metals on the basis of valence bond theory
- 6) Write a short note on
 - a) Conductor
 - b) Semi-conductor
 - c) Insulator
- 7) What are n-type and p-type semiconductors? Explain their formation
- 8) Explain why the electrical conductivity of a metal decreases as the temperature is raised, but the opposite occurs with semiconductors.

Unit - 10**Structure**

- 10.0 Objectives of the unit
- 10.1 Introduction
- 10.2 Hydrogen bond
- 10.3 Condition for hydrogen bond formation
- 10.4 Strength of Hydrogen bond
- 10.5 Hypes of hydrogen bonds
 - a) Intramolecular hydrogen bonds
 - b) Intermolecular hydrogen bonds
- 10.6 Importance of intra and inter-molecular hydrogen bonding
- 10.7 Detection of Hydrogen bonding
 - 1. Infrared spectroscopy
 - 2. Proton magnetic resonance (PMR)
 - 3. Electronic spectroscopy
- 10.8 Properties and effects of hydrogen bonds
- 10.9 Consequences of intermolecular hydrogen bonding
- 10.10 Consequences of intra-molecular hydrogen bonding
- 10.11 Illustrations of hydrogen bonding
- 10.12 Summary of the unit
- 10.13 Key words
- 10.14 References for further study
- 10.15 Questions for self under standing

10.0 Objectives of the unit

After studying this unit you are able to

- ❖ Explain hydrogen bonding
- ❖ Recognize conditions for hydrogen bond formation
- ❖ Illustrate Strength of hydrogen bond
- ❖ Identify types of hydrogen bond
- ❖ Differentiate intra and inter-molecular hydrogen bonding
- ❖ Explain various methods available for detection of hydrogen bonding.
- ❖ Explain properties and effects of hydrogen bond

10.1 introduction

A hydrogen atom under appropriate conditions can be linked to two similar or dissimilar electronegative atoms. i.e., it is covalently bonded to one atom and attached to other atom by a weaker bond, which can be represented as follows $X-H\cdots Y$. The shorter $X-H$ bond is covalent bond and it is stronger. The longer dotted bond is weaker bond and it is called hydrogen bond. In order to understand the concept of hydrogen bond let us consider a molecule, say XA in which H atom is covalently linked with a strongly electronegative atom X (X may be N , O , Br or F). The bonding electron pair shared between H and X will lie far away from the H atom (i.e., $X-H$ bond become polarized). Therefore partially positive charge will be developed on H atom and negative charge will be developed on X atom. Thus HX molecule will behave as a dipole and it will be represented as $H^{\delta+} - X^{\delta-}$. If another molecule $H-Y$ which is also forms a dipole $H^{\delta+} - Y^{\delta-}$ is brought near $H^{\delta+} - X^{\delta-}$ dipole, these two dipoles will be linked together by a special type of bond. This type of bond is called Hydrogen bond and is represented by dotted lines. Thus the existence of hydrogen bond between $H-X$ and $H-Y$ molecule is shown as

$H^{\delta+} - X^{\delta-} \cdots H^{\delta+} - Y^{\delta-}$. Thus hydrogen atoms act as bridge between the electronegative atoms X and Y .

10.2 Hydrogen bond

It is a special type of dipole-dipole attraction which occurs when a hydrogen atom bonded to a strongly electronegative atom exists in the vicinity of another electronegative atom with a lone pair of electrons. These bonds are generally stronger than ordinary dipole-dipole and dispersion forces, but weaker than true covalent and ionic bonds. Eg: HF , H_2O , NH_3 , etc. Because of

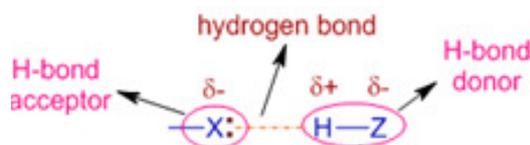
hydrogen bonding H_2O exist in a liquid form and it is a life saving liquid for all mankind animals, plant kingdom and aquatic life.

Definition: *The electrostatic attraction between partially positively charged hydrogen atom bonded to a relatively electronegative atom and another electronegative atom is referred to as hydrogen bond.*

Or

The attractive force that binds a hydrogen atom, which is already covalently attached with a strongly electronegative atom of a molecule with another electronegative atom of same or other molecule, is known as hydrogen bond.

It is represented by a dotted line as shown below.



Where, Z is an electronegative atom to which H atom is covalently bonded. The H-Z group is also called as donor group since it provides hydrogen atom for H-bonding. X is another electronegative atom that attracts positively charged H atom, and X is referred to as hydrogen bond acceptor since it accepts positive charge from the H atom. The acceptor atom, X may or may not be covalently bonded to another H atom but should contain at least one lone pair on it. The dotted line in the above figure represents the hydrogen bond.

10.3 Condition for hydrogen bond formation

In order for a hydrogen bond to occur there must be both a hydrogen donor and an acceptor present. The donor in a hydrogen bond is the atom to which the hydrogen atom participating in the hydrogen bond is covalently bonded, and is usually a strongly electronegative atom such as N, O, or F. The hydrogen acceptor is the neighboring electronegative ion or molecule, and must possess a lone electron pair in order to form a hydrogen bond. Hence the hydrogen bond formation is expected to occur under the following conditions.

1. There should be a hydrogen atom carrying an appreciable partial positive charge. Such a hydrogen atom would exist in any polar H-X group.
2. There should be another electronegative atom Y possessing an unshared electron pair.
3. X and Y should have high electronegativity, the electronegativities of X and Y should be equal or nearly equal.

Since the hydrogen donor is strongly electronegative, it pulls the covalently bonded electron pair closer to its nucleus thereby away from the hydrogen atom. The hydrogen atom is then left with a partial positive charge, creating a dipole-dipole attraction between the hydrogen atom bonded to the donor, and the lone electron pair on the acceptor.

Thus hydrogen bond is a weak attractive interaction between the polar molecules in which H is bonded to electro negative atoms such as N O or F etc. the name hydrogen bond is misnomer as it is not a true chemical bond but it is a strong dipole-dipole interaction but weaker than the conventional covalent or ionic bond.

10.4 Strength of Hydrogen bond

The energies of hydrogen bonds are in the range 2 to 10 kcal/mol as compare to the range of 30-130 kcal/mole for ordinary chemical bonds. The length of the hydrogen bond is of the order of 2.5 to 2.75 Å. The length and strength of hydrogen bonds depends on bond strength, temperature, pressure and environment. The typical length of a hydrogen bond in water is 197 pm. The ideal bond angle depends on the nature of the hydrogen bond donor. The following table gives hydrogen bond angles between a hydrofluoric acid donor and various acceptors.

acceptor...donor	VSEPR symmetry	Angle (°)
HCN...HF	linear	180
H ₂ CO...HF	trigonal planar	110
H ₂ O...HF	pyramidal	46
H ₂ S...HF	pyramidal	89
SO ₂ ...HF	trigonal	142

The energy of the hydrogen bond also depends on the electronegativities of atoms X and Y and it is usually decreases in the order F > O > N ≈ Cl. the hydrogen difluoride ion HF²⁻ possess the strongest known hydrogen bond (27kcal/mole). The heat of vaporization and sublimation are used to estimate the energy of the hydrogen bond involved.

Hydrogen bonding strongly affects the crystal structure of ice, helping to create an open hexagonal lattice. The density of ice is less than the density of water at the same temperature; thus, the solid phase of water floats on the liquid, unlike most other substances.

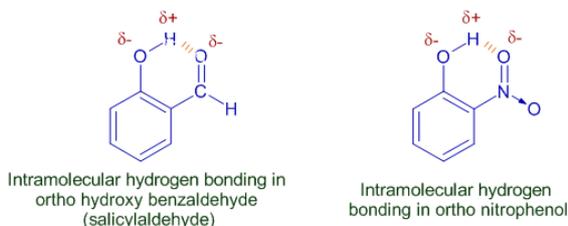
10.5 Types of hydrogen bonds

Hydrogen bonds can occur within one single molecule, between two like molecules, or in-between two unlike molecules. Hence, it has been classified into

- Intramolecular hydrogen bond and
- Intermolecular hydrogen bond.

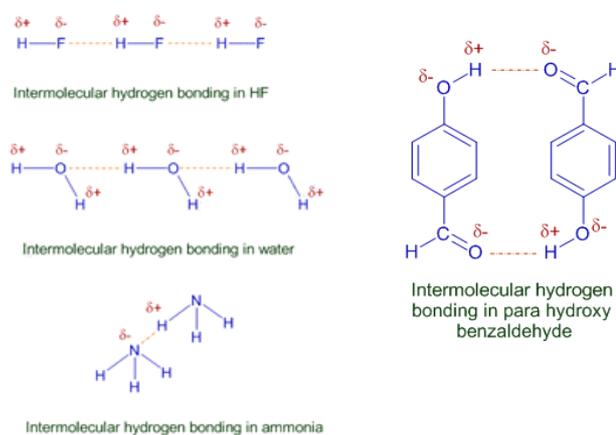
a) Intramolecular hydrogen bonds

Intramolecular hydrogen bonds are those which occur within one single molecule. This occurs when two functional groups of a molecule can form hydrogen bonds with each other. In order for this to happen, both a hydrogen donor and an acceptor must be present within one molecule, and they must be within close proximity of each other in the molecule. For example, intramolecular hydrogen bonding occurs in salicylaldehyde and o-nitrophenol etc.



b) Intermolecular hydrogen bonds

Intermolecular hydrogen bonds occur between separate molecules in a substance. They can occur between any numbers of like or unlike molecules as long as hydrogen donors and acceptors are present in positions in which they can interact. For example, intermolecular hydrogen bonds can occur between NH_3 molecules alone, between H_2O molecules alone, or between NH_3 and H_2O molecules, or between two p-hydroxy benzaldehyde. Eg.



10.6 Importance of intra and inter-molecular hydrogen bonding

Abnormal values of vapour pressure, osmotic pressure, surface tension, freezing point depression and elevation of boiling for compounds such as water, ammonia, formic acid, formaldehyde, hydrogen cyanide, etc., are indicated by whether they are associated through intra molecular or inter molecular hydrogen bonding

- i) The formation of the associated molecules of the hydrides of N and O i.e., (NH_3 and H_2O) is due to the existence of inter-molecular hydrogen bonding in NH_3 and H_2O molecules. Their formation can be shown as follows.
- ii) Cl, Br, and I are not so strongly electronegative as F therefore the molecules HCl, HBr, and HI do not behave as dipole. In these molecules the shared electron pair doesn't lie so far away from the H atom, hence it does not attract Cl, Br and I atoms of the neighbouring HCl, HBr and HI molecule. Thus there is no significant H-bonding is possible between these molecules. Hence KI.HI, KCl.HCl, KBr.HBr such associated molecules do not exist.
- iii) Cupric sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). In $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ one of the molecules of water of crystallization is different from the other four molecules and this suggests that the molecular formula is $\text{Cu}(\text{H}_2\text{O})_4\text{SO}_4 \cdot \text{H}_2\text{O}$. In the crystal structure of this compound each Cu^{2+} ion is surrounded octahedrally by six O-atoms. Four of which are from four water molecules and the two are from SO_4^{2-} ion. Thus four water molecules are associated with Cu^{2+} ion as co-ordinated water and remaining one molecule is held to SO_4^{2-} ion.
- iv) Meta and parahydroxy benzaldehyde and nitrophenol are less volatile than the corresponding ortho isomers. This is because the former molecules are associated through intermolecular hydrogen bonding whereas the latter molecule is associated through intramolecular hydrogen bonding. The intramolecularly hydrogen bonded substances are more soluble in organic solvents and have lower melting and boiling points than intermolecularly hydrogen bonded isomers.
- v) When intramolecular hydrogen bonding links the two groups of a compound to form a stable ring structure as in the case of o-hydroxy benzaldehyde, the characteristic frequency of –OH group disappears in its infrared spectrum. The spectra of meta- and para hydroxyl benzaldehyde however show this line because in these isomers no such ring formation occurs.

10.7 Detection of Hydrogen bonding

The various spectroscopic techniques such as (FTIR), proton magnetic resonance (PMR), electronic etc...., have been used to detect the presence of hydrogen bonding in molecules.

The most important experimental evidence for hydrogen bonding is the high values of melting and boiling points and heat of vapourization of HF, H₂O and NH₃ as compared to the hydrides of other elements

Example, boiling point of CH₄ is -164⁰, NH₃ is -33⁰, H₂O is 100⁰, HF is 20⁰, SiH₄ is -112⁰, PH₃ is -88⁰, H₂S is -61⁰

1. Infrared spectroscopy

When a complex of type A-H.....X containing hydrogen bond is formed, several changes are observed in the IR spectra of the compound. To mention few,

a. The absorption bands due to H –H stretching vibrations are found to be shifted to lower frequency by about 30cm⁻¹ to several hundred cm⁻¹ or even more. This shift is because of weakening of the force constant associated with A—H bond, due to the formation of hydrogen bond.

b. IR spectroscopic technique can also be used to distinguish the presence of intermolecular and intramolecular hydrogen bonding. The frequency of absorption for free -OH stretching is found to be 3600 cm⁻¹. If such -OH group forms intramolecular hydrogen bonding, an additional band appears around 3300cm⁻¹. The increase in temperature or dilution of solution, weaker the intensity of the band near 3300 cm⁻¹ and increases the same around 3600 cm⁻¹. If an intramolecular hydrogen bond is formed within the same molecule, as in salicylaldehyde, the signal corresponding to free –OH around 3600cm⁻¹ totally disappears and the only band which observed is at 3300 cm⁻¹.

2. Proton magnetic resonance (PMR)

Because of formation of hydrogen bond in the molecule, it modifies the electron density around the proton of A-H group and hence its shielding also. In most of the cases because of the hydrogen bonding shielding around proton decreases (because of drift of electron density towards the more electro negative atom) and hence one can observe the shift towards the lower magnetic field i.e deshielded range/ down field range or higher chemical shift value. If the hydrogen bonding is of intermolecular type the shift is concentration dependent and intramolecular type, it is concentration independent.

3. *Electronic spectroscopy*

UV –Vis spectra (200-800nm) involves the excitation of electrons in energy levels. Experimentally it has been observed that, electronic transitions are shifted to blue region (hypsochromic shift) when the chromophores is involved in hydrogen bonding as an acceptor and are shifted to red region (bathochromic shift) when chromophores acts as donor.

10.8 Properties and effects of hydrogen bonds

When we consider the boiling points of molecules, we usually expect molecules with larger molar masses to have higher normal boiling points than molecules with smaller molar masses. This, without taking hydrogen bonds into account, is due to greater dispersion forces. Larger molecules have more space for electron distribution and thus more possibilities for an instantaneous dipole moment.

We see that H₂O, HF, and NH₃ each have higher boiling points than the same compound formed between hydrogen and the next element moving down its respective group, indicating that the former have greater intermolecular forces. This is because H₂O, HF, and NH₃ all exhibit hydrogen bonding, whereas the others do not. Furthermore, H₂O has a smaller molar mass than HF but partakes in more hydrogen bonds per molecule, so its boiling point is consequently higher.

i) Viscosity

The same effect that is seen on boiling point as a result of hydrogen bonding can also be reflected in the viscosity of certain substances. It has been observed that, those substances which are capable of forming hydrogen bonds tend to exhibit a higher viscosity than those that do not. Substances which have the possibility for multiple hydrogen bonds exhibit even higher viscosities.

10.9 Consequences of intermolecular hydrogen bonding

1) The boiling point, melting point, sublimation point as well as enthalpy of vaporization of compounds increase due to intermolecular H-bonding.

E.g. The boiling point of H₂O is high (373 K) due to intermolecular hydrogen bonding and hence it exist as liquid at room temperature, whereas H-bonds are absent in H₂S and hence it has low boiling point and exists as a gas at room temperature.

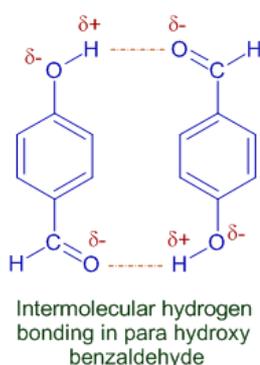
Though sulfur is an electronegative element, it cannot form hydrogen bonds due to larger size. There is no ample charge density on either sulfur or hydrogen to make a H-bond.

2) The solubility of compounds, showing intermolecular H-bonding, in water increases due to formation of intermolecular H-bonds with water.

E.g. Ethyl alcohol, methyl alcohol, ammonia, HF, acetic acid etc., are fairly soluble in water due to their ability to form intermolecular hydrogen bonds with water molecules.

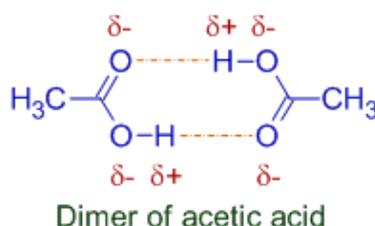
3) Due to intermolecular H-bonding, para isomers have higher boiling points and are fairly soluble in water. Therefore they cannot be separated by steam distillation.

E.g. Para hydroxy benzaldehyde has high boiling point and is more soluble in water, than its ortho isomer, due to intermolecular H-bonding and hence cannot be separated by steam distillation.



4) Some molecules exist as dimers or trimers or polymers in non-aqueous medium or in vapor state due to strong intermolecular H-bonding.

E.g. Acetic acid exists as dimer in benzene.



10.10 Consequences of intra-molecular hydrogen bonding

1) The boiling point, melting point and solubilities of isomers containing intra-molecular hydrogen bonds are lower than their isomers showing intermolecular H- bonds.

E.g. The boiling point and solubility of o-hydroxy benzaldehyde (salicylaldehyde) are lower than those of p- hydroxy benzaldehyde. In ortho hydroxy benzaldehyde, there are intra-molecular hydrogen bonds, whereas para hydroxy benzaldehyde forms inter molecular H-bonds. Hence ortho hydroxy benzaldehyde is steam volatile and can be separated easily from other isomers by steam distillation.

In general, boiling point, melting point and solubility in water are lower for ortho isomers due to intra-molecular hydrogen bonding when compared to their para isomers. This also explains why p-nitro phenol has higher boiling point than that of the o-nitro phenol.

10.11 Illustrations of hydrogen bonding

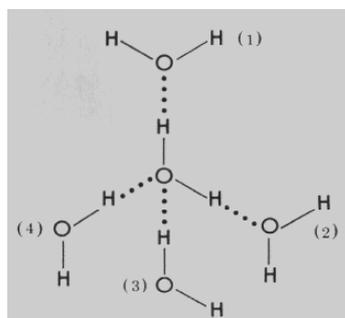
Unique Properties of Water

Water has some unique properties. Two of these are:

1. Density in the solid state (ice) is less than that in the liquid state. This is quite unusual as in most substances density in the solid state is higher than that in the liquid state.
2. Further water contracts when it is heated in-between 0°C to 4°C. This is again quite unusual as most substances expand when they are heated in all temperature ranges.

Both these peculiar properties which are due to hydrogen bonding are discussed below:

1. In ice, the hydrogen bonding between H₂O molecules is more extensive than in liquid water. A substance in solid state has a definite structure and the molecules are more rigidly fixed relative to one another than in liquid state. In ice, the H₂O molecules are tetrahedrally oriented with respect to one another as shown in the figure.



At the same time, each oxygen atom is surrounded tetrahedrally by four hydrogen atoms, two of these are bonded covalently and the other two by hydrogen bonds.

The hydrogen bonds are *weaker* and, therefore, *longer* than the covalent bonds. This arrangement gives rise to an *open cage-like structure*, as shown in the figure. There are evidently a number of 'holes' or open spaces in this structure. These 'holes' are formed because the hydrogen bonds holding the H₂O molecules in ice are *directed at certain definite angles*. In liquid water such hydrogen bonds are fewer in number. Therefore, as ice melts, a large number of hydrogen bonds are broken. The molecules, therefore, move into the 'holes' or open spaces and come closer to one another than they were in the solid state. This results in a sharp increase in the density. The density of liquid water is, therefore, higher than that of ice.

2. As liquid water is heated from 0° to 4°C, hydrogen bonds continue to be broken and the molecules come closer and closer together. This leads to *contraction*. However, there is also some expansion of water due to rise in temperature as in other liquids. It appears that upto 4°C, the former effect predominates and hence there is net *contraction in volume*. Above 4°C, however, the normal expansion effect, due to rise in temperature, predominates and hence the volume increases as the temperature rises.

density of ice is less than water

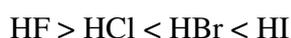
Solid water (ice) has less density than water due to stable hydrogen bonding which forces the crystalline structure to be very open (hexagonal type of) creating some extra interstitial space. Hence ice occupies more volume and hence less density than water.

Boiling points of hydrides of 15, 16 & 17 groups

The boiling points of compounds increase with increase in the molecular weight since the van der Waal's forces of attraction also increases with increase in the size of molecule.

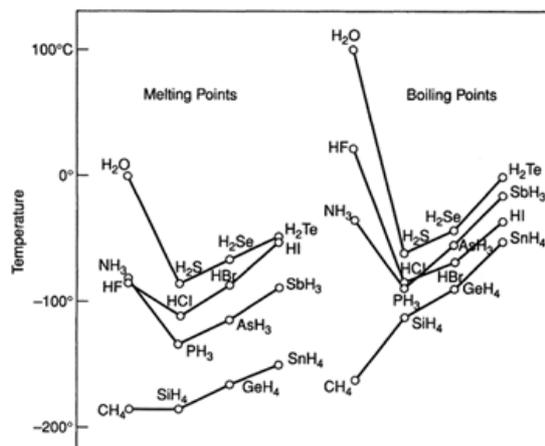
Hence we expect smooth increase in the boiling points of hydrides down the group. However, contrary to the expectation, the BP's of hydrides of group 15, 16 and 17 of the periodic table, is decreased from the first member to the next and then shows regular increment while going down in each group.

The trend in BP's of hydrides of group 15, 16 and 17 is in the order as mention below:



The unusual higher boiling points of NH_3 , H_2O and HF are due to intermolecular hydrogen bonding. However the second hydride in each group i.e. PH_3 , H_2S and HCl have low boiling points since they cannot form H-bonds due to larger size of central atoms which cannot get significant charge density to interact with a δ^+ hydrogen atom even though they are also electronegative elements.

The boiling points and melting points of various molecules containing hydrogen is given in the following diagram.



Boiling points and solubility of alcohols and ethers

Alcohols, R-OH can form intermolecular hydrogen bonds due to presence of -OH group that acts as donor group for H-bonding, whereas ethers, R-O-R lack such groups and cannot exhibit H-bonding. Hence alcohols possess high boiling points and are fairly soluble in water. However, ethers show lower boiling points than their isomeric alcohols and are sparingly soluble in water.

Comparison of boiling points of HF and H₂O

H₂O has more boiling point than HF even though the H-bonds in HF are stronger and molar mass of HF is greater. Because (1) In H₂O, there are twice the numbers of hydrogen bonds per molecule than in HF. (2) HF exists as (HF)₆ cluster of molecules even in vapor state. Hence it requires less energy for transition from liquid state to vapor state. Less number of bonds has to be broken while liquid HF is converted to gaseous HF.

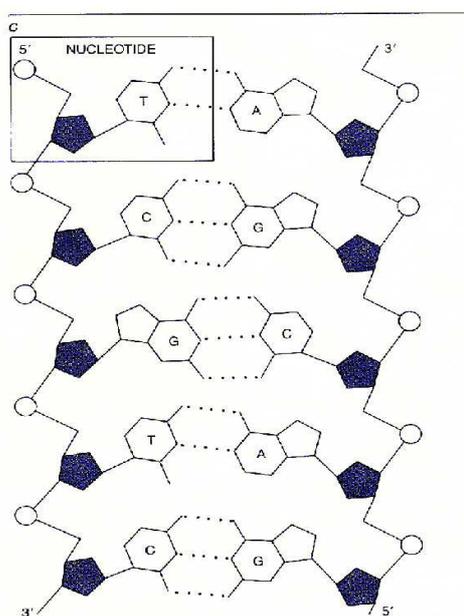
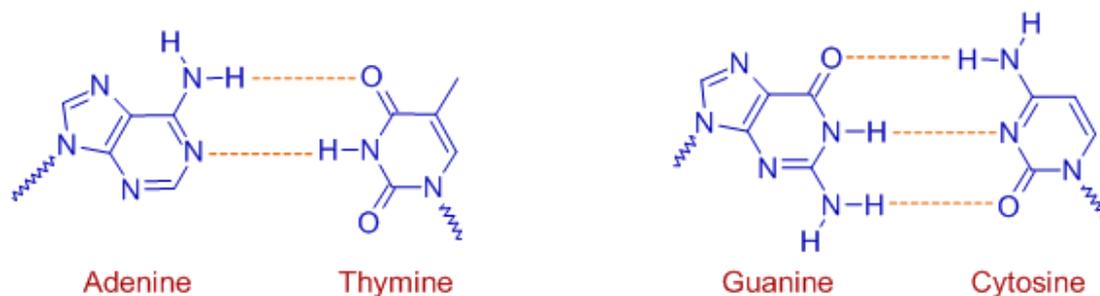
Thus, the boiling point of H₂O is higher than HF. Because of this, perhaps water is used as a universal solvent to sustain living organisms in this universe.

Hydrogen bonding in DNA

H-bonds play a major role in the formation of double helical structure of DNA. The hydrogen bonding between base pairs are responsible for the double stranded structure and those between phosphates cause the DNA strand to twist.

In DNA, it is observed that Adenine (A) always pairs with Thymine (T) and Guanine (G) always pairs with Cytosine (C) and hence the number of Adenine molecules is always equal to the number of Thymine molecules and the number of Guanine molecules is same as that of Cytosine molecules in DNA.

It is because; A forms two H-bonds with T, whereas G forms three hydrogen bonds with C. Other combinations will result in less number of H-bonds.



Hydrogen bonding in DNA molecule

Hydrogen bonding in Proteins

The hydrogen bonds also play major role in the secondary and tertiary structures of proteins. The oxygens of carboxylic group and hydrogens of amide group participate in the H-bonding and confer stable and specific structural conformations to the proteins. Many carbohydrates like mono and disaccharides are soluble in water due to formation of intermolecular H-bonds with water. For example, glucose, fructose, sucrose, maltose, lactose etc. are fairly soluble in water.

Some polysaccharides also show strong affinity with water and form lyophilic colloids. E.g. Starch

The fibrous nature of cellulose and extra ordinary strength of nylon are due to the formation of hydrogen bonds.

10.12 Summary of the unit

The covalency of hydrogen is limited to one because only two electrons can be accommodated in the first shell. Therefore the possibility of hydrogen being bivalent in hydrogen bonded compounds is unlikely. Hydrogen bond is basically purely electrostatic in nature. Covalent bond formation between H and strongly electronegative atom X results a strong dipole with X as the negative end and H as positive end. A second electronegative atom Y attached to another atom or molecule will also become the negative end of a dipole. The two dipoles with facing of opposite charge end close together because of electrostatic attraction. The presence of lone pair electrons on the electronegative atoms plays an important part in determining the strength and direction of the hydrogen bonds. The hydrogen bond formation is indicated by the fact that a hydrogen bond $X-H\cdots Y$ is formed most readily if X and Y have high electronegativities. The ability of hydrogen bond formation by X-H with another atom Y increases from C-H through N-H and O-H to F-H. And it decreases passing from O-H to S-H and from F-H to Cl-H. Solubility and miscibility of many organic solvent in water is readily explained on the basis of hydrogen bonding. The complete miscibility of $[(CH_3)_2O]$ and slight miscibility of $[(CH_3)_2S]$ in water is explained by the fact that there is much greater hydrogen bonding ability in dimethyl ether due to greater electronegativity of oxygen than sulphur in dimethylsulphide.

Hydrogen bonding is important in investigating molecular association, crystal structure and spectra. Analysis of many compounds is based on the formation of hydrogen bonding. Hydrogen bonding plays a very significant role in biochemical processes.

10.13 Key words

Hydrogen; Intramolecular; Intermolecular; Infrared spectroscopy; Proton magnetic resonance; Electronic spectroscopy.

10.14 References for further study

1. Concise inorganic chemistry – J D Lee , 5th Ed' n , ELBS - 1996.
2. Inorganic chemistry- principles of structure and applications. Huhey Keither and Keither 4th Ed' n , Pearson education - 2006
3. Inorganic chemistry – Sharpe , 3rd Low price Ed'n - 2005.
4. Principles of inorganic chemistry – Puri ,Sharma , Khalia,-2008
5. Solid state chemistry and its applications – A R west, John Wiley and sons - 1998.

10.15 Questions for self understanding

- 1) What is hydrogen bond?
- 2) Explain the conditions for hydrogen bond formation
- 3) Write a note on Strength of hydrogen bond
- 4) What are the types of hydrogen bond exists? Discuss in brief with example.
- 5) Explain the importance of intra and inter-molecular hydrogen bonding.
- 6) Discuss in brief about detection of hydrogen bonding.
- 7) Explain properties and effects of hydrogen bonds.
- 8) What are the consequences of intermolecular hydrogen bonding?
- 9) What are the consequences of intra-molecular hydrogen bonding?
- 10) Explain the biological importance of hydrogen bonding.

Unit - 11**Structure**

- 11.0 Objectives of the unit
- 11.1 Introduction
- 11.2 Perfect and imperfect crystals
- 11.3 Defects in Stoichiometric crystals
 - 1) Schotky defect
 - 2) Frenkel defect
- 11.4 Consequences of Schotky and Frenkel defects
- 11.5 Defects in the non stoichiometric compounds
 - 1) Metal excess defect
 - 2) Metal deficiency defect
- 11.6 Conductivity in ionic Solids
- 11.7 Ionic conduction in solid state
- 11.8 Summary of the unit
- 11.9 Key words
- 11.10 References for further study
- 11.11 Questions for self under standing

11.0 Objectives of the unit

After studying this unit you are able to

- ❖ Identify Perfect and imperfect crystals
- ❖ Reasoning for defects in stoichiometric crystals
- ❖ Explain and identify the difference between Schotky defect and Frenkel defect
- ❖ Reasoning for defects in the non stoichiometric compounds
- ❖ Explain and identify the difference between Metal excess defect and Metal deficiency defect
- ❖ Explain Conductivity in ionic Solids

11.1 Introduction

simple crystals of inorganic compounds consists of positive and negative ions packed in such a way that oppositely charged ions are as near as possible and the ions of the same charge are separated as far as possible. Such an arrangement provides the maximum attractive forces and the minimum repulsive forces. The essential feature of crystalline solids is that constituent molecules, ions or atoms are arranged in a completely regular three dimensional pattern. Since the atom or ions have a considerable degree of thermal variations, the crystalline state is far from static and the pattern is seldom perfect. Many of the most useful properties of solids are related to the thermal vibrations of atom, the presence of impurities and the existence of defects.

11.2 Perfect and imperfect crystals

Crystalline materials are made up of solid regions of ordered matter. These regions are known as crystals. *A perfect crystal is one in which all the atoms are at rest on their correct lattice positions in the crystal structure.* Such perfect crystal can be obtained hypothetically, only at absolute zero. At all real temperature, crystals are considered to be imperfect.

Apart from the fact that, atoms are vibrating (which may be considered as one form defect) it has been observed that the number of atoms/ions are found to misplaced/missing in the real crystal. Such phenomenon introduces defect in the perfect crystal, wherein the regular arrangements of atom/ions are situated as per the ideal requirement of the crystal structure.

In some crystals, it has been observed that the number of defects present is very small, may be less than 1%. In other words, in a crystal lattice the atoms /ions have considerable degrees of thermal vibrations the crystalline state is far from static and hence the pattern is seldom perfect one.

The number “n” of such defects present per cm^3 at a given temperature T (absolute scale) is given by

$$n = Ne^{-w/2R}$$

Where,

N= total number of sites per cm^3

W= work energy required to produce a defect, and

R= gas constant

In general defects have been classified into

1. Defects in Stoichiometric crystals
2. Defects in non Stoichiometric crystals

11.3 Defects in Stoichiometric crystals

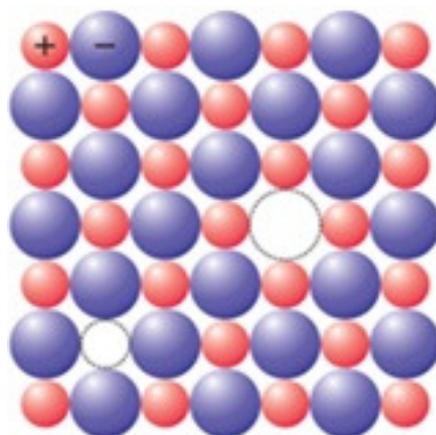
Stoichiometric crystals are those crystals in which the number of positive ions is exactly in the same ratio as indicated by their chemical formulae.

Eg-In AB crystal it has got equal number of A^+ and B^- ions. In such type of crystals generally two types of defects are observed. They are

1. Schotky defect
2. Frenkel defect

1) Schotky defect

It arising because of formation of holes in the crystal lattice or some of the lattice points is unoccupied. Hence hole is created because of missing of one positive ion and one negative ion in the crystal lattice, as shown below.

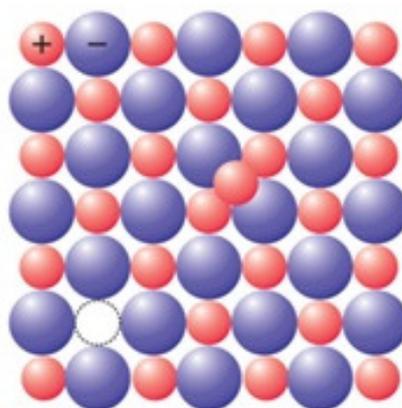


Schottky defect

Because in this type of defect, crystal will remain neutral since the number of positive ions and number of negative ions missing in the lattice points are the same. In general Schotky defects appears in ionic compounds having high coordination number 6 or 8, where, in radius ratio r_+/r_- is not far below unity. In such cases positive and negative ions will have more or less nearly same size eg NaCl, CsCl, KCl, KBr etc. .

2) Frenkel defect

This defect arises when an ion occupies an interstitial position between the lattice points, as shown in the fig.



Frenkel defect

Here, the ion which should have been occupied the lattice site, occupies the interstitial position and consequently hole has been created in the lattice. Still, the crystal remains the neutral as the numbers of positive ions are the same as that of negative ions.

Frenkel defect generally favored in the compounds in which the anions are much larger than cations and in such cases the radius ratio r_+/r_- is low. The coordination number in such types of compounds is 4 or 6. Hence, fewer attractive forces between the oppositely charged ions are broken by causing movement of a positive ion from its appropriate site to the interstitial position. Further, in such compounds, small +ve ions are highly polarizing and large negative ions readily polarized and thus such compounds are having some covalent character.

In silver bromide AgBr, some of the Ag^+ ions are generally missing from its regular position and thus occupy the interstitial position in the lattice. The crystals where one can observe the Frenkel defect are ZnS, AgI, AgCl etc..

The energy required to form either Schotky defect or Frenkel defect depends on the work (energy) needed to form the defect and the temperature.

The number of defects formed is relatively small and it has been observed that , at room temperature, NaCl has only one defect in 10^{15} lattice sites and this value rising to one in 10^6 sites at 500°C and one in 10^4 site at 800°C .

11.4 Consequences of Schotky and Frenkel defects

1. The closeness of similar charges brought about by the Frenkel defects, generally tends to increase the dielectric constant of the crystals.
2. The presence of holes in the crystal generally lowers the density as well as lattice energy (i.e. stability) of the crystal.
3. Because of both type of defects in the crystals, it may conduct electricity to small extent. Electrical conductivity in chemically pure, stoichiometric semiconductors is known as intrinsic semiconductors. In this case, such type of conduction occurs through ionic mechanism and when an electric field is applied, a nearby ion moves from its lattice 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 there by migrates from one end to another end. Hence it conducts the electricity in the entire crystal.

Crystals with Frenkel defect have only one type of hole but crystals containing Schotky defects have holes from negative and positive ions and conduction may due to either one type of hole or both types. Migration of smaller ions (generally positive ion) in to the appropriate holes is favored at low temperature, since moving a small ion requires low energy. However, migration of both types of ions is opposite directions, generally occurs at high temperatures'.

It has been observed that alkali halides conduct by the migration of cations, generally at temperature below 500°C . But at high temperature both anions and cations migrate.

11.5 Defects in the non stoichiometric compounds

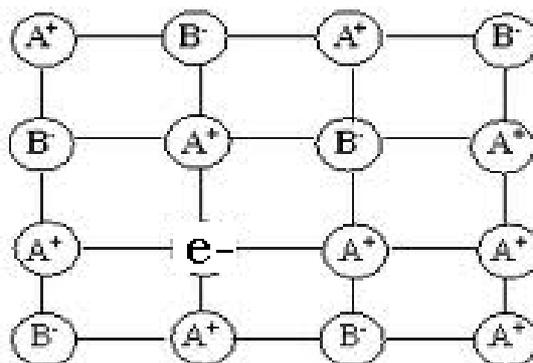
In non stoichiometric compounds generally the number of negative ion and positive ions present in such complexes are different from that of their ideal chemical formula, i e. there may either excess of positive charge or negative charge in the crystal. But crystal behaves as neutral. If negative charge is in excess it is balanced by extra positive ions and if positive charge is in excess, it is balanced by the presence of extra electrons. Hence the crystal structure appears to be irregular and hence forms the basis for defects. The defects in such crystal are known as non stoichiometric defects.

In non stoichiometric compounds generally there are two types of defects

1. Metal excess defects
2. Metal deficiency defects

3) Metal excess defect

In this case the negative ion may be absent from its crystal lattice leaving a 'hole', which is occupied by an electron and hence electrical balance, is maintained as shown in the fig.

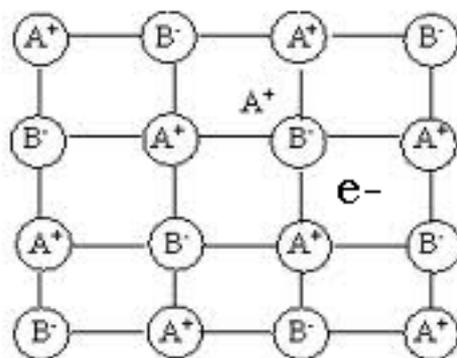


Metal excess defect because of absence of anion

It has been observed that in these crystals, defects formed are very similar to Schottky defect, but only hole is formed instead of formation of pair. Further this type of defect is generally exhibited by the crystals which would expect from Schottky defect. When compounds like NaCl, KCl are heated in the excess of their constituents metal vapors, they become deficient in metal ions, and such compounds may be represented by $AX_{(1-\delta)}$, where the δ value is very small, The non stoichiometric form NaCl is yellow and that of KCl is lilac in color.

The crystal lattice has vacant anion sites, which are occupied by electrons. Anionic sites occupied by electrons in this way is generally called F-center (F is an abbreviation for *Farbe*, the word for color). These F-centers impart the color to the compound and the more F-centers are present, more the intensity of the color of the compound. Compounds containing F-centers are paramagnetic in nature, as they contain more un paired electron occupying in vacant sites. When materials with F-center irradiated with light, it has been observed that such materials will behave as photoconductors. When they absorb sufficient light energy, the electron in such compound will be promoted to conduction band, rather similar to the conduction band present in metals. Since conduction is by electrons, such materials act as n -type semiconductors.

Metal excess defects can also be caused because an ion occupies an interstitial position in the lattice, and to maintain neutrality an electron is also present in the interstitial site, as shown in the fig.



Metal excess effects caused by interstitial cations

This type of defect is quite similar to Frenkel defect in that ions occupy interstitial position, but there are no 'holes' and there are also interstitial electrons. The compounds like ZnO, CdO, Fe₂O and Cr₂O₃ one can encounter such type of defects.

In this type, when defect oxide is heated in dioxygen, and then cooled to room temperature, its conductivity is found to decrease. This is because of the fact that when such compounds are heated, the dioxygen oxidizes some of interstitial ions and subsequently remove interstitial electrons and hence reduce the conductivity.

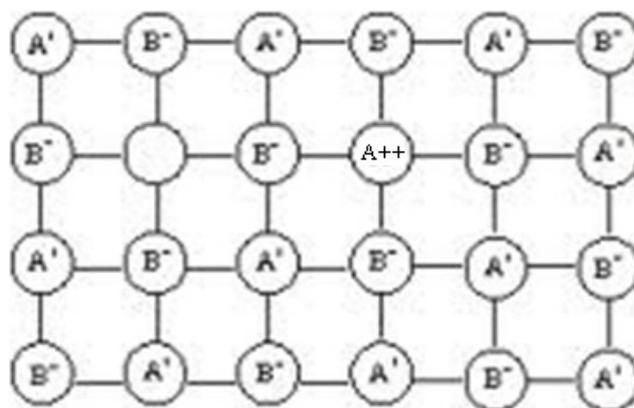
Crystals with either type of metal excess defect contain free electrons and if they migrate they conduct electric current. Since there are only a small number of defects, only few electrons are available to conduct electricity and magnitude of the current is relatively very small compare to metals. This type of defect materials will behave as semiconductors and mechanism of conduction is by normal electrons, and such semiconductors are n-type semiconductors.

4) **Metal deficiency defect**

Such type of defect is generally exhibited by the compounds, where metal can exhibit variable valency and hence generally occurs in compounds containing transition metal ions.

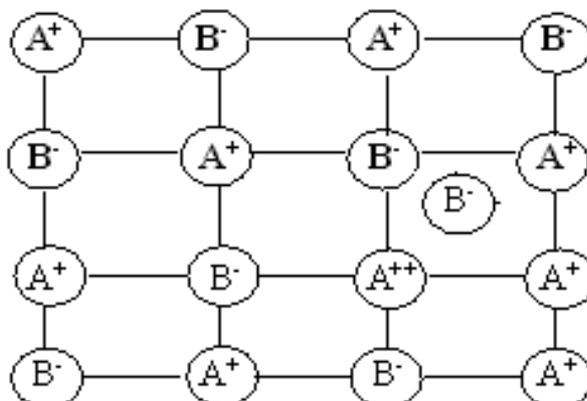
There are two possible ways in which metal excess defect can occur:

1. In the first case, one of the positive ion may be missing from its lattice site. The extra negative charge caused may be balanced by one of the nearby metal ions by acquiring an additional positive charge, as shown in the fig



Hence this type of defect is generally exhibited by transition metal compounds like FeO, FeS, CuI etc.. If Fe^{+2} is missing, in the lattice site of FeO, then there may be Fe^{+3} ions in the crystal to balance the electrical charge.

In the second case, an extra negative ion may occupies the interstitial position. The extra negative charge is balanced by acquiring extra charge by one of the adjacent metal ions, and this metal ion should exhibit a variable valency and may be transition metal ion as shown in the fig.



The crystals with metal deficiency defect are also behaved as semiconductors. The conductivity is because of hopping of electron from A^+ to A^{++} metal ions [i.e. if lattice ion contain A^+ and A^{++} metals ions, then electron hops from A^+ ion to the positive centre, (an A^{++} ion), and the original A^+ ion becomes a new positive centre. Hence there is an apparent movement of A^{++} . As a result of series of electron hops, an electron may be transferred from one end to another, and at the same time a positive 'hole' migrates in the opposite direction. Hence the conduction is by a positive hole or p-type conduction.

If defect oxide of this type is heated in dioxygen, its room temperature conductivity increases as dioxygen oxidizes some of the metal ions, and hence increases the number of positive centers i.e 'holes' are made available for conduction. Hence conductivity increases.

11.6 Conductivity in ionic Solids

In a material in general electrical conduction occurs because of long range migration of either electrons or ions (cations/anions). But generally in many cases the conduction is only by electrons. However, in many inorganic materials it has been observed that, in the same material the conduction is both by ions and electrons.

In solid materials, one is usually interested in specific conductivity, σ , which is the conductivity of the crystal or pellet, that has a cell constant of unity (i.e. unit cross sectional area and unit length) and the associated unit are ohm cm^{-1} and S m^{-1} where 1 Siemen, $\text{S} = 1\text{ohm}^{-1}$.

In general for any material, the specific conductivity, σ is given by

$$\sigma = \sum_i n_i e_i \mu_i$$

where,

n_i = number of charge carriers/unit volume

e_i = their charge, and μ_i = mobility of ions (carriers)

(e is the charge of an electron.)

The typical conductivity range of material is given below

Conductor	Material	Conductivity [σ , ohm cm^{-1}]
Ionic	Ionic crystals	$< 10^{-18} - 10^{-4}$
	Solid electrolytes	$10^{-3} - 10^1$
	Strong liquid electrolytes	$10^{-3} - 10^1$
Electronic	Metals	$10^1 - 10^5$
	Semiconductors	$10^{-5} - 10^2$
	Insulators	$< 10^{-12}$

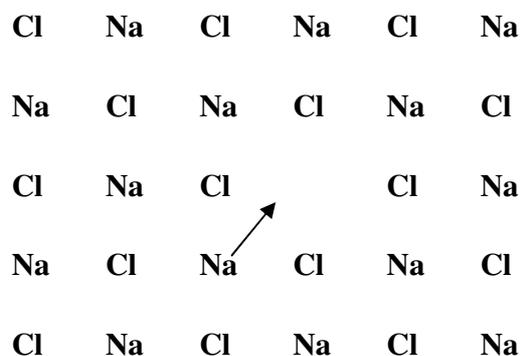
The conductivity (either ionic or electronic) of material is temperature dependent. For all materials, except metal, the conductivity increases with the rise in temperature. In general, migration of ions does not occur to any appreciable extent in most ionic and covalent solids such as oxides and halides, because in such solids, the atoms tend to be essentially fixed on their

lattice sites and can only move through crystal defects. At high temperatures, where the defect concentration is relatively large and thus possesses higher thermal energy and hence the conductivity is considerably high. Eg. The conductivity of NaCl crystal at is 800 °C, (just below its melting point) is $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ whereas at room temperature, it is found to be an insulator. Further, it has been observed that, in some solids, ions can move relatively freely and such materials are known as “solids electrolytes”, “fast ion conductors” or “super ionic conductors”. Such materials generally have special crystal structures in that with open tunnel or layers through which the mobile ions may move. Such solid state ionic conductors are very important from an industrial view point as well as in diverse industrial applications such as in the fabrication of fuel cells, dry batteries, electrochemical cells. The examples for such type of materials are $\text{Na}_3\text{Zr}_2\text{PSiO}_{12}$, NASICON (Sodium Superionic conductors). $\text{Li}_{14}\text{ZnGe}_4\text{O}_{16}$ LISICON (lithium Superionic conductors) RbAg_4I_5 , AgI , $\text{Ag}_2\text{Se-Ag}_3\text{PO}_4$, lime stabilized zirconia ($\text{Ca}_x \text{Zr}_{1-x} \text{O}_{2-x}$: $0.1 \leq x \leq 1.2$ etc.

11.7 Ionic conduction in solid state

Ionic conductivity is nothing but ion transport under the influence of an external electric field. Now the question is how ions are created/ generated in the ionic solid/crystal.

In crystal of alkali halides eg. NaCl, the cations are usually more mobile than anions. In the NaCl structure as shown in the below figure,



Migration of cation vacancies (Na^+ ions) in NaCl

Wherein Na^+ ion is moving into adjacent vacant cation site and thereby leaving its own site vacant. The Na^+ ion that has moved can't travel further vacant site. However the cation vacancy may continue to move, because it is always surrounded by twelve Na^+ ions. Hence one can assume that in such ionic crystals the cation vacancies are the main current carriers in general

and Na^+ ions in particular in NaCl. In NaCl, anion vacancies may also appear but it is relatively less mobile than cation vacancies.

The temperature dependence of ionic conductivity is given by the equation

$$\sigma = Ae^{(-E/RT)}$$

Where, E = activation energy.

R= gas constant

T = Temperature in absolute scale

A = constant

The magnitude of ionic conductivity in NaCl depends on the number of cations vacancies present which in turn depends very much on purity and thermal history of the crystals. The vacancy and generally created by one of the two methods. On heating the crystal, the number of vacancies present in thermodynamic equilibrium increases and this number is intrinsic to pure crystals.

Secondly by introducing aliovalant impurities in the system: vacancies may be created, to maintain the charge balance. eg. By doping MnCl_2 into NaCl and at equilibrium, a solid solution is formed with formula, $\text{Na}_{(1-2x)}\text{Mn}_x\text{Cl}$, where for each Mn_x ion, there will be a corresponding cation vacancy. Such vacancies are extrinsic because they are not present in the pure NaCl crystal.

In general at low temperature, the number of thermally generated vacancies is very small and (unless the crystal is very pure) is much less than the concentration of extrinsic vacancies. The change over from extrinsic to intrinsic behavior occurs at higher temperature that is determined generally by concentration of impurities.

11.8 Summary of the unit

Stoichiometric compounds have positive and negative ions exactly in the same ratios indicated by their chemical formula. They obey the law of constant composition which states that the same chemical compound always contains the same elements in the same composition by weight. Two types of defects are observed in stoichiometric compounds, they are Schottky and Frenkel defect. At the absolute zero crystals tend to have a perfectly ordered arrangement. As the temperature increases the amount of thermal vibration of ions in their lattice sites increases. If the vibration of the particular ion becomes large enough, it may jump out of its lattice site. The number of defects depends on the temperature hence as temperature increases, great the chance that lattice sites become unoccupied. A schottky defect consists of a pair of holes in the crystal lattice. This

defect occurs mainly in highly ionic compounds where the positive and negative ions are of a similar size. A Frenkel defect consists of a vacant lattice site and the ion which ideally should have occupied the site now occupies an interstitial position. This type of defect is favored by a large difference in size between the positive and negative ions. A consequence of these defects is that a crystalline solid that has defects may conduct electricity to a small extent. Crystal with Frenkel defect has only one type of hole but crystal with Schottky defects has holes from both positive and negative ions. Presence of holes should lower the density of the crystalline solid.

11.9 Key words

Stoichiometric crystals; Schotky defect; Frenkel defect; non stoichiometric; Metal excess defect; Metal deficiency defect.

11.10 References for further studies

1. Concise inorganic chemistry – J D Lee , 5th Ed' n , ELBS - 1996.
2. Inorganic chemistry- principles of structure and applications. Huhey Keither and Keither 4th Ed' n , Pearson education - 2006
3. Inorganic chemistry – Sharpe , 3rd Low price Ed'n - 2005.
4. Principles of inorganic chemistry – Puri ,Sharma , Khalia,-2008
5. Solid state chemistry and its applications – A R west, John Wiley and sons - 1998.

11.11 Questions for self understanding

- 1) What are Perfect and imperfect crystals?
- 2) What type of defects present in stoichiometric crystals?
- 3) What is Schotky defect? Which type of crystal exhibit this defect?
- 4) What is Frenkel defect? Why this defect present these?
- 5) Explain the difference between Schotky defect and Frenkel defect.
- 6) What are the consequences of Schotky and Frenkel defects?
- 7) What is meant by non stoichiometric compounds?
- 8) Write a note on defects in the non stoichiometric compounds.
- 9) Explain in details
 - a) Metal excess defect
 - b) Metal deficiency defect
- 10) What are the difference between Metal excess defect and Metal deficiency defect?
- 11) Explain in brief about conductivity in ionic Solid.

Unit - 12**Structure**

12.0 Objectives of the unit

12.1 Introduction

12.2 Van der Waal's Forces

12.3 Intermolecular forces

1. Ionic forces

2. Dipole forces

3. Hydrogen bonding

4. Induced dipole forces

12.4 Supramolecular Chemistry and Supramolecular Architecture

12.5 Molecular self assembly

12.6 Molecular recognition

12.7 Nature of Supramolecular interactions

1. Ion-Ion interactions

2. Ion -Dipole interactions

3. Dipole–Dipole interactions

4. Dipole–induced-dipole interaction

5. Cation – π interactions

6. π – π interactions

12.8 Applications

12.9 Summary of the unit

12.10 Key words

12.11 References for further study

12.12 Questions for self under standing

12.0 Objectives of the Unit

After studying this unit you are able to

- ❖ Explain intermolecular forces
- ❖ Explain Van der Waal's Forces
- ❖ Explain the supramolecular chemistry and supramolecular architecture
- ❖ Identify significance the molecular self assembly

12.1 Introduction

Molecules attract each other without forming chemical bonds. When this attraction is stronger than the molecule's average kinetic energy, the molecules aggregate and form a condensed phase (liquid, solid, etc.). Most intermolecular forces, or *nonbonded forces*, are electrostatic. This means that the electrostatic potentials around a molecule are a good measure of nonbonded "bond strength" and we can use potential maps to study nonbonded interactions. Although most nonbonded forces are electrostatic, chemists like to distinguish between different types of forces according to the types of charges involved. The strongest nonbonded forces occur when both molecules contain permanently charged, or partially charged, atoms capable of generating large electrostatic potentials. Forces of this type are called *ion-ion*, *ion-dipole*, and *dipole-dipole* forces ("dipole" means any *neutral* molecule containing partially charged atoms capable of generating large potentials). Nonpolar molecules can also generate significant nonbonded forces, but these forces are much weaker (on a per atom basis) than the ones listed above. One important force acts between an ion (or dipole) and a *polarizable* nonpolar molecule (this means a molecule whose electron density cloud changes shape in response to electrostatic forces). The approach of permanently charged ion (or dipole) *induces* temporary changes in the electron density cloud of the polarizable molecule. This leads to forces called *ion-induced dipole* and *dipole-induced dipole* forces. Since these forces rely on a *change* in the electron density cloud, they cannot be assessed using potential maps.

12.2 Van der Waal's Forces

Vander Waal's Forces, intermolecular forces and molecular self assembly, super molecular architectures formed by weak chemical forces

Vander Waal's forces: The forces of attraction between two non bonded atoms are called as the Vander Waals forces .These forces are extremely weak forces (≤ 20 KJ/ mol) compared to the other types of interactions. The liquefaction and eventual solidification of noble gases is

explained by postulating so called Vander Waals forces (the same forces account for the deviation of actual gases from ideal behavior). These are the types of forces essentially operating between the electric dipoles.

In case of noble gases, which clearly have no permanent dipoles, it is suggested that, electron motion around the central nucleus can establish a fluctuating dipoles; and forces are set up by means must be necessarily a weak ones. Further Vander Waal's forces operate between the individual molecular crystals, eg iodine, naphthalene which are characterized by low melting points.

Thus, in general the Vander Waal's forces (or London dispersion forces) are the weak forces present in all atoms, molecules or ions attractive interactions between oscillating dipoles in adjacent atoms.

There is evidence that the Vander Waal's force, completely independent from the normal valance forces exists in real molecules. Some of the facts arising because of Vander Waal's interactions may be summarized as follows

Non ideality of real gases

Joule Thomson effect, where by the gas gets cooled on sudden expansion due to work done against inter molecular forces

The inert gases which are not capable of forming a stable chemical compound can be condensed to liquid. And solid states, where the cohesive force must operative. A similar situation exist for those molecules which are no residual; valance and non polar eg: H_2 , CO_2 , CH_4 , N_2 , O_2 , etc

The Vander Waal's forces may arise mainly from three sources

1. The molecules of some materials although electrically neutral, may possess permanent electric dipole, because of fixed distribution of electric charge in the very structure of some molecules one side of the molecule may have the positive charge and other may be negative charge. The tendency of such permanent dipoles to align with each other results in net attractive force.
2. The molecules that are having permanent dipoles, temporarily distorts the electron charge in other nearby polar or non polar molecules, thereby inducing permanent polarization. Hence an additional attractive force results from the interaction of permanent dipole with neighboring induced dipole.

3. When the molecules do not possess any permanent dipole (eg: In the Nobel gas molecule, argon and organic molecule like benzene) a force of attraction exist between the molecules responsible for condensing to the liquid state at sufficiently low temperature.

The nature of the attractive force in molecules, which requires quantum mechanics for its correct description, it has been recognized (1930) by the Polish-born physicist Fritz London who observe the electron motion within molecules. Further, London pointed out that at any instant the centre of negative charge of the electrons and the positive charge of the atomic nuclei would not be likely to coincide. Hence this fluctuation of electrons makes molecules to have time-varying dipoles. Such time-varying dipoles, or instantaneous dipoles, cannot orient themselves into alignment to account for the actual force of attraction, but they do induce properly aligned polarization in adjacent molecules, resulting in attractive forces. These specific interactions, or forces, arising from electron fluctuations in molecules are (known as London forces, or dispersion forces), and they are present even between permanently polar molecules.

It is evidenced that molecules held together mainly by London dispersion forces melt at comparatively low temperature and the resulting liquid vaporizes at more easily. Example for this type of molecules are the Nobel gases which boils at temperature ranging from -269°C (Helium) to -62°C (Radon) all these elements are mono atomic molecules. The reason for increase of boiling points as we go down the group in noble gases is because of the fact that, the number of electrons increases from helium to radon and also there is a corresponding increase in the radius of the noble gas atoms. If the number of electrons are more, the more distance they can move and hence the bigger the possible temporary dipole thus bigger the dispersion forces. Because of greater temporary dipoles, xenon molecules are stickier than neon molecules. Hence neon molecules will break away from each other at much lower temperature than xenon molecules. Hence neon has a low boiling point than xenon.

In general bigger molecules have higher boiling points than small ones. Bigger molecules have more electrons and more distance over which temporary dipole can develop and hence bigger molecules are stickier -more energy needed to separate.

It is also observed that long chain molecules can develop bigger temporary dipoles due to electron movement than short fat ones (branched molecules) consisting the same number of electrons. Eg. The hydrocarbons molecules butane and 2-methyl propane both have a molecular formula C_4H_{10} with difference in arrangement of atoms. In butane, the carbon atoms are arranged

in a single chain, but in 2-methyl propane has branching with a shorter chain length. Whenever molecules have generally a long thin molecular chain, they can lie close together and hence effective dispersion forces. This explains why butane has higher bp -0.5°C and 2-methyl propane lower bp -11.7°C .

Further, many organic molecules and inorganic molecules with zero dipole moments such as CH_4 (bp -116.6°C), BF_3 (bp -101°C), and SF_6 (sublimes at -64°C) fall into this category. As London forces increase greatly with polarisability, many larger molecules from liquids or even solids at room temperature. Despite of having only this type of attraction between the molecules. Eg; $\text{Ni}(\text{CO})_4$ (bp $=43^{\circ}\text{C}$), CCl_4 (bp 77°C) borazene, $\text{B}_3\text{N}_3\text{H}_3$ (bp $=53^{\circ}\text{C}$) and trimeric phosphazene $\text{P}_3\text{N}_3\text{H}_6$ (mp $=114^{\circ}\text{C}$). Even though, in above examples all the molecules contain very strong covalent bonds during melting or vaporization none of the bonds will be broken (i.e bonds will remain intact), and hence these bonds play no role in determining melting and boiling points.

12.3 Intermolecular forces

The term 'intermolecular forces' are used to describe all the forces, both attractive and repulsive, between groups of neutral molecules or atoms. Forces between atoms within a molecule ('intramolecular forces') are usually called chemical bonds, however there can be forces between atoms in a molecule (particularly large molecules) that are not classified as chemical bonds.

The various physical properties such as melting point, boiling point, vapor pressure, evaporation, viscosity, surface tension, solubility etc. are related to the strength of attractive forces/cohesive forces present between the molecules. These attractive forces are known as Intermolecular Forces.

Intermolecular forces are caused by the attractions and repulsions between the charged particles that make up the atoms in molecules. As two molecules approach each other, the negatively charged electrons in one molecule are attracted to the positively charged nuclei in the other molecule. But at the same time these electrons are repelled by the electrons in the other molecule. This complex combination of attraction and repulsion can result in the temporary distortion of the electron cloud around one molecule so that a weak overall attraction exists between the two molecules. This is called a dispersion force and it exists between all molecules. Basically there are four types of intermolecular forces.

1. Ionic forces

The forces holding ions together in ionic solids are electrostatic forces. Opposite charges attract each other. These are the strongest intermolecular forces. Ionic forces hold many ions in a crystal lattice structure.

2. Dipole forces

Polar covalent molecules are sometimes described as "dipoles", meaning that the molecule has two "poles". One end (pole) of the molecule has a partial positive charge while the other end has a partial negative charge. The molecules will orientate themselves so that the opposite charges attract principle operates effectively.

3. Hydrogen bonding

The hydrogen bond is really a special case of dipole forces. A hydrogen bond is the weak attractive force between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule.

4. Induced dipole forces

Forces between essentially non-polar molecules are the weakest of all intermolecular forces. "Temporary dipoles" are formed by the shifting or deformation of electron clouds within molecules. These temporary dipoles attract or repel the electron clouds of nearby non-polar molecules.

The temporary dipoles may exist for only a fraction of a second but a force of attraction also exist for that fraction of second. The strength of induced dipole forces depends on how easily electron clouds can be distorted.

12.4 Supramolecular Chemistry and Supramolecular Architecture

Supramolecular chemistry is the chemistry of the intermolecular bond, covering the structures and functions of the entities formed by the association of two or more chemical species'. The Supramolecular Chemistry may also be explained in contrast to molecular chemistry, which is predominantly based

Upon the covalent bonding of atoms, supramolecular chemistry is based upon intermolecular interactions, i.e. on the association of two or more building blocks, which are held together by intermolecular bond. Thus supramolecular chemistry is a new and novel domain of chemistry beyond that of convention chemical molecules and focuses the chemical systems made up of a discrete number of assembled molecular subunits or components.

The importance of supramolecular chemistry was established by pioneers D. Jeram (USA), J M Lehn (FRANCE) and C J Pedersen., they shared the Nobel prize in 1987 for the development and use of high selectivity. The selectivity of host –guest complexes in particular in which the host molecule recognizes and selectively binds a certain guest, was cited as an important contribution.

In 1990s, supramolecular chemistry became more sophisticated, with researcher developing molecular machinery and highly complex self assembled structure, sensors and methods of electronic and biological interfacing. During this period electro chemical and photochemical motifs' became integrated in to supra molecular systems in order to increase functionality, research into synthetic self replicating system and work on molecular information. The emerging science of nanotechnology also had a strong influence on the subject with building blocks such as fullerenes nanoparticles and dendrimers becoming involved in synthetic systems.

The concepts in supramolecular chemistry:

12.5 Molecular self assembly

Molecular self assembly is the construction system, without guidance or management from outside the source (other than to provide suitable environment.) the molecules are directed to assemble through non covalent interactions. Further self assembly may be divided into inter molecular self assembly (to form a supra molecular assembly) and intra molecular self assembly (or folding as exhibited by polypeptides and foldamers). Molecular self assembly also allows the construction of larger structures such as micelles, membranes, liquid crystals etc.

12.6 Molecular recognition

Molecular recognition is the specific binding of a guest molecule to a complementary host molecule to form host-guest complexes. In many instances the definition of which species is the host or which is the guest is arbitrary.

The important applications of this field are in construction of new molecular sensors and catalysis.

12.7 Nature of Supramolecular interactions

The various types supramolecular interactions are roughly classified and given the following table and they are the driving forces for formation of Supramolecular structures.

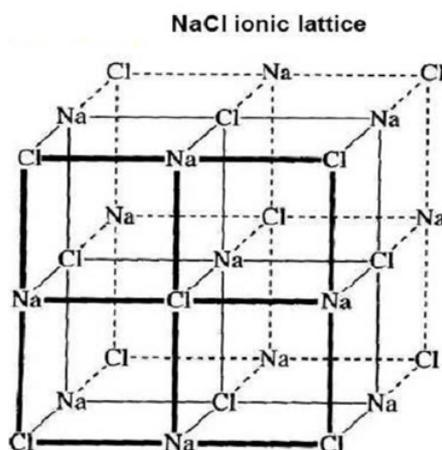
Sl.No	Interaction	Strength (KJ/mol)
1	Ion-Ion	200 – 300

2	Ion - Dipole	50 -200
3	Dipole–Dipole	5 -50
4	Hydrogen bonding	4 - 120
5	Cation - π	5 -80
6	π - π	0 - 50
7	Vander Waal's	< 5
8	Hydrophobic	Related to solvent –solvent interaction energy

Few interactions have been discussed with suitable examples.

7. Ion-Ion interactions

As mentioned earlier, ion-ion interactions are strong intermolecular forces between molecules due to complete separation of discrete opposite charges. Ion has complete charge so attraction between A^- and B^+ is called ion-ion interaction. The thermodynamic properties of electrolyte solutions exhibit marked deviations from ideal behaviour. This is because strong electrolytes are completely dissociated into ions and the deviation from ideal behaviour is due to the operation of electrical interactions between the ions. They are long range (they vary with distance as $1/r$) and are essentially Coulombic. The short range (r^{-6}) ion-ion interaction also exists and this short range effects arising either from incomplete dissociation or ion association. The latter factor becomes important in non-aqueous solutions where the dielectric constant is low. Also in more concentrated ionic solutions ion/solvent interactions become important. The energy of this interaction is comparable to that of energy of covalent bonding

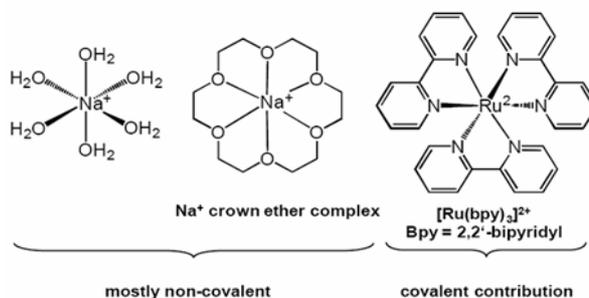


8. Ion -Dipole interactions

An ion-dipole force is an attractive force that results from the electrostatic attraction between an ion and a neutral molecule that has a dipole. The ion-dipole interaction, similarly to van der Waals interactions of neutral molecules, refers to weak noncovalent bonds. It is due to interactions between ions and polar groups of molecules (or induced dipoles). The energy of the ion-dipole bond typically lies within the range of 50-200 kJ/mol. There are two main types of ion-dipole interactions.

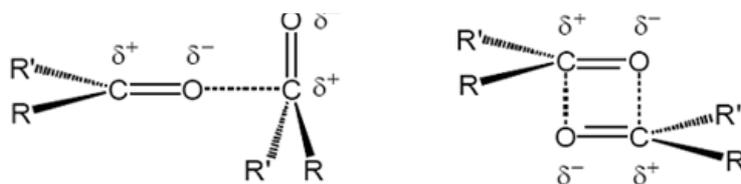
1. Orientation interaction (ion– permanent dipole). Potential of ion-dipole interaction (U), when the dipole can rotate (almost) freely, such as in liquids, the magnitude of interaction is inversely proportional to the fourth power of the distance and to the temperature.

2. Induction interaction (ion – induced dipole). The dipole moment induced by an external field, in this particular case the field of the ion, has permanent orientation determined by the field. It is proportional to the charge of the ion and polarisability of the molecule and inversely proportional to the square of the distance. Correspondingly, the interaction potential is inversely proportional (as in the case of a permanent dipole moment) to the fourth power of the distance and directly proportional to the square of the charge and (isotropic) polarisability of the molecule:



9. Dipole–Dipole interactions

A polar molecule has an electric dipole moment by virtue of the existence of partial charges on its atoms. Opposite partial charges attract one another if two polar molecules are orientated so that the opposite partial charges on the molecules are closer together. Then there will be a net attraction between the two molecules. This type of intermolecular force contributes to the condensation of hydrogen chloride to a liquid at low temperatures. The dipole–dipole interaction also contributes to the weak interaction between molecules in gases. because, although molecules rotate, they tend to linger in relative orientations in which they have low energy—namely, the mutual orientation with opposite partial charges close to one another.



Dipole – dipole interactions in carbonyl compounds

10. Dipole–induced-dipole interaction

The second type of attractive interaction is dipole-induced dipole interaction. It also depends on the presence of a polar molecule. The second participating molecule need not be polar (if it is polar, then the resulting interaction is called the dipole–dipole interaction described above). In the dipole–induced-dipole interaction, the presence of the partial charges of the polar molecule causes a polarization or distortion of the electron distribution of the other molecule. As a result of this distortion, the second molecule acquires regions of partial positive and negative charge, and thus it becomes polar. The partial charges so formed behave just like those of a permanently polar molecule and interact favourably with their counterparts in the polar molecule that originally induced them. Hence, the two molecules cohere. This interaction also contributes to the intermolecular forces that are responsible for the condensation of hydrogen chloride gas.

11. Cation – π interactions

Cation- π interaction is a potent intermolecular interaction between a cation and an aromatic system. Which is viewed as a new kind of binding force and compared with the classical interactions like hydrogen bonding, electrostatic and hydrophobic interactions. Cation- π interactions have been observed in a wide range of biological contexts. In this paper cation- π interactions in biological systems, the experimental and theoretical investigations on cation- π interactions, as well as the research results on cation- π interactions in our group.

Cation- π interactions are ubiquitous in biological systems. Theoretical and experimental investigations have proved that cation- π interactions are central to protein structures and functions, protein-nucleic acid interactions, ligand-acceptor recognition, as well as drug-target binding. This is a very important kind of nonbonding interactions in structural biology. Based on the cation properties, cation- π interactions can be classified into three different types.

- 1) The interaction between inorganic metal cations such as Na^+ , K^+ , Mg^{2+} and Ca^{2+} with aromatic systems
- 2) The interaction between organic cations and aromatic systems

3) The interaction between the atoms possessing partial positive charges (e.g. H in an N—H bond) and aromatic systems. The first class cation- π interaction is mainly involved in the binding of proteins or nucleic acid with inorganic metal cations.

6. $\pi - \pi$ interactions

$\pi - \pi$ interactions takes between aromatic moieties they have consists of both hydrophobic and electrostatic forces. Despite extensive reviews on $\pi - \pi$ interactions, no systematic study of different factors implied in this interaction is done.

Aromatic $\pi - \pi$ interactions between benzene-like chemical groups play a key role in many important scientific phenomena, including the stereochemistry of organic reactions, organic host-guest chemistry and crystal packing, protein folding and structure, DNA and RNA base stacking, protein-nucleic acid recognition, drug design, and asphaltene (heavy crude oil) aggregation and fouling.



12.8 Applications

Supramolecular chemistry has got tremendous applications in materials technology, catalysis, medicines and in other fields including green chemistry, host-guest chemistry, biomimetics etc.

12.9 Summary of the unit

As the name implies non-bonded interactions act between atoms which are not linked by covalent bonds. Intermolecular attractions are the attractions between one molecule and a neighbouring molecule. The force of attraction which holds an individual molecule together are known as intramolecular attraction (ex. Covalent bond). The term 'intermolecular forces' is used to describe all the forces, both attractive and repulsive. The simplest non-bonded interaction is the van der Waals interaction. Electrostatic attraction between electrically-charged particles is the strongest of all the intermolecular forces. The attractive forces that exist between molecules are responsible for many of the bulk physical properties exhibited by substances. Some compounds are gases, some are liquids, and others are solids. The melting and boiling points of

pure substances reflect these intermolecular forces, and are commonly used for identification. Of these two, the boiling point is considered the most representative measure of general intermolecular attractions. Thus, a melting point reflects the thermal energy needed to convert the highly ordered array of molecules in a crystal lattice to the randomness of a liquid. The distance between molecules in a crystal lattice is small and regular, with intermolecular forces serving to constrain the motion of the molecules more severely than in the liquid state. Molecular size is important, but shape is also critical, since individual molecules need to fit together cooperatively for the attractive lattice forces to be large. Spherically shaped molecules generally have relatively high melting points, which in some cases approach the boiling point, reflecting the fact that spheres can pack together more closely than other shapes. This structure or shape sensitivity is one of the reasons that melting points are widely used to identify specific compounds.

12.10 Key words

Van der Waal's Forces; Intermolecular forces; Supramolecular Chemistry; self assembly; Ion-Ion interactions; Ion -Dipole interactions; Dipole–Dipole interactions; Dipole–induced-dipole interaction; Cation – π interactions; π – π interactions.

12.11 References for further study

1. Concise inorganic chemistry – J D Lee , 5th Ed' n , ELBS - 1996.
2. Inorganic chemistry- principles of structure and applications. Huhey Keither and Keither 4th Ed' n , Pearson education - 2006
3. Inorganic chemistry – Sharpe , 3rd Low price Ed'n - 2005.
4. Principles of inorganic chemistry – Puri ,Sharma , Khalia,-2008
5. Solid state chemistry and its applications – A R west, John Wiley and sons - 1998.

12.12 questions for self understanding

- 1) What are Intermolecular forces? Explain their importance.
- 2) What is Van der Waal's Forces?
- 3) Write a note on Supramolecular Chemistry and Supramolecular Architecture
- 4) Explain Molecular self assembly.
- 5) Discuss in brief on nature of Supramolecular interactions.
- 6) Write short notes on
 1. Ion-Ion interactions

2. Ion -Dipole interactions
3. Dipole–Dipole interactions
4. Dipole–induced-dipole interaction
5. Cation – π interactions
6. π – π interactions

Unit - 13**Structure**

- 13.0 Objectives of the unit
- 13.1 Introduction
- 13.2 Arrhenius theory
- 13.3 Bronsted-Lowry theory
- 13.4 Conjugate acids and bases
- 13.5 Lux - Flood Concept
- 13.6 Lewis Concept
- 13.7 Usanovich Concept (Positive – negative definition)
- 13.8 Solvent system definition
- 13.9 Summary of the unit
- 13.10 Key words
- 13.11 References for further study
- 13.12 Questions for self under standing

13.0 Objectives of the Unit

- ❖ After studying this unit you will be able to
- ❖ Explain the definition of Acid and Base
- ❖ Classify the given substances as acid and base
- ❖ Explain the different theories of acids and bases
- ❖ Recognize their advantages and limitations

13.1 Introduction

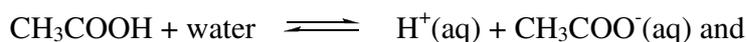
Acids and bases are encountered frequently both in chemistry and in everyday living. They have opposite properties and have the ability to cancel or neutralize each other. Acids and bases are carefully regulated in the body by the lungs, blood, and kidneys through equilibrium processes. Acid-base theories are in fact definitions of acids and bases. All of the current definitions of acid-base behaviour are compatible with each other. One of the objectives of presenting different definitions to acids and bases is to give a cosmopolitan attitude towards acids and bases. Different concepts have been put forth by different investigator to characterise acid and bases.

13.2 Arrhenius theory

A framework to observations on the chemistry of compounds that react in water was proposed by S. A. Arrhenius. At that time, the approach was limited to aqueous solutions only. According to him, *an acid is a substance whose water solution contains H_3O^+ while base is a substance which gives OH^- ions in aqueous solution.*



Similarly



Similarly



Accordingly, HCl, HNO₃, H₂SO₄, HClO₄, H₃PO₄, HC₂H₃O₂ are acids while NaOH, KOH, Ca(OH)₂, are all bases.

The high dielectric constant of water lowers the force of attraction between the oppositely charged ion and thus causes the dissociation of electrolyte. The greater the number of H⁺ or HO⁻ ions given by acid or bases in water the greater is strength of the acid or the base. In order to

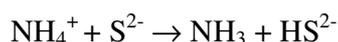
describe acid-base reactions in the gas phase or in solvents other than water, a different approach is necessary.

13.3 Bronsted-Lowry theory

In 1923, J. N. Bronsted and T. M. Lowry independently suggested that *an acid is a proton donor while a base is proton acceptor*. For aqueous solutions, the Bronsted-Lowry definition does not differ from the Arrhenius theory of acids and bases. The usefulness of the Bronsted-Lowry definition lies in its ability to handle any protonic solvent such as liquid ammonia or sulfuric acid.

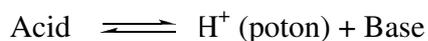


Further, proton-proton transfer reactions that would not normally be called neutralization reactions but which are obviously acid-base in character may be treated as readily



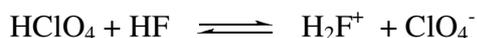
Acid Base Base Acid

When an acid loses a proton, i.e., an H^+ ion, the residual part of it has a tendency to regain the proton. Therefore it behaves as a base, hence



In liquid ammonia all ammonium salts act as acids since they can donate protons, and the sulphide ion acts as a base since it accepts protons. The reaction is reversible and it will proceed in the direction that produces the weaker species.

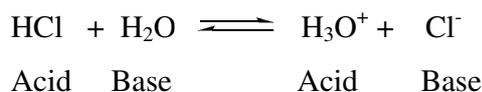
A limitation of the Bronsted-Lowry theory is, the extent of dissolved substance to act as acid or base depends largely on the solvent. The solute only shows acid properties if its proton donating properties exceed those of the solvent. For example, HClO_4 is an extremely strong proton donor, if liquid HClO_4 is used as a solvent, then HF dissolved in this solvent is forced to accept protons, thus act as a base



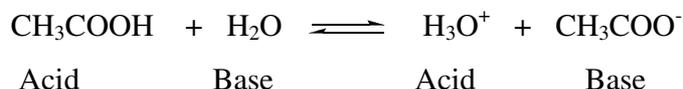
In a similar way H_2O is forced to accept protons and thus act as a base in both HClO_4 and liquid HF as a solvent.

13.4 Conjugate acids and bases

The dissociation of hydrochloric acid in water may be represented as follows



Similarly the dissociation of acetic acid in water may be represented as follows



In the above reaction it is evident that acetic acid and Hydrochloric acid donate proton to water thus acts as an acid. Water accepts a proton and therefore acts as a base. In reverse reaction, hydronium ion (H_3O^+) donates a proton to acetate and chloride ions and therefore acts an acid. The acetate and chloride ions accept a proton and therefore behave as a base. The chemical species differ from each other only in terms of transferred proton such pairs of substances which can be formed from one another by the gain or loss of a proton are known as conjugate acid-base pairs. Thus acetic acid is the conjugate acid of acetate ion and acetate ion is base of acetic acid. Similarly water is conjugate bade of hydronium ion and hydronium ion is the conjugate acid of water.

The following conclusions are drawn with regard to acids and bases according to the Bronsted-Lowry characteristics of the reactions

1. There is no acid without a base. The proton must be donated to something else.
2. The stronger an acid is, the weaker its conjugate will be as a base. The stronger a base is, the weaker its conjugate will be as an acid.
3. A stronger acid reacts to displace a weaker acid. A stronger base reacts to displace a weaker base.
4. The strongest acid that can exist in water is H_3O^+ . If a stronger acid is placed in water, it donates protons to water molecules to produce H_3O^+ .
5. The strongest base that exists in water is OH^- . If a stronger base is placed in water, it accepts protons from water to produce OH^- .

13.5 Lux - Flood Concept

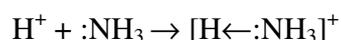
This concept was proposed by Lux in 1939 and extended by Flood in 1947. In contrast to the Bronsted-Lowry theory that emphasizes the proton as the principal species in acid-base reactions, the definition proposed by H. Lux and extended by H. Flood describes the acid-base behaviour in terms of oxide ion.

Let us consider the reactions of acidic and basic anhydrides in the absence of water or H^+ ions.

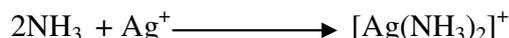
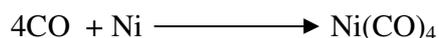
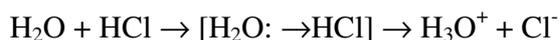
(ii) It is limited to systems such as molten oxide.

13.6 Lewis Concept

In 1923, G. N. Lewis proposed a definition of acid-base behaviour in terms of electron-pair donation and acceptance. Lewis definition of acid-base concepts did not depend on the presence of protons, nor involve reactions with the solvent. This is widely used especially in the field of organic reactions. Lewis defined *an acid as an electron-pair acceptor and a base as an electron-pair donor*. Lewis definition also includes reactions in which no ions are formed and no H⁺ ions or other ions are transferred.



Similarly hydrogen chloride is a Lewis acid because it can accept a lone pair from a base such as water through this is followed by ionization.



In view of the above, Lewis definition encompasses all reactions entailing H⁺ION, oxide ion or solvent interactions besides the formation of acid-base adducts such as R₃NBF₃ and all coordination compounds.

Though this is a more general approach than those involving protons, it has following drawbacks

- i) Many substances like BF₃ or metal ions that are not normally regarded as acids behaves as Lewis acids. This theory also includes reactions where no ions are formed and neither hydrogen ions nor any other ions are transferred. For example Ni(CO)₄
- ii) There is no scale of acid or basic strength, since the strength of an acid or base compound is not constant and varies from one solvent to another and also from one reaction to another
- iii) Almost all reactions become acid-base reaction under this system.

13.7 Usanovich Concept (Positive – negative definition)

Usanovich, a Russian Scientist Summarized the previous concepts and gave a new definition in 1939. According to him, *an acid is any species which forms salts with base through neutralization or gives up cations or combines with anions or electrons. A base is any species which neutralizes acids, gives up anions or electrons or combines with cations*. For Ex:

Acid	Base	Salt	Justification
SO ₃	Na ₂ O	Na ₂ SO ₄	Na ₂ O yields O ²⁻ ion SO ₃ combines with O ²⁻ ion
Fe(CN) ₂	4KCN	K ₄ [Fe(CN) ₆]	KCN yields CN ⁻ ion Fe(CN) ₂ combines with CN ⁻ ion
Sb ₂ S ₅	3(NH ₄) ₂ S	2(NH ₄) ₃ SbS ₄	(NH ₄) ₂ S yields S ²⁻ ion Sb ₂ S ₅ Combines with S ²⁻ ion
Cl ₂	2Na	2NaCl	Na loses an electron Cl gains an electron

This is a very wide definition and includes all the Lewis acid-base type of reactions and in addition it includes redox reactions involving the transfer of electrons.

Advantages

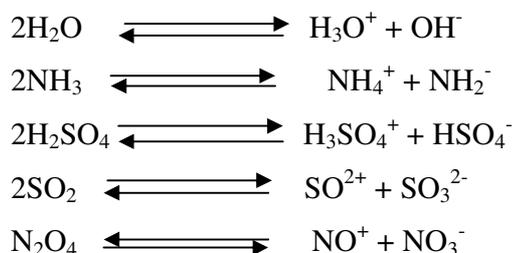
- (i) This includes all oxidation reduction reactions as acid – base reactions and
- (ii) It classifies together all examples of acidity and basicity.

Limitations

- (i) Usanovich places considerable emphasis on the degree of coordination unsaturation on the central atom in the compound as well as emphasizing the general trends of the periodic table. For Eg: In SO₃, the central atom Sulphur is coordinately unsaturated. This is why, it is capable of accepting an anion such as O²⁻, thereby acting as an acid.
- (ii) If we accept this concept, we find that virtually all chemical reactions fall into the acid – base category and one begins to wonder at the purpose of using any name other than chemical reactions.

13.8 Solvent system definition

It was proposed by E. Franklin in 1924 and extended by H. Cady and H. Elsey in 1928. This is the most convenient and general definition of acids and bases. It can be applied in all cases where the solvent undergoes self-ionization regardless whether it contains protons or not. Many solvents autoionize with the formation of a cationic and anionic species as does water.



According to Franklin, *an acid a substance that increases the concentration of the characteristic cation of the solvent* (H_3O^+ in case of water, NH_4^+ in liquid ammonia and NO^+ in N_2O_4) *while base is a substance that increases the characteristic anion of the solvent* (OH^- in water, NH_2^- in ammonia and NO_3^- in N_2O_4).

Examples:

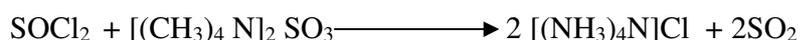
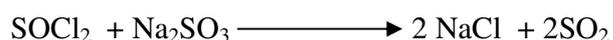


Thus water ionizes to give H_3O^+ and OH^- ions. The substances produce H_3O^+ ions in water (ex: HCl , KNO_3 , H_2SO_4) are acids. Similarly the substances produce OH^- ions in water (ex: NaOH , NH_4OH) are bases

Similarly liquid ammonia ionizes to give NH_4^+ and NH_2^- ions. Thus ammonium salt are acids since they produce NH_4^+ ions in liquid NH_3 while sodamide (NaNH_2) is a base because it produces NH_2^- ions.

N_2O_4 undergo self-ionization to NO^+ and NO_3^- . Thus in N_2O_4 solvent NOCl is an acid because it increases the concentration of NO^+ while NaNO_3 is a base since it increases NO_3^- ion concentration.

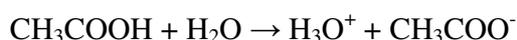
H. Cady and H. Elsey extended this concept to non protic solvents. According to them, *an acid is a solute that either by direct dissociation or by reaction with the solvent gives the cation characteristic of the solvent and a base is a solute that either by direct dissociation or by reaction with the solvent gives the anion characteristic of the solvent.*



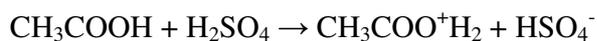
Advantages

1) This definition applies equally to both protic and non-protic solvents. Therefore this broader definition also has advantages when protic solvent is considered, because it explains about why the acidic and basic properties of a solute are not absolute and depend in part on the solvent

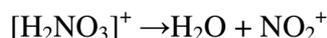
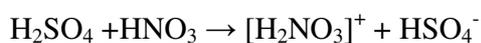
For example, normally acetic acid behaves as acid in aqueous media and produces H_3O^+ ion



However in H_2SO_4 acetic acid behaves as a base, this is because sulphuric acid is a stronger proton donor than the CH_3COOH . Hence



Similarly HNO_3 is forced to behave as a base in H_2SO_4 , this is important in producing nitronium ions NO_2^+ in the nitration of organic compounds by a mixture of concentrated H_2SO_4 and HNO_3



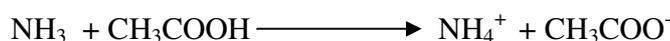
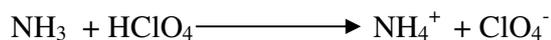
2) Construction of a scale similar to pH scale

$$K_W = [\text{H}_3\text{O}^+] [\text{OH}^-] = 10^{-14}$$

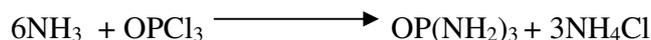
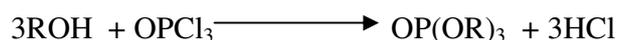
$$K_{AB} = [\text{A}^+] [\text{B}^-]$$

where $[\text{A}^+]$ and $[\text{B}^-]$ are the concentrations of cations and anions characteristic of a particular solvent.

3) The leveling effect can be explained. All acids and bases stronger than the characteristic cation and anion of the solvent will be leveled to the latter. For example



3) The solvent system concept has been used extensively as a method of classifying solvolysis reactions. For example, it is possible to compare the hydrolysis of nonmetal halides with their solvolysis by non-aqueous solvents:



13.9 Summary

In earlier stage of chemistry acids were distinguished by their sour taste and their effect on certain plant extracted pigments. Same way bases were treated as substances which reacted with acids to form a salt. As subject grown several theories are put forward to explain behavior of acids and bases. They are not theories but they are different definitions of acids and bases. No theory is more right or wrong than any other and one can use the most convenient theory for a particular situation.

13.10 Keywords

Acid; Base; Solvent; Arrhenius theory; Bronsted-Lowry theory; Lux-Flood theory; Lewis theory; Solvent theory; Usanovich theory; conjugate acids; conjugate bases.

13.11 References for further study

1. Inorganic Chemistry, 4th Ed., J. E. Huheey, E.A. Keiter and R. L. Keiter, O. K. Medhi, Pearson Education, 2009.
2. Theoretical Inorganic chemistry – M. C. Day and J.Selbin.
3. Concepts and Methods of Inorganic Chemistry – B. E. Douglas and D. H. McDaniel.
4. Inorganic chemistry – An Advanced Text book – Therald Moeller.

13.12 Questions for self understanding

- 1) Write three general properties of acid and bases.
- 2) What is Arrhenius theory of acid and base?
- 3) Discuss the advantage and limitations of Arrhenius theory of acid and bases
- 4) What is Bronsted-Lowry theory of acid and base?
- 5) What are conjugate acids and bases?
- 6) Explain how Bronsted-Lowry theory of acid and base has advantage over Arrhenius theory.
- 7) What are the limitations of Bronsted-Lowry theory of acid and base?
- 8) Explain Lux - Flood concept of acid and base.
- 9) What are acid and base according to Lewis Concept?
- 10) Explain the advantages and limitations of Lewis Concept acid and base.
- 11) Write a note on Usanovich Concept.
- 12) Define Solvent system definition of acid and base.
- 13) Discuss the advantages of solvent system definition of acid and base.

Unit - 14**Structure**

- 14.0 Objectives of the unit
- 14.1 Introduction
- 14.2 Hard and soft acids and bases (HSAB)
 - 1) *Ionic and covalent bonding theory*
 - 2) *Pi-bonding theory*
- 14.3 Applications of hard and soft acid and base concept
- 14.4 Relative strengths of acid and bases
 - a) *Gas-phase basicities (Proton affinities)*
 - b) *Gas-phase acidities(Proton loss)*
- 14.5 Periodic variation of acidic and basic properties
 - i) Hydrides
 - ii) Oxyacids
- 14.6 Irving- William series
- 14.7 Summary of the unit
- 14.8 Key words
- 14.9 References for further study
- 14.10 Questions for self under standing

14.0 Objectives of the unit

After studying this unit you are able to

- ❖ Explain hard and soft acid and bases
- ❖ Explain the characteristics of hard and soft acid and bases
- ❖ Identify the hard and soft acid and bases for given set of ions and molecules
- ❖ Give the reasoning for relative strength of acid and bases
- ❖ Explain the periodic variation of acidic and basic properties
- ❖ Explain the Irving-William series of ions

14.1 Introduction

Coordination chemists have been aware of certain trends in the stability of metal complexes. According Irving – Williams correlations, the stability of the complexes of dipositive ions for a given ligand follows the order, $Ba^{+2} < Sr^{+2} < Ca^{+2} < Mg^{+2} < Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$. This order arises in part from a decrease in size across the series and in part from ligand – field effects. Another correlation was given by Ahrlund, Chatt and Davies in 1958. According to these workers, ligands and metal ions were classified as class (a) and class (b). Class (a) metals are those, they form their most stable complexes with ligands containing nitrogen, oxygen or fluorine as a donor atom. The class (b) metals are those, they form their most stable complexes with ligands containing heavier member of these families as a donor atom.

Class (a) metal ions include those of alkali metals, alkaline earth metals and lighter and more highly charged ions. ex: Ti^{4+} , Fe^{3+} , Co^{3+} , Al^{3+} ...

Class (b) metal ions include transition metals such as Hg^{2+} , Pt^{4+} , Pt^{2+} , Ag^{+} , Cu^{+}, and low valent metal ion such as the formally zero valent metals in metal carbonyls. This empirical ordering proved very useful in classifying and predicting the relative stabilities of complexes.

Thus halide complexes of cations with inert gas type configurations {class (a)} decrease in stability in the order $F^{-} > Cl^{-} > Br^{-} > I^{-}$. The reverse order of stability is observed for the cations of class (b) such as Hg^{2+} . R.G. Pearson in 1963 introduced a more generalized correlation to include broader range of acid-base interactions. According to their preferences towards either class (a) or class (b) metal ions, ligands may be classified as class (a) or (b) respectively. Stability of these complexes may be summarized as follows

<u>Class (a) ligands</u>	<u>Class (b) ligands</u>
N >> P > As > Sb	N << P > As > Sb
O >> S > Se > Te	O << S < Se ~ Te
F > Cl > Br > I	F < Cl < Br < I

Class (a) ligands exhibit the tendency to complex with class (a) metal ions and Class (b) metal ions. For example: R₃P and R₂S have a much greater tendency to coordinate with Hg²⁺, Pd²⁺ but NH₃, R₃N, H₂O and F⁻ prefer Be⁺², Ti⁺⁴ and Co⁺³.

Ahrland, Chatt and Daries correlations have been explained and generalized by Pearson along with a change in terminology as hard and soft acids and bases in 1963.

14.2 Hard and soft acids and bases (HSAB)

Pearson defines a *soft base* as one in which the donor atom is of high polarizability and of low electronegativity and is easily oxidized or is associated with empty low lying orbitals. A *hard base* is defined as one with opposite properties. The donor atom is of low polarizability and high electronegativity, is hard to reduce and is associated with empty orbitals of high energy.

The acceptor atom of soft acid is defined by Pearson to be one that has one or more of the following properties, large size, low or zero positive charge and presence of several easily excited outer electrons. A hard acid on the other hand is distinguished by small size, higher positive oxidation state and the absence of outer electrons which are easily excited to higher states.

It is generalized that the stable complexes are formed from the combination of hard acids with hard base and soft acid with soft bases and vice versa cannot form stable complexes. This means that if there is a choice of reaction between an acid and two bases, or a base with two acids a hard acid will prefer to combine with a hard base and a soft acid with a soft base. Thus it is possible to predict the more stable complex formation in each case. For example,

For the following reaction,



B₁ is softer than B₂ if K > 1.

On this basis, a list of hard and soft acids and bases are given in the following table.

Hard	Soft
H ⁺ , Li ⁺ , Na ⁺ , K ⁺	Cu ⁺ , Ag ⁺ , Au ⁺ , Tl ⁺ , Cs ⁺
Ba ⁺² , Mg ⁺² , Ca ⁺² , Sr ⁺² , Mn ⁺²	Pd ⁺² , Cd ⁺² , Pt ⁺² , Hg ⁺²
Al ⁺³ , Sc ⁺³ , Ga ⁺³ , In ⁺³ , La ⁺³	Tl ⁺³ , Tl(CH ₃) ₃ BH ₃
Cr ⁺³ , Co ⁺³ , Fe ⁺³ , As ⁺³	Ga(CH ₃) ₃ GaCl ₃ , GaI ₃ , InCl ₃ , CH ₃ H ⁺ , RS ⁺ , RSe ⁺ , RTe ⁺
Si ⁺⁴ , Ti ⁺⁴ , Zr ⁺⁴ , Th ⁺⁴ , U ⁺⁴	I ⁺ , Br ⁺ , HO ⁺ , RO ⁺
UO ₂ ²⁺ , (CH ₃) ₂ Sn ²⁺ , VO ²⁺ , MoO ₃ ³⁺	I ₂ , Br ₂ ICN, [Co(CN) ₅] ⁻² , Pt ⁺⁴ , Te ⁺⁴
Border Line: Fe ⁺² , Co ⁺² , Ni ⁺² , Cu ⁺² , Zn ⁺² , Pb ⁺² , Sn ⁺² , Sb ⁺³ , Bi ⁺³ , Rh ⁺³ , Ir ⁺³ , B(CH ₃) ₃ , SO ₂ , NO ⁺ , Ru ⁺² , Os ⁺² , R ₃ C ⁺ , C ₆ H ₅ ⁺ , GaH ₃ .	

Classification of hard and soft bases

Hard	Soft
H ₂ O, OH ⁻ , F ⁻	I ⁻ , CN ⁻ , SCN ⁻ , RS ⁻ , R ⁻ , H ⁻
Ac ⁻ , PO ₄ ⁻³ , SO ₄ ⁻²	S ⁻² , S ₂ O ₃ ⁻² , R ₂ S, RSH, R ₃ P
Cl ⁻ , CO ₃ ⁻² , ClO ₄ ⁻ , NO ₃ ⁻	R ₃ As, (RO) ₃ P, RNS, CO
ROH, RO ⁻ , R ₂ O	C ₂ H ₄ , C ₆ H ₆
NH ₃ , RNH ₂ , N ₂ H ₄	

Border Line: C₆H₅NH₂, C₆H₅N, N₃⁻, Br⁻, NO₂⁻, SO₃⁻²

The two simple theories have been used to explain the preference of hard acids for hard bases and soft acids for soft bases. They are,

3) Ionic and covalent bonding theory

According to this theory hard complexes prefers to form ionic bonding and soft complexes prefers to form covalent bonding. The high positive charge and small size of the hard ions favour ionic bonding and bases of high negative charge and small size would be expected to be held most strongly by these acids. The hard and soft combination suffer from mismatch in their binding tendencies and are thus generally unstable.

4) Pi-bonding theory

The important feature of soft acids is the presence of loosely held outer d-electrons capable of being donated to ligands, thus most soft acids are π-bond donors. Generally the soft bases are π-bond acceptors and soft bases including ligands containing P, As or I donor atoms and unsaturated ligands such as CO. On the other hand hard acids are π-bond acceptors and hard bases

(ex, N, P, F) are π -bond donor. Thus pi-bonding formation is possible between soft acids and soft bases or hard acids and hard bases. The hard and soft combinations suffer from a mismatch in their bonding tendencies.

14.3 Applications of hard and soft acid and base concept

The concepts of hardness and softness help to rationalize a great deal of inorganic chemistry, for example they are relevant to the compounds that constitute the structure of the earth.

1) Relative stabilities of compounds and complexes

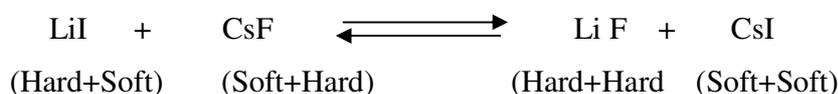
Thermodynamic stability of simple compounds and complex ions can be nicely rationalized in terms of hard and soft acid-base principle

For example, AgI_2^- (Soft+Soft) is stable while AgF_2^- (Soft+Hard) is not. The reverse is true for Cobalt (III), i.e., CoF_6^{3-} is more stable than CoI_6^{3-} . This is because soft acids prefer to combine with soft bases and hard acids with hard bases.

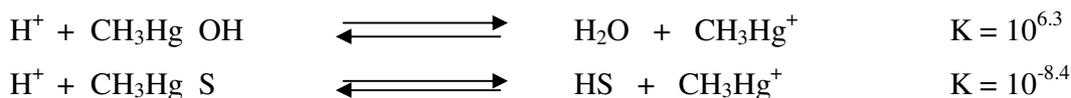
2) Coordinating power of the halide ions towards Al increases in the order $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^-$ while the order is $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ for Hg^{+2} ion.

For Ex: $[\text{AlF}_4]^-$ (Hard+Hard) $[\text{HgI}_4]^{2-}$ (Soft+Soft)

3) In solution the following reactions proceed right but not left.



4) Relative stabilities of the complexes



Both CH_3Hg^+ and H^+ form stable complexes with OH^- and S^{2-}

5) Hard bases tend to group together and soft bases tend to group together on a given acid.

Ex: $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$ (Hard+Hard) $[\text{Co}(\text{CN})_5\text{I}]^{3-}$ (Soft+Soft)

6) Synthetic inorganic chemistry

This principle has many applications in synthetic inorganic chemistry. For example, in order to obtain stable compounds of elements in a very high oxidation state, it is necessary to coordinate with hard bases such as O^{2-} , OH^- or F^- . Similarly to obtain stable compounds of elements with very low oxidation state. It is necessary to coordinate with very soft bases such as CO , PR_3 and

CN. The metal coordination compounds containing olefins and aromatic hydrocarbons are prepared using transition metals in low oxidation state. Compounds containing metal-metal bonds are stabilized by ligands such as CO in combination with transition metals in low oxidation state.

7) *Poisoning of metal catalyst*

The HSAB principle has also been used to explain the poisoning of metal catalyst.

For example, certain soft metal like platinum and palladium are used as catalyst, since species such as CO and olefins are first adsorbed on the metal surface and then undergo reaction at the metal surface. Bases containing phosphorus, arsenic, antimony, tellurium and selenium in low oxidation states poison the metallic catalyst, because they are strongly adsorbed on the surface and thus block the active site. Thus soft metal catalysts are poisoned by impurities of soft bases and not by those of hard bases such as nitrogen, oxygen and fluorine.

8) *Solubility*

Hard solvents tend to dissolve hard solutes and soft solvents tends to dissolve soft solutes

14.4 Relative strengths of acid and bases

The relative strength of an acid is measured by its tendency to donate a proton (according to Bronsted concept). A stronger acid has a stronger tendency to donate a proton. Similarly the strength of a base is measured by its tendency to accept a proton. A stronger base has a stronger tendency to accept a proton.

There are two general methods mainly employed for the comparison of relative acidity.

First one is a comparison of proton donating tendencies of different acids towards same base. Water is commonly used as base for moderately strong acids. For example, the ionization or acidity constant K_a for acetic acid at 25°C is 1.8×10^{-5} , whereas for hydrogen cyanide is 4.0×10^{-10} . Therefore acetic acid is a stronger acid than hydrogen cyanide.

Second method is the competitive protolysis method. In this method one acid is added to the conjugate base of the other and equilibrium concentrations are determined experimentally.

For example, when sodium ethoxide is added to water, it is experimentally seen that ethoxide ion (the conjugate base of ethanol) react fairly completely with water to form ethylalcohol and hydroxide ion.



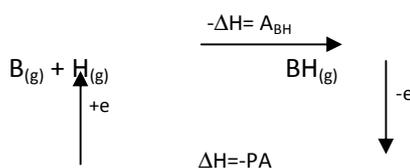
Therefore ethoxide ion is stronger base than hydroxyl ion and water is stronger acid than ethanol

a) Gas-phase basicities (Proton affinities)

The most fundamental measure of the inherent basicity of a species is the proton affinity. It is defined as the energy released for the reaction shown below:



Note that the proton affinity has the opposite sign from the enthalpy of reaction. Proton affinities are always listed as positive numbers despite referring to exothermic reactions. Proton affinities may be obtained in a number of ways which include Born-Haber cycle.



In this case, BH is expected to be sufficiently stable that its bond energy/enthalpy of atomization and ionization potential (IE_{BH}) can be measured. The greatest proton affinity estimated is that of N_3^- due to the large electrostatic attraction of the -3 ion. The dinegative imide, NH_2^{2-} has a very large but somewhat lower value, followed by amide, NH_2^- and NH_3 . Inductive effects are readily observed with values ranging from $NF_3 = 604$ kJ/mol through $NH_3 = 872$ kJ/mol to trimethylamine, $(CH_3)_3N = 974$ kJ/mol.

b) Gas-phase acidities (Proton loss)

Proton affinity of a cation is its ability to attract and hold a proton. Its value will also be the enthalpy of dissociation of its conjugate acid in the gas phase. Consider HF^- which has PA_{F^-} of 1554 kJ/mol.



Higher the endothermic nature of the above equation, weaker will be the acid. HF is a weaker acid in the gas phase and aqueous solution compared to other HX acids. Similarly, acetic acid ($PA_{CH_3COO^-}$ of 1459 kJ/mol) is a weaker acid than trifluoroacetic acid ($PA_{CF_3COO^-}$ of 1351 kJ/mol).

14.5 Periodic variation of acidic and basic properties

To better understand the relationship between acid strength and molecular structure, acids are divided into two types, they are

- i) Hydrides
- ii) Oxyacids

- i) Hydrides. Two factors are mainly influences the acid strength of the hydride of an element
- The electronegativity and
 - Atomic size of the element.

These may be understood by making a comparison of the hydrides of the element in a period and group

- 1) Hydrides of the elements of a period

Consider the hydrides of the elements of 2nd period viz. CH₄, NH₃, H₂O and HF.

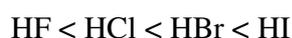
These hydrides become increasingly acidic as we move from CH₄ to HF. i.e., the electronegativity of these element increases in the order C < N < O < F, the acid strength of the hydrides increases in the same order CH₄ < NH₃ < H₂O < HF.

Thus CH₄ has negligible acidic properties but NH₃ can donate a proton to stronger bases to form NH₂⁻. H₂O loses a proton even more readily and HF is a fairly strong acid. The increase in acidic properties of these hydrides is due to the stability of their conjugate base. i.e., as we move from CH₄ to HF the stability of conjugate bases follows the order CH₃⁻ < NH₂⁻ < OH⁻ < F⁻.

Similarly the electronegativites of the elements of the third period changes in the order P < S < Cl, and the strength of the hydrides of elements increases in the same order PH₃ < H₂S < HCl. Thus PH₃ does not react with water, H₂S is a weaker acid and HCl is a strong acid.

- 2) Hydrides of the elements in a group

The acidity of the hydrides of the elements of a group increases with increasing size of the central atom. For example, consider the hydrides of group 16 and 17 elements



This is the reverse order to that of expected on the basis of electronegativity. The first hydride of the each series i.e., (H₂O and HF) is the weakest acid of the series and is formed by the element with the highest electronegative element.

The increasing acidic character reflects decreasing trend in the electron donor ability of OH⁻, HS⁻, HSe⁻ or HTe⁻ ions. The increasing acidic character is due to the decreasing charge density on the conjugate base from OH⁻ to HTe⁻, the proton is less tightly held in higher members and therefore acidic character increases.

The aqueous solutions of group 17 hydrides show acidic character increases in the order, HF < HCl < HBr < HI. This is due to the fact that as we move from HF to HI, there is a gradual

decrease in the bond energies of H-X bonds (H-F = 135 kcal/mole, H-Cl = 103, H-Br = 88, H-I = 71). This decreasing bond energy increases the tendency of H-X molecule to split up into H⁺ and X⁻ ions in aqueous solution. Thus the acidic character increases from HF to HI.

As we know, two factors influence the acid strength of the hydrides, they are electronegativity of the central atom and size of the central atom. When these factors work against each other, the effect of atomic size outweighs the electronegativity effect. Hence a proton is more easily removed from hydrides of larger central atom is larger than the smaller central atom.

For example, the hydrides of carbon, sulphur and iodine, the electronegativity of C, S and I, which belongs to different groups, are approximately same (2.5). But atomic radius of carbon is 77pm, sulphur is 103pm and iodine is 133pm. Thus there is a marked increase in the acidity of the hydrides with increase in size of the central atom. CH₄ does not dissociate in water, H₂S is weak acid and HI is a strong acid.

Hydrides of group 15 elements (NH₃, PH₃, AsH₃, SbH₃, BiH₃) all show a basic character. The basic character decreases as we move from N to Bi. This is because, with the increase in size and decrease in electronegativity from N to Bi, there is a decrease in electron density in sp³ hybrid orbital and thus electron donor capacity (i.e., basic character) decreases.

ii) Oxyacids

Oxyacids are the compounds derived from H-O-Z. The hydrogen atom is attached to an oxygen atom and the acidity of the oxyacids depends on the electronegativity of the atom Z. If Z is a metal atom with low electronegativity, the O-Z bond will be an ionic bond and the compound is a metal hydroxide, i.e., a base. For example, NaOH, KOH, Ca(OH)₂, etc....

Otherwise if Z is a non-metal atom with high electronegativity, the electron pair of O-Z bond will be a strong covalent bond. The Z will tend to reduce the electron density around O atom. Thus, H-O bond electrons are drawn towards Z atom, which will allow the proton to dissociate and make the compound acidic. For example HOCl, HOBr, etc....

The higher the electronegativity of Z atom, the O atom will draw O-H electrons towards itself, hence more readily proton will be lost. i.e., as the electronegativity of Z increases, the acid strength also increases. Therefore acidity is of the order HOI < HOBr < HOCl

The acidic strength of oxyacids of the same elements with different oxidation states increases with the increase of its oxidation state.

For example, HOCl < HClO₂ < HClO₃ < HClO₄

Similarly, $\text{H}_2\text{SO}_3 < \text{H}_2\text{SO}_4$ and $\text{HNO}_2 < \text{HNO}_3$

The acidic character of the oxyacids of different elements with same oxidation state decreases with the increase in the atomic number of the central atom.

For example, $\text{HOCl} > \text{HOBr} > \text{HOI}$

Similarly $\text{HClO}_4 > \text{HIO}_4$ and $\text{H}_2\text{SO}_3 > \text{HSeO}_3$

This is because, as the atomic number of the central atom increases, its electronegativity decreases and its size increases. As a result the tendency of the acid to lose a proton decreases.

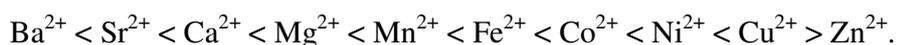
This makes the acid weaker.

Under favourable conditions hydrated metal ions dissociate one or more protons from the coordinated aquo groups

$[\text{M}(\text{H}_2\text{O})_6]^{n+} + \text{H}_2\text{O} \rightarrow [\text{M}(\text{H}_2\text{O})_5(\text{OH})]^{(n-1)+} + \text{H}_3\text{O}^+$ Thus hydrated metal ions also exhibit acidity. The acidity increases with the increase of positive charge and basicity increases with the increase of negative charge. Thus $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion is a stronger acid than $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ion and $[\text{Ni}(\text{OH})_4]^{2-}$ is a stronger base than $[\text{Ni}(\text{OH})_4]^-$ ion.

14.6 Irving-William series

The Irving-Williams Series refers to the relative stabilities of complexes formed by a metal ion. The magnitude of the stability constants depend upon the identity of the metal center. The stability constants of complexes of the first row divalent metal ions, it is found that they fall in the order below, and this is largely independent of the nature of the ligand.



This series is referred as Irving-Williams Series. This is essentially due to decreasing size of the cation, and in the case of the transition metal ion ligand field effect also contributes.

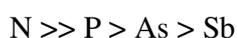
It is noted that certain ligands prefer certain metals, for example Al^{3+} , Ti^{4+} and Co^{3+} favour one type of ligand while Ag^+ , Hg^{2+} and Pt^{2+} favour another type. Therefore metal ions are classified as type-a or type-b.

Type-a, metal ions are largely of group 1, 2 and lighter transition metals in high oxidation states.

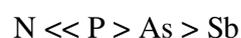
Type-b, metal ions are heavier transition metals in lower oxidation state.

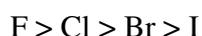
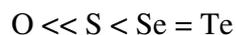
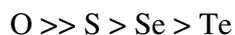
Ligands are also be classified based on their preference for forming complexes with type- a or type-b metal ions.

Tendency for a



Tendency for b

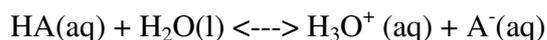




Later the metal ions and ligands are classed as Hard (a) and Soft (b). Thus a hard acid is a type-a metal ion, while hard base are the ligands, NH_3 , F^- etc., which have stronger tendency to form a complexes with type-a, metal ions. A soft acid is a type-b metal ion, while soft base are the ligand, phosphine, iodide etc... which have stronger tendency to form a complexes with type-b metal ions. Generally Hard – tend to be small, slightly polarisable and soft – tend to be larger, more polarisable.

14.7 Summary of the unit

Acids are characterized by releasing H^+ ions in aqueous solutions, having a sour taste, having a pH level ranging from zero (strong) to seven (weak), reacting with metals, and having the ability to alter the color of indicators. An acid added to water (and at equilibrium) can be represented by the following equation:



In this equation, HA is acid, water is the base, H_3O^+ is the **conjugate acid** and A^- is the **conjugate base**. This is a representation of **conjugate pairs** where an acid and its conjugate base are a pair, and a base and its conjugate acid are a pair. By knowing strengths of one or more of these acid/base pairs, it is possible to predict to the strength of an acid. Bases are compounds that break apart to form a negatively charged hydroxide ion (OH^-) in water. The strength of a base is determined by the concentration of Hydroxide ions (OH^-). The greater the concentration of OH^- ions, the stronger is the base. Bases taste bitter and feel slippery. The Strong bases are very dangerous and can burn the skin.

All acids and bases do not ionize or dissociate to the same extent. This leads to the statement that acids and bases are not all of equal strength in producing H^+ and OH^- ions in solution. The terms "strong" and "weak" give an indication of the strength of an acid or base. The terms strong and weak describe the ability of acid and base solutions to conduct electricity. If the acid or base conducts electricity strongly, it is a strong acid or base. If the acid or base conducts electricity weakly, it is a weak acid or base. Basicity is proportional to charge density. When comparing atoms of equal formal charge the larger atom provides more space for the charge. Therefore, in a larger atom the negative charge is more dispersed and the charge density decreases. As a result negative charges prefer to rest on large atoms rather than being localized on a small atom (due to

increase stability). Therefore smaller atoms have a greater driving force to share electron density because of increased charge concentration and are thereby stronger bases. It is important to understand that this principle applies when considering atoms in the same column of the period table (as size changes are significant). Because size does not greatly change across a period, this principle does not apply. When comparing atoms across a period, we consider electronegativity.

14.8 Key words

Hard and soft acid and bases; pi-Bonding theory; strength of acid and bases; Hydrides; Oxyacids; Irving-William series.

14.9 References for further study

1. Inorganic Chemistry, 4th Ed., J. E. Huheey, E.A. Keiter and R. L. Keiter, O. K. Medhi, Pearson Education, 2009.
2. Theoretical Inorganic chemistry – M. C. Day and J.Selbin.
3. Concepts and Methods of Inorganic Chemistry – B. E. Douglas and D. H. McDaniel.
4. Inorganic chemistry – An Advanced Text book – Therald Moeller.

14.10 Questions for self understanding

- 1) What are hard and soft acid and bases give three examples?
- 2) Classify the given set of ions and molecules as hard and soft acid and bases and give the reason. Be^{2+} , Cs^+ , NH_3 , PH_3
- 3) Explain ionic and covalent bonding theory
- 4) Explain pi-bonding theory
- 5) What are the applications of hard and soft acid and base concept?
- 6) Write a note on relative strength of acid and bases
- 7) Discuss periodic variations of acidic and basic properties.
- 8) Write a note on Irving –William series.
- 9) Explain the periodic variation of acidic and basic properties
- 10) Explain the Irving-William series of ions

Unit - 15**Structure**

- 15.0 Objectives of the unit
- 15.1 Introduction
- 15.2 *Inorganic solvents*
 - 1) *Non aqueous solvents*
 - 2) *Ionizing solvents*
 - 3) *Non-ionizing solvents*
- 15.3 Physical properties of solvents
 - (a) *Melting point and boiling point*
 - (b) *Polarity of the solvent*
 - (c) *Dielectric constant*
 - (d) *Viscosity*
 - (e) *Electrical conductivity*
- 15.4 Effect of chemical properties of the solvent
 - a) *Effect of acidic or basic characteristics of the solvent*
 - b) *Chemical effects on solubility*
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- 15.5 Metal-Ammonia solutions
- 15.6 Solvated electron
- 15.7 Hydrated electron
- 15.8 Super acids
- 15.9 Summary of the unit
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15.0 Objectives of the unit

After studying this unit you are able to

- ❖ Explain the importance of solvents as reaction media
- ❖ Recognize the important physical properties of solvents
- ❖ Classify the solvent based on their physical and chemical properties
- ❖ Explain the effect of chemical properties of solvents on reaction
- ❖ Recognize the different reactions occurs in metal ammonia solution
- ❖ Differentiate the properties of Hydrated and ammoniated electron

15.1 Introduction

A solvent is a substance that is capable of dissolving another substance (called a solute) into a uniform mixture known as a solution. In order for a solvent to be able to accomplish this task it must overcome the forces that bind the solute (the substance being dissolved) together. Ability of a substance to dissolve another substance is determined by compatibility of their molecular structures. The following classifications of solvents are made on the basis of their molecular structure.

Polar protic solvents

A polar protic solvent consists of a polar group -OH and a non-polar tail. The structure may be represented by a formula R-OH. These solvents dissolve other substances with polar protic molecular structure and miscible with water (H-OH), acetic acid (CH₃CO-OH), methanol (CH₃-OH), ethanol (CH₃CH₂-OH), n-propanol (CH₃CH₂CH₂-OH), n-butanol (CH₃CH₂CH₂CH₂-OH) etc.....

Dipolar aprotic solvents

Dipolar aprotic solvents consists a large **dipole moment** (a polarity of a chemical bond). They do not contain -OH group. For example, acetone ((CH₃)₂C=O), ethyl acetate (CH₃CO₂CH₂CH₃), dimethyl sulfoxide ((CH₃)₂SO), acetonitrile (CH₃CN), dimethylformamide ((CH₃)₂NC(O)H).

Non-polar solvents

These classes of solvents have low dielectric constant, because electric charge in the molecules of non-polar solvents is evenly distributed. Non-polar solvents are hydrophobic (immiscible with water), are lipophilic as they dissolve non-polar substances such as oils, fats, greases. For example, carbon tetrachloride (CCl₄), benzene (C₆H₆), and diethyl ether (CH₃CH₂OCH₂CH₃), hexane (CH₃(CH₂)₄CH₃), methylene chloride (CH₂Cl₂).

15.2 Inorganic solvents

The most popular inorganic (not containing carbon) solvents are water (H₂O) and aqueous solutions containing special additives (surfactants, detergents, PH buffers, inhibitors). Other inorganic solvents are anhydrous liquid ammonia (NH₃), concentrated sulfuric acid (H₂SO₄), sulfuryl chloride fluoride (SO₂ClF), etc.....

Inorganic solvents are classified as aqueous and non aqueous solvent. Water is called aqueous solvent and solvents other than water are called non aqueous solvents. Similarly solutions prepared by using water as solvents are called aqueous solutions and solutions prepared by using solvents other than water are called non aqueous solution.

a) Non aqueous solvents

Almost all of the reactions that the inorganic chemist observes in the lab take place in solution. Although water is the best known solvent, it is not the only one of importance to the chemist. By changing the solvent, the products from a given set of reactants can be completely changed and in some cases, reactions may be reversed. For example, in aqueous solution, AgNO₃ and BaCl₂ react to form a precipitate leaving Ba(NO₃)₂ in solution whereas in liq.NH₃, AgCl combines with Ba(NO₃)₂ to yield a precipitate of BaCl₂ leaving AgNO₃ in solution.

Solvents are classified in different ways as shown below depending on their physical and chemical properties

(a) Based on proton donor and proton acceptor properties of solvents (aprotic or non-protonic solvents; protic or protonic solvents; amphi-protic or amphoteric solvents)

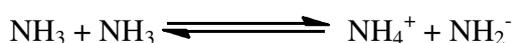
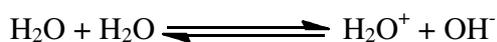
(b) Based on the fact that like dissolves like (Ionising solvents; non-ionising solvents).

b) Ionizing solvents

Ionizing solvents are polar or ionic in nature and dissolve ionic compounds and initiate ionic reactions. Ions are exists in their pure state and thus are weak weak conductors of electricity. These solvents have high values of dielectric constants, because of their polar nature. These have strong tendency to form associated structure.

For example, H₂O, NH₃, HF, SO₂, etc....

The main characteristic of these solvents is, these solvents undergo self ionization as shown below.





c) *Non-ionizing solvents*

These are non-polar solvents and dissolve only non-polar or neutral compounds and do not initiate ionic reactions. These solvents have low dielectric constants and have little associating and solvating tendency between solute and solvents.

For example, C₆H₆, CCl₄, Cl₂CH-CHCl₂ etc..... Unlike ionizing solvents, these solvents do not undergo self ionization

We can also conveniently place non-aqueous solvents into the

- protic solvents (e.g. HF, H₂SO₄, MeOH)
- aprotic solvents (e.g. SO₂, N₂O₄, BrF₃)
- coordinating solvents (e.g. MeCN, Et₂O, Me₂CO)

15.3 Physical properties of solvents

There are several physical properties of a solvent that are of importance in determining its behaviour. Some of these are discussed below

(a) *Melting point and boiling point*

Since most reactions in solvent system are most conveniently carried out in the liquid phase, the temperature range between the MP and BP of the solvent virtually establishes the temperature range of usefulness of the solvent as far as the reactions at atmospheric pressure are concerned. This range can be extended by use of a diluent to lower the freezing point and raise the BP of the solvent or by operating at increased pressure to raise the BP.

Important physical properties of some ionizing solvents are tabulated in below Table 1.

Table 1. Physical properties of some ionizing solvents

<i>Solvent</i>	<i>Viscosity (millipoise)</i>	<i>Dipole moment (in Debye units)</i>	<i>Dielectric constants</i>	<i>Auto-ionisation</i>	<i>Ionic product</i>
Water	10.08	1.84	78.5 (25°C)	$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$	10^{-14}
Ammonia	2.65	1.46	22.0 (-33.5°C)	$2\text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-$	10^{-33}
Hydrogen fluoride	2.40	1.90	83.6 (0.0°C)	$3\text{HF} \rightleftharpoons \text{H}_2\text{F}^+ + \text{HF}_2^-$	$> 10^{-14}$
Hydrogen cyanide	2.00	2.93	106.8 (25°C)	$2\text{HCN} \rightleftharpoons \text{H}_2\text{CN}^+ + \text{CN}^-$	10^{-19}
Sulphur dioxide	2.28	1.61	17.27 (-16.5°C)	$2\text{SO}_2 \rightleftharpoons \text{SO}^{\oplus 2} + \text{SO}_3^{\ominus 2}$	10^{-13}

(b) Polarity of the solvent

Polarity of a molecule results when unsymmetrical molecules contain bonds in which the electron pair forming the bond is shared between the two bonded atoms. Another way of expressing this is that polar molecules are molecules in which the center of negative and the center of the positive charge do not coincide.

One effect of polarity of a solvent is that polar solutes tend to be much more soluble in liquids of high polarity than they are in non-polar solvents. Polar substance like glucose is highly soluble in water but is virtually insoluble in CCl_4 .

(c) Dielectric constant

Coulombic force of attraction, F between a cation and anion in an ionic crystal is given by

$$F = \frac{q^+ q^-}{4\pi r^2 \epsilon_0}$$

where q^+ and q^- are the charges, r is the distance of separation and ϵ_0 is the permittivity of the medium (dielectric constant). ϵ_0 depends upon the nature of the medium in which the two charged ions are suspended. That is, a solvent having a high dielectric constant will weaken the force holding the ions of ionic compound and ultimately will dissolve the ionic compound in it. In general, ion-solvent interactions are favoured (e.g. to facilitate the dissolution of an ionic salt) by using a solvent with a large dipole moment, but for maximum effect, the solvent molecule should also be small, and both ends of it should be able to interact with the ions in the same way that water interacts with cations through the oxygen atoms. Thus, ammonia is a better solvent for ionic salts than dimethylsulfoxide or nitromethane.

(d) Viscosity

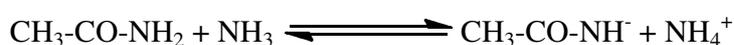
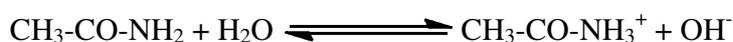
One of the striking differences of various liquids is the differences in their rates of flow. Generally speaking lowering the temperature, increasing the molecular size or making the molecule less symmetrical increases the viscosity of the liquid. Of particular interest is the fact that increasing the viscosity the liquid lowers the mobility of ions and molecules in the liquid and thus reducing the electrical conductance of solutions of electrolytes and increasing the difficulty of such operations as precipitation, crystallization and filtration involving that liquid.

e) *Electrical conductivity*

One of the striking features of ionizing solvents is, these solvents undergo self-ionization, and hence electrical conductance gives an idea about the extent of such ionization. Generally greater the ionization, easier it is for acid-base reaction to occur in the solvent.

f) *Proton affinity*

This property of ionizing solvent is applicable only for protonic solvent like, H₂O, HN₃, etc..... It greatly affects the behaviour of solute in a given solvent system. For example, NH₃ has greater proton affinity than H₂O, therefore acetamide which behaves as a very weak base in aqueous solutions display acidic properties in Liq. NH₃

**15.4 Effect of chemical properties of the solvent***(a) Effect of acidic or basic characteristics of the solvent*

When discussing protonic solvents, we shall use the Bronsted-Lowry definitions and when discussing non-protonic solvents we shall use the somewhat more general Lewis definitions. The acidity or basicity of a protonic solvent exerting a more profound effect on its usefulness as a solvent, because of what is known as the leveling effect of the solvent. This effect results from the self-ionisation of the solvent.



The apparent strength of a protonic acid is dependent on the solvent in which the acid is dissolved. When all the acids, which are stronger than H₃O⁺ ion (example, HClO₄, H₂SO₄, HCl, HNO₃, HBr, HI) are added to water, they donate a proton to water to form H₃O⁺ ion and appear to have equal strength since all these acids are levelled to the strength of H₃O⁺ which is left in solution. This phenomenon namely *the strength of all the acids becomes equal to that of H₃O⁺ is called as levelling effect of the solvent* and here, water is called as levelling solvent for all those acids. The acids stronger than H₃O⁺ are levelled to strength of H₃O⁺ when placed in aqueous solution.

(b) Chemical effects on solubility

The solubility of a specific solute in a specific solvent can be greatly increased by chemical interactions between solute and solvent species. Protogenic solvents such as H₂O, C₂H₅OH are miscible with CH₃COCH₃ in all proportions due to interaction of molecules of H₂O with CH₃COCH₃ through the mechanism of H-bonding.

(c) Effects of oxidizing and reducing characteristics

The usefulness of the solvent on the nature of chemical processes which may be carried out in solution in it also extends to the field of oxidation-reduction processes. In liq NH₃ strong oxidizing agents may not be used because NH₃ itself is a reducing agent and undergoes oxidation with oxidizing agents to elementary N₂ and other oxidation products.

15.5 Metal-Ammonia solutions

If there is one radical difference between chemistry in water and liquid ammonia, it is in the behavior toward group IA metals. When placed in water these metals liberate hydrogen in vigorous reactions such as



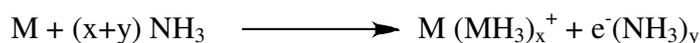
In contrast, these metals dissolve and undergo reaction very slowly in liquid ammonia. Solutions containing alkali metals in liquid ammonia have been known for more than 140 years and they have extraordinary properties. The extent of alkali metals dissolved in liquid ammonia itself is very interesting. And their solubilities are shown in Table 2.

The dissolution does not involve a chemical change in the metal as evident from the fact that evaporation of the solutions regenerates the metal. If the product is not placed under thermal stress, the metal can be recovered as a solvate having the formula M(NH₃)₆. Moreover, the solutions of alkali metals in liquid NH₃ have lower densities than the solvent alone and hence, some expansion of the liquid occurs when the metal dissolves. The dilute solutions appear as blue in color irrespective of alkali metal dissolved in it, but are bronze colored when concentration is more than approximately 1M. The solutions exhibit conductivity which is higher than that of 1:1 electrolyte. The conductivity decreases as the concentration of the metal increases, but the conductivity of concentrated solutions is characteristic of metals. Further, the solutions are paramagnetic, but the magnetic susceptibility decreases for concentrated solutions. The magnitude of the magnetic susceptibility is in agreement with there being one free electron produced by each metal atom.

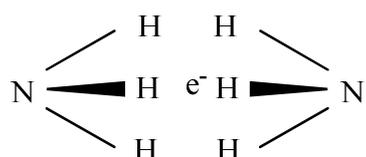
Table 2 Solubility of Alkali Metals in liquid Ammonia

Metal	Temp. °C	Molarity of saturated solution	Temp. °C	Molarity of saturated solution
Li	0	16.31	-33.2	15.66
Na	0	10.00	-33.5	10.93
K	0	12.41	-33.2	11.86
Cs	0	----	-50.0	25.1

The model of metal-ammonia solutions that has emerged is based on ionization of the metal atoms to produce metal ions and electrons, both are solvated. The solvated electron is believed to reside in a cavity in ammonia, and thus it may behave as a particle in a three-dimensional box with quantized energy levels. Transitions between the energy levels may give rise to absorption of light and thereby cause the solutions to be colored. The dissolution process can be represented as

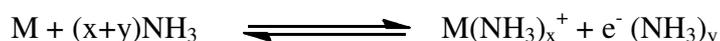


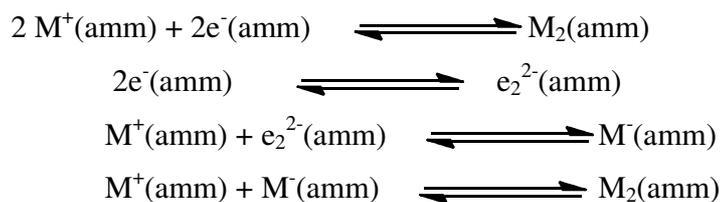
The form of the cavity in which an electron resides is not known, but it is reasonable to expect that the hydrogen atoms are directed around the electron in some way because of their slight positive charge. Although there may be several molecules of ammonia forming the cavity, it is reasonable to represent it as shown below



In this representation, somewhat positive hydrogen atoms form a cage around the electron. The solvated electron in liquid ammonia exhibits a maximum at approximately 1500 nm.

Solutions of alkali metals in liquid ammonia have been studied by electrical conductivity, magnetic susceptibility, nuclear magnetic resonance, volume expansion, spectroscopy (visible and infrared), and other techniques. The data obtained indicate that the metals dissolve with ionization and the metal ion and electron are solvated. Equilibria that have been postulated to explain the unique properties of the solutions are represented as follows:

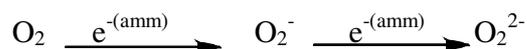




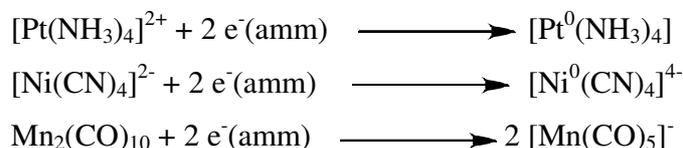
The expansion of the solution has been accounted for by considering the electron as residing in a hole in the solvent. Although it is not likely that all of these steps are involved, it is likely that the relative importance of these reactions depends on the particular metal dissolved and the concentration of the solution. In addition to dissolving, alkali metals also react slowly by the liberation of hydrogen,



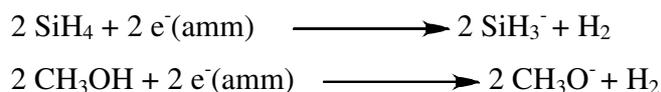
This reaction is accelerated photochemically and is catalyzed by transition metal ions. Since, the solutions of alkali metals in liquid ammonia contain free electrons, they act as strong reducing agents. This fact has been exploited in a number of reactions. For example, oxygen can be converted to super-oxide or peroxide ions as shown below



The solutions can also convert transition metals to unusual oxidation states.



Many compounds react in liquid ammonia by loss of hydrogen and produce an anion. Some examples of this type of reaction are



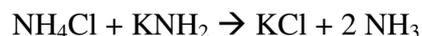
It has also been found that alkali metals dissolve in solvents such as methylamine and ethylenediamine. These solutions have similar characteristics of the solutions containing ammonia, and they undergo similar reactions.

Dilute solutions of alkali NH_3 have many applications as reducing agents in inorganic syntheses. The group 2 metals Ca, Sr and Ba dissolve in liquid NH_3 to give bronze-coloured $[\text{M}(\text{NH}_3)_x]$ species, and for $\text{M} = \text{Ca}$, neutron diffraction data confirm the presence of octahedral $[\text{Ca}(\text{NH}_3)_6]^{2+}$ complex ion. Although pale blue solutions are obtained when Mg is added to NH_3 , complete dissolution is not observed and no ammine adducts of Mg have been isolated from

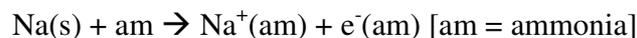
these solutions. However, combining an Hg/Mg (22:1 ratio) alloy with liquid NH₃ produces crystals which contain octahedral [Mg(NH₃)₆] units, hosted within an Hg lattice. This material is superconducting with a critical temperature, T_c, of 3.6 K.

15.6 Solvated electron

Liquid ammonia, (obtained by cooling the gas to below -33°C) is an example of a non-aqueous solvent which will dissolve ionic species. Many similarities are there between reactions occur in ammonia and in water. Both solvents are slightly self-ionizing. In water, alkali (base) as a substance which gives OH⁻ ions, whereas in liquid ammonia alkali as a substance which gives NH₂⁻ ions. Thus NaNH₂ is an alkali in ammonia (equivalent in water: NaOH), and so is K₂NH (equivalent to K₂O). Ammonium salts are regarded as acids in liquid ammonia, and a typical neutralization reaction is represented as



The remarkable property of alkali metals is their ability to dissolve in liquid ammonia and resulting solution formed resembles liquid metals. Solid metal is reformed (except in the case of lithium) after evaporation of the solvent. These solutions contain alkali metal cations and electrons, i.e.,



It is important to note that, the removal of an electron from an alkali metal in the gas phase is highly endothermic, but in solution both the metal cation and the electron are heavily solvated (i.e., surrounded by ammonia molecules which are tightly held by ion-dipole forces) hence the reaction is exothermic.

The properties of the solutions are determined largely by the properties of the solvated electron. This solvated electron is highly mobile therefore the solution has a high conductivity. The magnitude of conductance is higher than solutions of corresponding alkali metal salt. Alkali metal ions are colorless, but the solution of alkali metals in ammonia is blue in colour. The blue color is due to solvated electron which absorbs in the red and infra-red region of the electromagnetic spectrum.

We were discussed about few similarities between the actions of water and ammonia on the alkali metals. Ammonia produces a solution containing electrons, whereas water reacts vigorously and high exothermically with alkali metals and evolving hydrogen as well as enormous amount of heat. The reason for this difference is the variation in the stability of the

solvated electron in the two solvents. The lifetime of an electron in water is less than one thousandth of a second. It reacts as follows



Therefore the reaction of sodium with water as involving the formation of Na^+ ions and electrons, followed by reaction of the electrons with the solvent. In contrast, the electron is stable almost indefinitely in ammonia and if a suitable catalyst such as iron(III) oxide is added then decomposition is rapid which is precisely analogous to the reaction in water.



The reaction of ammonia with the electron is energetically favourable, but in the absence of a suitable catalyst the activation energy is too high for the reaction to occur at a suitable rate. The catalyst reduces the activation energy by providing an alternative pathway, and decomposition then occurs rapidly.

15.7 Hydrated electron

Hydrated electrons form when excess electrons are injected into water. i.e, when high-energy radiation passes through aqueous media, hydrated electrons are formed. Such electrons are designated as $e^-(aq)$, and are confined to cavities within liquid water. They are central to radiation chemistry and are as diverse as environmental chemistry, charge-induced reactivity, nuclear waste reprocessing, and biological radiation damage. Since their discovery, their reactivity has been intensely studied in bulk water.

Hydrated electrons are extra electrons solvated in water. The process of solvation may be envisaged as the polarization of the solvent molecules owing to electron-dipole interactions. The electric field of the extra electron, inducing a potential well which then traps and stabilizes the electron. The study of solvation energy, diffusion coefficient and interaction distance indicates that a charge distribution is even larger than that of an iodide ion, and probably extending 2.5-3.0 Å from the centre as shown in figure.

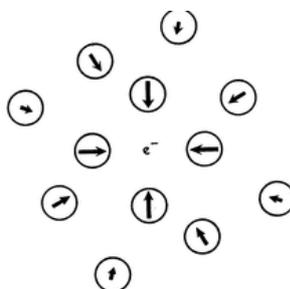


Figure 2. Diagrammatic representation of a solvated electron

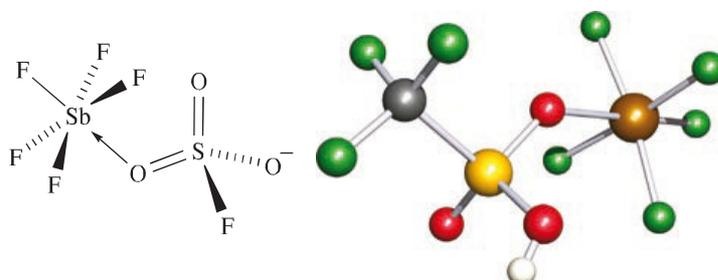
15.8 Super acids

Super acid is a medium having high acidity generally greater than of 100% sulfuric acid.

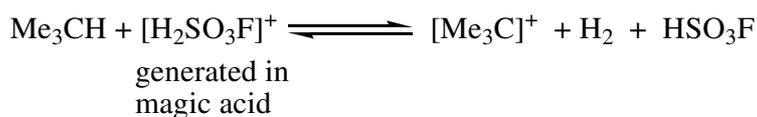
Or

A super acid is any acid with greater in strength than sulphuric acid, because sulphuric acid is undergo 100% ionization. The common superacids are made by dissolving a powerful Lewis acid (e.g. SbF_5) in a suitable Bronsted acid such as HF or HSO_3F (an equimolar mixture of HSO_3F or HF and SbF_5 is known by the trade name Magic acid). Which is the strongest acid known in the world, the molecular formula is HSbF_6 . It is rapidly and explosively decomposes in water. Another example of super acid is trifluoromethylsulphonic acid also known as triflic acid. Its molecular formula is $\text{CF}_3\text{SO}_3\text{H}$, it is a colorless liquid at room temperature. It is used in many organic reactions.

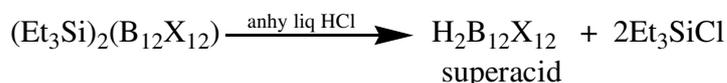
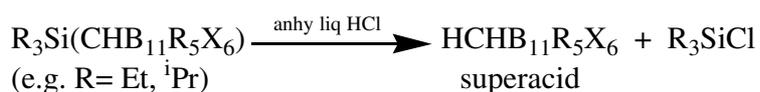
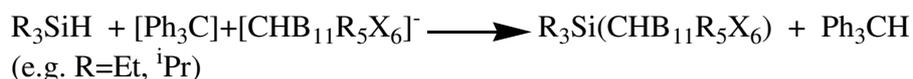
Superacids are extremely potent acids and capable of protonating even hydrocarbons. They are including mixtures of HF and SbF_5 , and HSO_3F and SbF_5 . The latter mixture is called magic acid and is available commercially under the name Antimony (V) fluoride. It is a strong Lewis acid and forms an adduct with F^- (from HF) or $[\text{SO}_3\text{F}]^-$ (from HSO_3F).



Equilibrium is an over-simplification of the $\text{SbF}_5\text{-HSO}_3\text{F}$ system, but represents it sufficiently for most purposes. The species present depend on the ratio of $\text{SbF}_5\text{:HSO}_3\text{F}$, and at higher concentrations of SbF_5 , species including $[\text{SbF}_6]^-$, $[\text{Sb}_2\text{F}_{11}]^{2-}$, $\text{HS}_2\text{O}_6\text{F}$ and $\text{HS}_3\text{O}_9\text{F}$ may exist. In superacidic media, hydrocarbons act as bases, and this is an important route to the formation of carbenium ions.



Superacids have a wide range of applications and have been used to access species such as $[\text{HPX}_3]^+$ (X=halide), $[\text{C}(\text{OH})_3]^+$ (by protonation of carbonic acid), $[\text{H}_3\text{S}]^+$, $[\text{Xe}_2]^+$ and metal carbonyl cations. However, the conjugate bases of traditional superacids are typically strongly oxidizing and strongly nucleophilic, and are not necessarily innocent bystanders in a reaction mix-mixture. A recently developed class of superacids involves icosahedral CB_{11} (carbaboranes) or B_{12} cluster cages. An advantage of these acids is that they possess chemically inert, extremely weak conjugate bases. The carbaborane anions $[\text{CHB}_{11}\text{R}_5\text{X}_6]^-$ (R = H, Me, Cl and X = Cl, Br, I) and $[\text{B}_{12}\text{X}_{12}]^{2-}$ (X = Cl, Br) are the conjugate bases of members of this family of superacids. While the anions $[\text{CHB}_{11}\text{R}_5\text{X}_6]^-$ and $[\text{B}_{12}\text{X}_{12}]^{2-}$ are chemically unreactive, their conjugate acids are an extremely potent Brønsted acids, stronger than fluorosulfonic acid. The superacids $\text{HCHB}_{11}\text{R}_5\text{X}_6$ and $\text{H}_2\text{B}_{12}\text{X}_{12}$ are prepared in two steps.



Above reactions show the formation of intermediate silylium species which are of interest in their own right. The Si–Cl distance is 232 pm which is significantly greater than the sum of the covalent radii (217 pm). This indicates that $i\text{Pr}_3\text{Si}(\text{CHB}_{11}\text{H}_5\text{C}_{16})$ is tending towards an $[i\text{Pr}_3\text{Si}]^+[\text{CHB}_{11}\text{H}_5\text{C}_{16}]^-$ ion-pair, although well separated ions are clearly not present. Similarly, the solid state structure of $(\text{Et}_3\text{Si})_2(\text{B}_{12}\text{Cl}_{12})$ reveals Et_3Si units associated with the B_2Cl_{12} cage through long Si–Cl bonds (231 pm). The Et_3Si units are flattened and the sum of the C–Si–C bond angles is 348° which approaches the 360° expected for an isolated $[\text{Et}_3\text{Si}]^+$ ion. Treatment of the intermediates with anhydrous liquid HCl yields anhydrous $\text{HCHB}_{11}\text{R}_5\text{X}_6$ and $\text{HB}_{12}\text{X}_{12}$. These super acids protonate most solvents. They can be handled in liquid SO_2 , although complete ionization appears to take place, probably with the formation of $[\text{H}(\text{SO}_2)_2]^+$.



The exceptional acid strength of these superacids is illustrated by their ability to protonate arenes (e.g. C_6H_6 , $\text{C}_6\text{H}_5\text{Me}$, C_6Me_6). The resultant salts are remarkably thermally stable, e.g. $[\text{C}_6\text{H}_7]^+[\text{CHB}_{11}\text{Me}_5\text{Br}_6]^-$ is stable to 423 K.

Also super acids are used in chemical engineering and petrochemistry to produce plastics and high octane gasoline. The superacids are also used to form and sustain organic cations, these cations are used in intermediate reactions as well as to make final product.

15.9 Summary of the unit

Water is the most commonly used solvents because its ability to dissolve wide variety of substances and its availability in high purity. Also water is more convenient for handling and it has ability to ionize many substances. Due to these reasons water is referred to as universal solvent. But it also has limitations the more important limitations of water as a reaction medium are i) reactions involving acids stronger than H_3O^+ ion cannot be carried out in aqueous solution, similarly reactions involving bases stronger than OH^- ion cannot be carried out in aqueous solution. ii) Reaction involving strong reducing agents cannot be carried out in aqueous solution because such reagents react with water causing evolution of hydrogen. The choice of a solvent for carrying out chemical reactions is determined by the chemical properties of the solvent. The melting and boiling points determine the temperature range within which the solvent is useful. Similarly the magnitude of molar heat of fusion and vapourization gives an idea of the associable forces between molecules of a solvent. Generally the solvents of high dielectric constant will be much better reaction media for ionic substances than the solvents of low dielectric constant. Solvents have been classified in a number of ways depending upon some chemical or physical properties.

15.10 Keywords

Non aqueous solvents; Ionizing solvents; Non-ionizing solvents; Polarity of the solvent; Dielectric constant; Viscosity; oxidizing and reducing character of solvent; Metal-Ammonia solutions; Solvated electron; Hydrated electron; Super acids

15.11 References for further study

1. Inorganic Chemistry, 4th Ed., J. E. Huheey, E.A. Keiter and R. L. Keiter, O. K. Medhi, Pearson Education, 2009.
2. Theoretical Inorganic chemistry – M. C. Day and J.Selbin.
3. Concepts and Methods of Inorganic Chemistry – B. E. Douglas and D. H. McDaniel.
4. Inorganic chemistry – An Advanced Text book – Therald Moeller.

15.12 Questions for self understanding

- 1) What are the physical properties a liquid must possess in order to act as an ionizing solvent?
- 2) Discuss the role of physical properties in the solvent action of water and one of the non-aqueous solvents.
- 3) Explain the importance of solvents as reaction media
- 4) What are the important physical properties of solvents? Discuss briefly
- 5) What are the Classification of the solvent based on their physical and chemical properties? Give one example each,
- 6) Write a note on
 - A) Non aqueous solvents
 - B) Ionizing solvents
 - C) Non-ionizing solvents
- 7) Explain the effect of chemical properties of solvents on reaction
- 8) Discuss the different reactions occurs in metal ammonia solution.
- 9) Write a note on metal-ammonia solution
- 10) What is hydrated electron and discuss its applications and
- 11) What are the differences between ammoniated and hydrated electron.
- 12) What are super acids? Give two examples

Unit - 16**Structure**

- 16.0 Objectives of the unit
- 16.1 Introduction
- 16.2 Chemistry in Liquid ammonia (Liquid ammonia as a solvent)
 - A) *Ammoniation Reactions*
 - B) *Ammonolysis Reactions*
 - C) *Metathesis (Precipitation) Reactions*
 - D) *Acid-Base Reactions*
- 16.3 Liquid Hydrogen Fluoride as a solvent
- 16.4 Liquid Sulfur dioxide as a solvent
 - a) *Reactions with organic compounds*
- 16.5 Anhydrous sulphuric acid as a solvent
- 16.6 Liquid Dinitrogen Tetraoxide as a solvent
 - a) *Acid-Base reactions*
 - b) *Solvolytic reactions*
 - c) *Reaction with metals*
 - d) *Formation of molecular compounds*
 - e) *Applications*
- 16.7 Liquid Bromine trifluoride as a solvent
 - a) *Reactions in BrF_3*
- 16.8 Summary of the unit
- 16.9 Key words
- 16.10 References for further study
- 16.11 Questions for self under standing

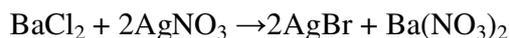
16.0 Objectives of the unit

After studying this unit you are able to

- ❖ Explain the different types of reactions studied in Liquid ammonia
- ❖ Explain the different types of reactions studied in Liquid Hydrogen Fluoride
- ❖ Explain the different types of reactions studied in Liquid Sulfur dioxide
- ❖ Explain the different types of reactions studied in Anhydrous sulphuric acid
- ❖ Explain the different types of reactions studied in Liquid Dinitrogen Tetraoxide
- ❖ Explain the different types of reactions studied in Liquid Bromine trifluoride
- ❖ compare different physical and chemical properties of non-aqueous solvents

16.1 Introduction

It is desirable to carry out chemical reaction in a solvent because, in a solvent it is possible to achieve intimate contact between reactants otherwise they would not react. For example, in the reaction



The reaction proceeds very much slowly in the solid state even though thermodynamic conditions are favour. However in solution state (example, aqueous solution) the reaction proceeds very rapidly to give the products. Usually it is possible to alter the course of the reaction (i.e, rate, direction, etc....) using suitable solvent. For example Barium chloride and silver nitrate react and form a precipitate of silver chloride in water. But reverse reaction is occurs in liquid ammonia. The reactions those are violent when pure reactants are taking part in reactions are slowdown and controlled using solvent. For example, the direct reaction between anhydrous stannic chloride and anhydrous hydrazine occurs with explosive violence but it occurs very smoothly in chloroform solvent. Also it is possible to separate the desire product form the reaction mixture by making use of suitable solvent. Since different substance have difference in solubility. For example, in the reaction between barium bromide and silver nitrate the desired product silver bromide can be separated from the other products i.e., $\text{Ba}(\text{NO}_3)_2$ by doing reaction in water. The sparing solubility of silver bromide and high solubility of $\text{Ba}(\text{NO}_3)_2$ in water make silver bromide to precipitate out and simple filtration and washing with water enable to get pure product.

Most of the chemical reactions are taking place in aqueous solutions. It is unfortunate that usually while carry out reaction, the importance was given only for the reacting substances and

ignore the importance of the solvent on the course of a chemical reaction. By changing the solvent, the reactant may give different products or even the direction of reaction can be reversed. LiNO_3 and NH_4Cl do not react in aqueous solution but give a precipitate of LiCl in liq. NH_3

16.2 Chemistry in Liquid ammonia (Liquid ammonia as a solvent)

In many of its properties, liquid ammonia resembles water except that of dielectric constant. The lower dielectric constant results in a decreasing ability to dissolve ionic compounds, especially those containing highly charged ions (carbonates, sulphates and phosphates). Both are polar and involve extensive hydrogen bonding in the liquid state. Hydrogen bonding in liquid ammonia is less extensive compare to in water, because in water the oxygen atoms can form hydrogen bonds to two other water molecules. This difference is evident from the fact that the heat of vaporization of water is 40.6 kJ/mol, but that of ammonia is only 23.26 kJ/mol. Although there are differences when specific types of compounds are considered, both water and liquid ammonia dissolve many types of solids. In some cases, the solubility is higher than might be expected on the basis of the dielectric constant alone. In these cases, there is a stabilizing interaction between the solute and the ammonia. It is necessary to work with liquid ammonia at low temperature or high pressure since its boiling point is $-33.4\text{ }^\circ\text{C}$. By storing liquid ammonia in a Dewar flask, it is possible to keep it for a reasonable length of time since the rate of evaporation becomes slow.

We have already mentioned that silver chloride is readily soluble in liquid ammonia. Because it is slightly less polar than water and has lower cohesion energy, intermolecular forces make it possible for organic molecules to create cavities in liquid ammonia as a result most organic compounds are more soluble in liquid ammonia than they are in water. Physical data for liquid ammonia are summarized in Table 1.

Table 1 Physical Properties of Liquid NH_3 .

Melting point	$-77.7\text{ }^\circ\text{C}$
Boiling point	$-33.4\text{ }^\circ\text{C}$
Density at $-33.1\text{ }^\circ\text{C}$	0.683 gcm^{-3}
Heat of fusion	5.98 kJmol^{-1}
Heat of vaporization	23.26 kJmol^{-1}

Dipole moment	1.4 D
Dielectric constant at -60 °C	26.7 ϵ_0
Specific conductance at -35 °C	2.94 x 10 ⁻⁷ ohm
Viscosity at -33 °C	0.254 g cm ⁻¹ s ⁻¹

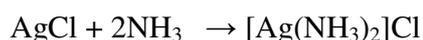
Liquid ammonia is a base, so reactions with acids generally proceed to a greater degree than do the analogous reactions in water. For example, *acetic acid is weak acid in water, but it ionizes completely in liquid ammonia*. Liquid NH₃ is an ideal solvent for reactions requiring a strong base, since the amide ion is strongly basic. Even though ammonia is base, it is possible for protons to be removed, but only when it reacts with exceedingly strong bases such as N³⁻, O²⁻, or H⁻. Solutions of *ammonium halides in liquid NH₃ may be used as acids*, in the preparation of Germane, GeH₄, from Mg₂Ge in a reaction analogous to the preparation of SiH₄.



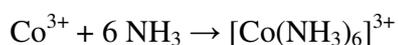
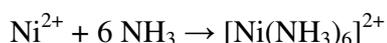
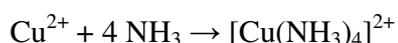
Some of the important types of reactions that occur in liquid ammonia are illustrated below

E) Ammoniation Reactions

Most solvents have unshared pairs of electrons, and they are polar therefore they have the ability to attach to metal ions or interact with anions. As a result, when many solids crystallize from solutions, they have induced a definite number of solvent molecules. Consider the behavior of AgCl in liquid ammonia.

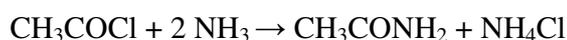


Because ammonia is the solvent, the solvated species is known as an *ammoniate*. Some other reactions of this type are shown below:



F) Ammonolysis Reactions

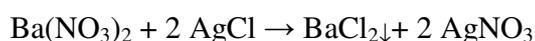
Reactions in which ammonia molecules split are known as ammonolysis reactions. Some examples of these reactions can be illustrated as follows



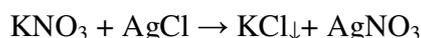
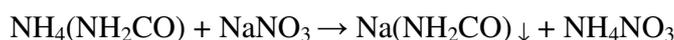
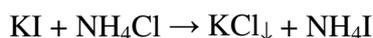
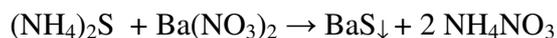


G) Metathesis (Precipitation) Reactions

In order for a metathesis reaction to occur in water, some products must be removed from the reaction. Generally, this involves the formation of a precipitate, the evolution of a gas or the formation of a unionized product. Because solubilities are different in liquid ammonia, reactions are often unlike those in water. Although silver halides are insoluble in water, they are soluble in liquid ammonia as a result of forming stable complexes with ammonia. Therefore, the reaction



takes place in liquid ammonia because BaCl_2 is insoluble, but in water, the reaction

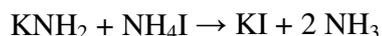
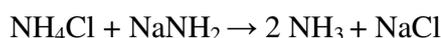


H) Acid-Base Reactions

Ammonia undergoes autoionization with the formation of NH_4^+ and NH_2^- ions as shown below



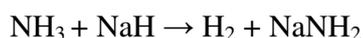
For liquid ammonia, NH_4^+ is the acidic species and NH_2^- is the basic species. Therefore, such a reaction can be shown as



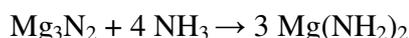
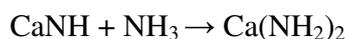
Acid-base reactions also include those in which the solvent itself functions as an acid or a base.

This can be shown as follows

Sodium hydride reacts with liquid ammonia to produce a basic solution as shown below



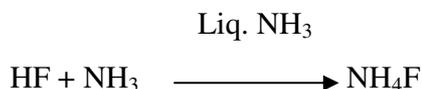
The imide and nitride ions are bases toward liquid ammonia. Both are too strong to exist in liquid ammonia, so they react to produce a weaker base, NH_2^- .



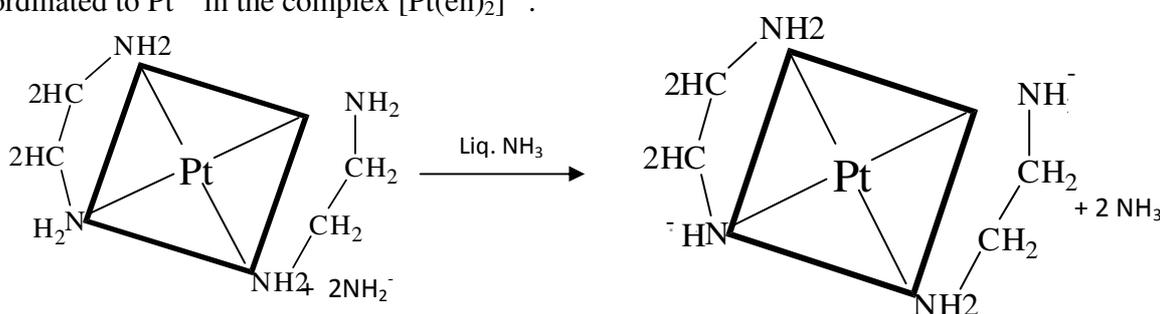
The oxide ion is also sufficiently strong as a base to remove protons from ammonia.



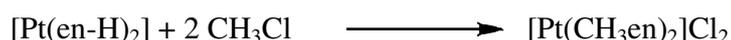
Because of the base strength of liquid ammonia, acids that are weak in water ionize completely in liquid ammonia.



A type of deprotonation reaction that takes place in liquid ammonia but not in water occurs because it is possible to utilize the base strength of the amide ion. The reaction involves removing H^+ from a molecule of ethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (written as en), that is coordinated to Pt^{2+} in the complex $[\text{Pt}(\text{en})_2]^{2+}$.

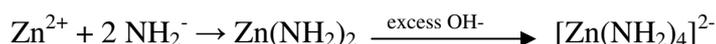
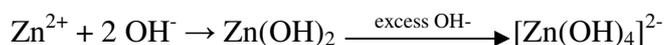


When the proton has removed from ethylenediamine, then it is designated as en-H, the complex can be written as $[\text{Pt}(\text{en-H})_2]$ and it is unchanged. This is a reactive species will undergo numerous reactions in liquid ammonia. This procedure was used by Watt and coworkers to produce derivatives of the ethylenediamine ligands by means of reactions such as

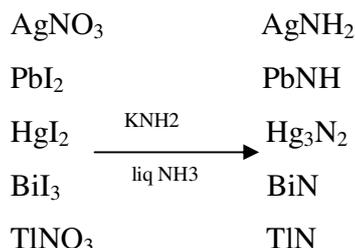


These interesting synthetic reactions are possible because of the basicity of NH_2^- , which cannot be utilized in aqueous solutions.

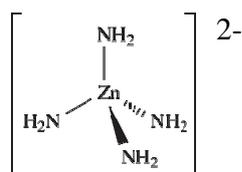
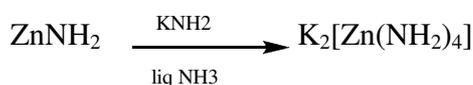
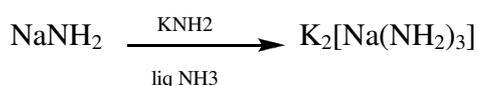
Amphoteric behaviour resulting from complex formation with excess amide also resembles that in water.



Reactions metal salts in liquid ammonia in the presence of KNH_2 result in the precipitation of metal amides, imides or nitrides.

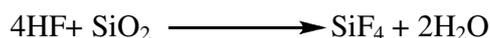


Many metal amides, imides and nitrides are similarly dissolved in solutions of KNH₂ in liquid NH₃. Infact because of the very strong basic character of the amide ion, the formation of amide complexes occurs for more metal ions than is true of hydroxo complexes.



16.3 Liquid Hydrogen Fluoride as a solvent

Early studies were hampered by the aggressive nature of anhydrous hydrogen fluoride towards glass and quartz, but the pure acid can now be safely handled without contamination using fluorinated plastics such as Teflon (polytetrafluoroethylene) or if absolutely free of water, in Cu or Monel metal (a nickel alloy) equipment.



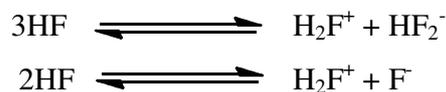
The molecule is polar, there is some autoionization, and it is a fairly good solvent for numerous ionic solids. Although the boiling point of liquid HF is rather low (19.5 °C), it has a liquid range that is comparable to that of water, because of extensive hydrogen bonding. The physical properties of HF are shown in Table 2.

Table 2 Physical properties of HF

Melting point	-83.1 °C
Boiling point	19.5 °C
Density at 19.5 °C	0.991 g cm ⁻³
Heat of fusion	4.58 KJ mol ⁻¹
Heat of vaporization	30.3 KJ mol ⁻¹

Equivalent conductance	$1.4 \times 10^{-5} \text{ ohm}^{-1}$
Dielectric constant at 0 °C	83.6
Dipole moment	1.83 D

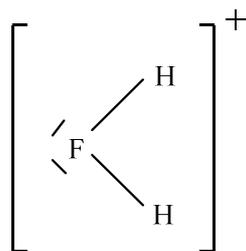
The autoionization of liquid HF can be represented by the equation



HF has an equivalent conductance of $1.4 \times 10^{-5} \text{ ohm}^{-1}$ at 25 °C. Therefore, the ion product constant for HF ionization is approximately 8×10^{-12} , which is larger than the value of 1.0×10^{-14} for water. The HF_2^- ion has a symmetric linear structure

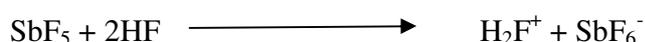


and it represents the strongest case of hydrogen bonding. It can be considered as a molecule of HF solvating a fluoride ion. The H_2F^+ cation has eight electrons around the central F atom, so it is isoelectronic with water, and the structure of the ion is

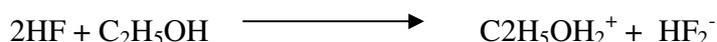
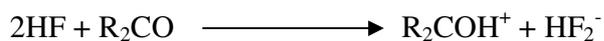


Both the dielectric constant and dipole moment are comparable to those of water, indicating that HF is a good solvent for inorganic compounds, but many organic compounds are also soluble. *The high dielectric constant, low viscosity and long liquid range of HF make it an excellent solvent for a wide variety of compounds.* In general, the fluorides of +1 metals are much more soluble than those of +2 or +3 metals.

The acidity of liquid HF is high enough that it can be function as an acid catalyst in many instances. The cation characteristic of the solvent, H_2F^+ , is generated when HF reacts with a strong lewis acid that is capable of forming stable fluoride complexes. The reaction with BF_3 , SbF_5 and AsF_5 are typical examples:



Equations such as these can also be written in the molecular form as



In addition to these types of reactions, liquid HF converts some oxides to oxyhalides. For example, the reaction of permanganate can be shown as follows:



It is apparent that liquid HF is a versatile and useful non-aqueous solvent.

16.4 Liquid Sulfur dioxide as a solvent

Liquid SO_2 is an important non-aqueous solvent. It is polar and aprotic, and readily solvates anions. Although the SO_2 molecule has a significant dipole moment, the liquid is a good solvent for many covalent substances. The molecule is polarizable because of the pi electrons, so the London forces between SO_2 and solute molecules lead to solubility. In accordance with the hard-soft interaction principle, compounds such as OSCl_2 , OPCl_3 and PCl_3 are very soluble. Although aliphatic hydrocarbons are not soluble in liq SO_2 , aromatic hydrocarbons are appreciably soluble in the liquid. This difference in solubility provides a way to separate the two types of hydrocarbons by means of solvent extraction. Ionic compounds are almost insoluble unless they consist of very large ions which contribute to polarizability and low lattice energy. The solubilities of metal halides decrease in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$. Metal sulphates, sulphides, oxides and hydroxides are insoluble. Physical properties for liq sulfur dioxide are shown in Table 3. As it is evident from the Table, SO_2 is a useful solvent for carrying out reactions utilizing super acids such as the $\text{HOSO}_2\text{F}/\text{SbF}_5$ mixture.

Table 3. Physical properties of SO_2 .

Melting point	-75.5 °C
Boiling point	-10.0 °C
Density	1.46 g/cm ³
Heat of fusion	8.24 kJ/mol
Heat of vaporisation	24.9 kJ/mol
Dipole moment	1.63 D
Dielectric constant	15.6
Specific conductance	3×10^{-8} /ohm

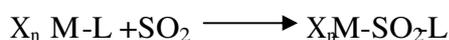
SO_2 can function as a very weak acid or a lewis base and thereby form a variety of solvates



With some very strong lewis acids, hydrolysis occurs to produce an oxyhalide



The SO_2 molecule has unshared pairs of electrons on both the sulfur and oxygen atoms. As a result, it forms numerous complexes with transition metals in which it is known to attach in several ways. These include bonding through the sulfur atom, through an oxygen atom, by both oxygen atoms, and various bridging schemes. In most cases, the complexes involve soft metals in low oxidation states. Another important reaction of sulfur dioxide is known as the insertion reaction in which it is placed between the metal and another ligand. This type of reaction is shown as

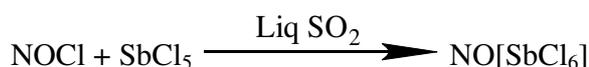
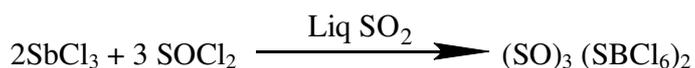


(where X and L are other groups bonded to the metal)

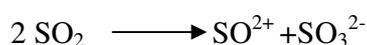
The solubility of I_2 in liq SO_2 is greatly increased by the addition of KI or RbI.



Similarly, the solubilities of Cd or mercuric iodides in SO_2 are increased by the presence of KI or RbI, thus indicating that complexes are formed.



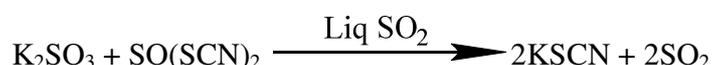
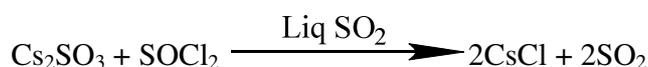
Liquid SO_2 undergoes autoionization as shown below



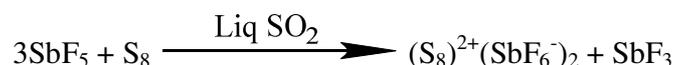
From the above equation, the acidic species would be SO^{2+} and the basic species would be SO_3^{2-} . Therefore, the neutralization reaction takes place as expected on the basis of the solvent concept.



The electrical conductivity of pure liq SO_2 ($4 \times 10^{-8} \text{ ohm}^{-1} \text{cm}^{-1}$ at -10°C) is commonly interpreted in terms of self-ionisation as shown above. The alkali metal sulphites which contain SO_3^{2-} ions act as bases in liq SO_2 and the compounds which contain or make available the SO^{2+} ion would be typical acids in liq SO_2 .

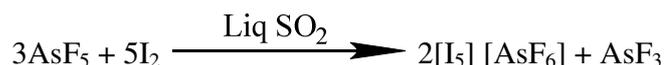


An illustration that a non-aqueous solvent such as liquid SO_2 is a versatile reaction medium for the following:

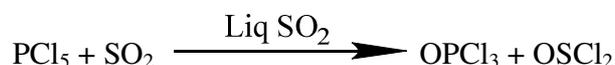


By increasing the ratio of SbF_5 to S_8 , it is also possible to generate the S_4^{2-} species.

$[\text{I}_3]^+$ and $[\text{I}_5]^+$ have been isolated as the $[\text{AsF}_6]^-$ salts from the reactions of AsF_5 and I_2 in liquid SO_2 , the product depending on the molar ratio of the reactants.



The reaction between PCl_5 and liquid SO_2 can be used to produce thionyl chloride and phosphoryl chloride.



The amphoteric behavior of Zn^{2+} and Al^{3+} can be demonstrated in liquid SO_2 . For example, the aluminium compound containing the anion characteristic of the solvent forms a precipitate, which is then soluble in either the acid or base in liquid SO_2 . This can be shown as



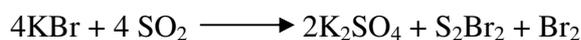
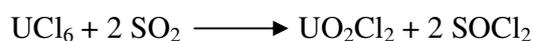
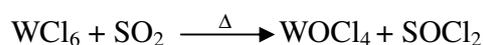
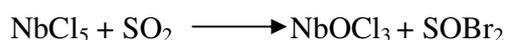
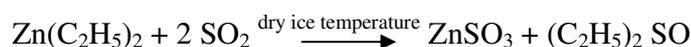
As we have already seen, SOCl_2 is an acid in liquid SO_2 , so the precipitate of $\text{Al}_2(\text{SO}_3)_3$ reacts as follows to give aluminum chloride and the solvent:



In liquid SO_2 the basic species is SO_3^{2-} so $[(\text{CH}_3)_4\text{N}]_2\text{SO}_3$ gives a basic solution in which aluminum sulfite dissolves by forming a sulfite complex, as shown in the equation

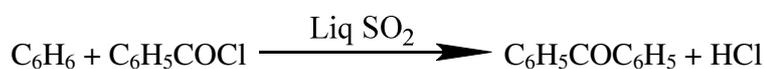
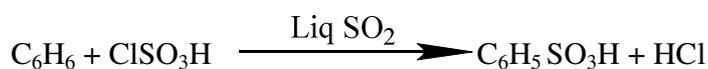


Solvolytic reactions of liquid SO_2 are much less common and are generally complex.

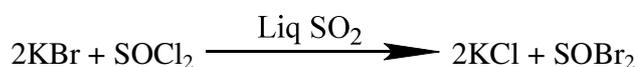


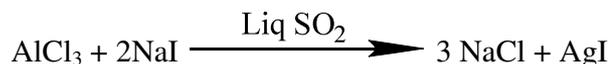
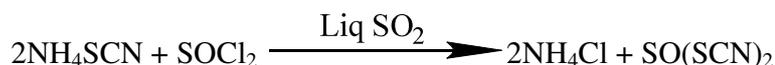
a) *Reactions with organic compounds*

Liquid SO_2 serves as suitable medium for a number of organic reactions. For example



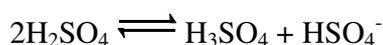
Precipitation reactions: Consider the following reactions that are carried out in liquid SO_2 :



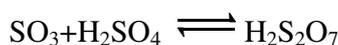
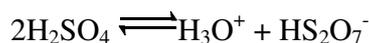


16.5 Anhydrous sulphuric acid as a solvent

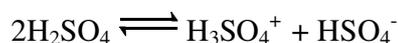
Another solvent that has been extensively investigated is sulfuric acid, which undergoes auto-ionization,



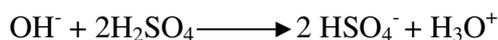
For this equilibrium, the ion product constant has a value of approximately 2.7×10^{-4} . However, the discussion is complex and other species are present in sulfuric acid as a result of equilibria that can be written as



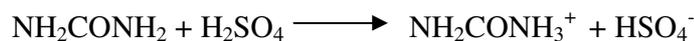
Disulfuric acid (also known as pyrosulfuric acid or oleum) also undergoes dissociation. Higher dielectric constant makes it a good solvent for ionic compounds and lead to extensive auto-ionisation. High viscosity of it introduces difficulties. For example, the solutes are slow to dissolve and slow to crystallize. Rate of filtration slows down. It is also difficult to remove adhering solvent from crystallized materials. Auto-ionization of sulphuric acid is shown below



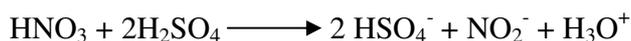
The solutes that are basic in water are also basic in sulphuric acid.



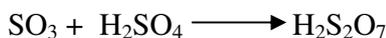
Urea which is a non electrolyte in water and acids in ammonia accept protons from sulphuric acid.



Acetic acid is a weak acid in aqueous solution and nitric acid a strong acid, but both behave as bases in sulphuric acid.



One of the compounds found to behave as an acid in sulphuric acid is disulphuric acid. It is formed from SO_3 and H_2SO_4 .



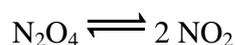
16.6 Liquid Dinitrogen Tetraoxide as a solvent

Liquid N_2O_4 has convenient liquid range. It is a suitable solvent due its low dielectric constant (and hence poor solvent for ionic compounds), it exhibits the variety of dissociation equilibria, it exhibit lewis acid character and oxidizing power. Physical properties of liquid N_2O_4 are given in Table 4.

Table 4. Physical properties of N_2O_4 .

Melting point	-12.3 °C
Boiling point	21.3 °C
Density	1.49 g/cm ³ at 0C
Dielectric constant	2.42 at 18 °C
Specific conductance	2.3x10 ⁻¹³ ohm ⁻¹ cm ⁻¹ at 17 °C

Equilibria in liquid and gaseous N_2O_4



Equilibrium constant, K for the above reaction in liquid phase at 20 °C $\text{N}_2\text{O}_4=1.0 \times 10^{-6}$ (which means that concentration of NO_2 in the liquid phase is quite low).



The dissociation in pure liquid N_2O_4 is very small as evident from the low specific electrical conductance. Solubilities in N_2O_4 are similar to the corresponding solubilities in ether. The strong oxidizing tendency of this solvent precludes its use as a solvent for many solvents with reducing properties. Alkanes, aromatic hydrocarbons, halo and nitro hydrocarbons and carboxylic compounds form addition compounds.

a) Acid-Base reactions

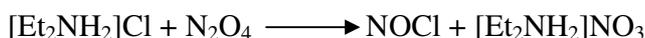


$NOCl$, $NOBr$ act as acids as they furnish NO^+ ions while $(Et_2NH_2)NO_3^-$ act as base. Low dielectric constant of N_2O_4 favours ionic reactions. However, a solution of $NOCl$ in liquid N_2O_4 reacts with $AgNO_3$.

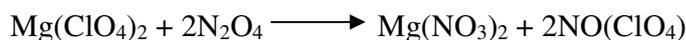


b) Solvolytic reactions

Preparation of anhydrous nitrates is an important reaction in liquid N_2O_4 (preparation of anhydrous nitrate is difficult in aqueous medium).



In the presence of small amounts of H_2O , Li_2CO_3 is solvolysed



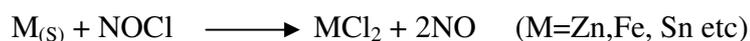
Similarly CaO , $CaCO_3$, Na_2CO_3 , $NaOH$, $ZnCO_3$, ZnS form anhydrous nitrates.

c) Reaction with metals

Very active metals react with liquid N_2O_4 in manner analogous to their reactions with water.



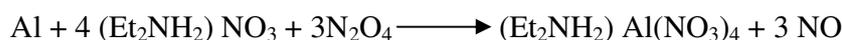
The addition of $NOCl$ to liquid N_2O_4 increases its reactivity toward metals.



Amphoteric metals such as Zinc behave toward liquid N_2O_4 in a manner analogous to their behavior towards aqueous acids and bases.



Diethyl ammonium nitrate zincate



d) Formation of molecular compounds

N_2O_4 forms molecular compounds with ether, 3^o amines and oxygenated compounds. BF_3 reacts with N_2O_4 in the gas phase and in liq. SO_2 to yield white crystalline solids of the type, $\text{N}_2\text{O}_4 \cdot \text{BF}_3$ and $\text{N}_2\text{O}_4 \cdot 2\text{BF}_3$

e) Applications

Liquid N_2O_4 as a fuel in the Apollo missions

During the Apollo Moon missions, a propulsion system was required that could be used to alter the velocity of the spacecraft and change its orbit during landing on and take-off from the Moon's surface. The fuel chosen was a mixture of liquid N_2O_4 and derivatives of hydrazine (N_2H_4). Dinitrogen tetroxide is a powerful oxidizing agent and contact with, for example, MeNHNH_2 leads to immediate oxidation of the latter:



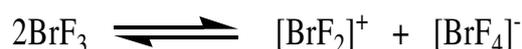
The reaction is highly exothermic, and at the operating temperatures, all products are gases. Safety is of utmost importance; the fuels clearly must not contact each other before the required moment of landing or lift-off. Further, MeNHNH_2 is extremely toxic.



The command module of Apollo 17 in orbit above the lunar surface

16.7 Liquid Bromine trifluoride as a solvent*Physical Properties*

Bromine trifluoride is a pale yellow liquid at 25 °C and is an aprotic non-aqueous solvent. Selected physical properties are given in Table 5. Bromine trifluoride is an extremely powerful fluorinating agent and fluorinates the compound that dissolves in it. However, massive quartz is kinetically stable towards BrF₃ and the solvent can be handled in quartz vessels. Apparatus made from Cu, Ni or Monel metal (68% Ni and 32% Cu) can also be used; the metal surface becomes protected by a thin layer of metal fluoride. The BrF₃ undergoes self-ionization to yield [BrF₂]⁺ and [BrF₄]⁻ ions and this has been demonstrated by the isolation and characterization of salt containing them, and by conductometric titrations of them. According to the solvent-based acid–base definitions, an acid in BrF₃ is a species that produces [BrF₂]⁺ and a base is one that gives BrF₄⁻

**Table 5. Physical properties of liquid BrF₃****Property / units Value**

Melting point /K -281.8

Boiling point /K- 408

Density of liquid / g cm⁻³ - 2.49

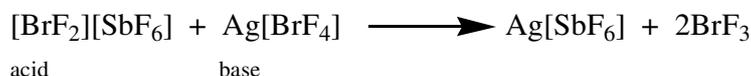
Relative permittivity - 107

Self ionization constant - 8.0x10⁻³ (at 281.8 K)

Fluoride salts and molecular fluorides in BrF₃ acts as a Lewis acid, readily accepting F⁻. When dissolved in BrF₃, alkali metal fluorides, BaF₂ and AgF combine with the solvent to give salts containing the [BrF₄]⁻ anion, e.g. K[BrF₄], Ba[BrF₄]₂ and Ag[BrF₄]. On the other hand, if the fluoride solute is a more powerful F⁻ acceptor than BrF₃, salts containing [BrF₂]⁺ are formed.

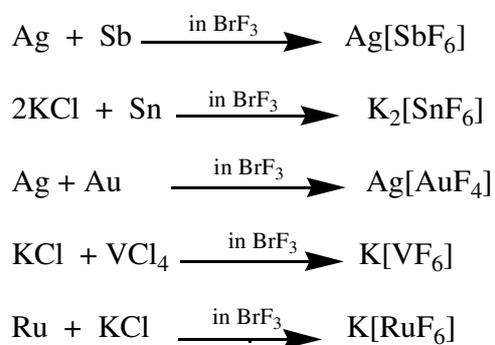


A conductometric titration of $[\text{BrF}_2][\text{SbF}_6]$ against $\text{Ag}[\text{BrF}_4]$ exhibits a minimum at a 1:1 ratio supporting neutralization reaction as shown below:



a) Reactions in BrF_3

Much of the chemistry studied in BrF_3 media involves fluorination reactions, and the preparation of highly fluorinated species. For example, the salt $\text{Ag}[\text{SbF}_6]$ can be prepared in liquid BrF_3 from Ag and Sb elements in a 1:1 molar ratio, and $\text{K}_2[\text{SnF}_6]$ is produced when KCl and Sn are combined in a 2:1 molar ratio in liquid BrF_3 . Some other examples are given below:



In contrast to the situation for H_2SO_4 , where we noted that it is difficult to separate reaction products from the solvent by evaporation, BrF_3 can be removed in vacuo ($\Delta_{\text{vap}}H^\circ = 47.8 \text{ kJ mol}^{-1}$). Some of the compounds prepared in liquid BrF_3 can also be made using F_2 as the fluorinating agent, but use of F_2 generally requires higher reaction temperatures and the reactions are not always product-specific.

16.8 Summary of the Unit

Although many inorganic reactions take place in aqueous solution, it is not always suitable to use water as a solvent. So, this chapter discusses the utility of non-aqueous solvents to carry out different types of reactions. As we discuss the properties and uses of some non-aqueous solvents, we must keep in mind that the extent to which non-aqueous solvents can be used is limited by the fact that many are highly reactive. Data are scarce for non-aqueous media especially in solvents of relative permittivity lower than that of water for which data are difficult to interpret because of ion-association. Therefore, much of the discussion centres on the properties and uses of selected non-aqueous solvents.

The Chemistry of the specific solvents discussed in this chapter illustrates the scope and utility of nonaqueous solvents. However, as a side note, several other nonaqueous solvents should at least be mentioned. For example, oxyhalides such as OSeCl_2 and OPCl_3 also have received a great deal of use as nonaqueous solvents.

16.9 Key words

Liquid ammonia; Liquid Hydrogen Fluoride; Liquid Sulfur dioxide; Anhydrous sulphuric acid; Liquid Dinitrogen Tetraoxide; Liquid Bromine trifluoride

16.10 References for further study:

1. Inorganic Chemistry, 4th Ed., J. E. Huheey, E.A. Keiter and R. L. Keiter, O. K. Medhi, Pearson Education, 2009.
2. Theoretical Inorganic chemistry – M. C. Day and J.Selbin.
3. Concepts and Methods of Inorganic Chemistry – B. E. Douglas and D. H. McDaniel.
4. Inorganic chemistry – An Advanced Text book – Therald Moeller.

16.11 Questions for self understanding

- a) Which of the following compounds behave as acids in liquid HF: ClF_3 , BF_3 , SbF_5 , SiF_4 ?
Write equations to explain this behaviour.
- b) Suggest explanations for the following observations
 - (i) In aqueous solution, AgNO_3 and KCl react to give a precipitate of AgCl , whereas in liquid NH_3 , KNO_3 and AgCl react to produce a precipitate of KCl .
 - (ii) NH_2 behaves as a base in liquid NH_3 .
 - (iii) $\text{CH}_3\text{CO}_2\text{H}$ behaves as a weak acid in aqueous solution, but is leveled to a strong acid in liquid ammonia.
 - (iv) Organic amines and amides can function as acids in liquid ammonia.
 - (v) Strong oxidizing agents apparently do not exist in liquid NH_3 . Give reasons.
 - (vi) SOCl_2 behaves as an acid in anhydrous SO_2 . Account for this.
 - (vii) Discuss the different types of reactions studied in liquid NH_3 . What are the limitations of this solvent?
 - (viii) Which properties of a non aqueous solvent determine its suitability as a medium for studying inorganic reactions? Discuss.
 - (ix) Discuss the advantages and disadvantages of using liquid SO_2 as a solvent. Give its solvolytic reactions.

- (x) Urea, a non-electrolyte in water, acts as an acid in liquid NH_3 and base in anhydrous H_2SO_4 . Account for this.
- (xi) Zinc amide is insoluble in liquid NH_3 , but dissolves on addition of KNH_2 . Explain.
- (xii) Outline the various types of reactions studied in anhydrous H_2SO_4 . What are the limitations of this solvent?
- (xiii) Describe the auto-ionization, solvolytic and solvation reactions of liquid ammonia, HF , SO_2 , BrF_3 and N_2O_4 .
- (xiv) Why N_2O_4 is a poor solvent for ionic compounds?
- (xv) Suggest how AgF behaves when dissolved in BrF_3 .