11082CH04

UNIT 4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Objectives

After studying this Unit, you will be able to

- understand Kössel-Lewis approach to chemical bonding;
- explain the octet rule and its limitations, draw Lewis structures of simple molecules;
- explain the formation of different types of bonds;
- describe the VSEPR theory and predict the geometry of simple molecules;
- explain the valence bond approach for the formation of covalent bonds;
- predict the directional properties of covalent bonds;
- explain the different types of hybridisation involving *s*, *p* and *d* orbitals and draw shapes of simple covalent molecules;
- describe the molecular orbital theory of homonuclear diatomic molecules;
- explain the concept of hydrogen bond.

> ***“Scientists are constantly discovering new compounds, orderly arranging the facts about them, trying to explain with the existing knowledge, organising to modify the earlier views or evolve theories for explaining the newly observed facts.”***

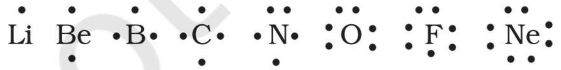
Matter is made up of one or different type of elements. Under normal conditions no other element exists as an independent atom in nature, except noble gases. However, a group of atoms is found to exist together as one species having characteristic properties. Such a group of atoms is called a molecule. Obviously there must be some force which holds these constituent atoms together in the molecules. **The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.** Since the formation of chemical compounds takes place as a result of combination of atoms of various elements in different ways, it raises many questions. Why do atoms combine? Why are only certain combinations possible? Why do some atoms combine while certain others do not? Why do molecules possess definite shapes? To answer such questions different theories and concepts have been put forward from time to time. These are Kössel-Lewis approach, Valence Shell Electron Pair Repulsion (VSEPR) Theory, Valence Bond (VB) Theory and Molecular Orbital (MO) Theory. The evolution of various theories of valence and the interpretation of the nature of chemical bonds have closely been related to the developments in the understanding of the structure of atom, the electronic configuration of elements and the periodic table. Every system tends to be more stable and bonding is nature’s way of lowering the energy of the system to attain stability.

4.1 KÖSSEL-LEWIS APPROACH TO CHEMICAL BONDING

In order to explain the formation of chemical bond in terms of electrons, a number of attempts were made, but it was only in 1916 when Kössel and Lewis succeeded independently in giving a satisfactory explanation. They were the first to provide some logical explanation of valence which was based on the inertness of noble gases.

Lewis pictured the atom in terms of a positively charged 'Kernel' (the nucleus plus the inner electrons) and the outer shell that could accommodate a maximum of eight electrons. He, further assumed that these eight electrons occupy the corners of a cube which surround the 'Kernel'. Thus the single outer shell electron of sodium would occupy one corner of the cube, while in the case of a noble gas all the eight corners would be occupied. This octet of electrons, represents a particularly stable electronic arrangement. **Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds.** In the case of sodium and chlorine, this can happen by the transfer of an electron from sodium to chlorine thereby giving the Na^+ and Cl^- ions. In the case of other molecules like Cl_2, H_2, F_2, etc., the bond is formed by the sharing of a pair of electrons between the atoms. In the process each atom attains a **stable outer octet of electrons**.

Lewis Symbols: In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as **valence electrons**. The inner shell electrons are well protected and are generally not involved in the combination process. G.N. Lewis, an American chemist introduced simple notations to represent valence electrons in an atom. These notations are called **Lewis symbols**. For example, the Lewis symbols for the elements of second period are as under:



Significance of Lewis Symbols : The number of dots around the symbol represents the number of valence electrons. This number of valence electrons helps to calculate the common or **group valence** of the element. The group valence of the elements is generally either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.

Kössel, in relation to chemical bonding, drew attention to the following facts:

- In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases;
- The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms;
- The negative and positive ions thus formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a particularly stable outer shell configuration of eight (octet) electrons, ns^2np^6.
- The negative and positive ions are stabilized by electrostatic attraction.

For example, the formation of NaCl from sodium and chlorine, according to the above scheme, can be explained as:

$$\underset{[Ne]\,3s^1}{Na} \rightarrow \underset{[Ne]}{Na^+} + e^-$$

$$\underset{[Ne]\,3s^2\,3p^5}{Cl + e^-} \rightarrow \underset{[Ne]\,3s^2\,3p^6 \text{ or } [Ar]}{Cl^-}$$

$$Na^+ + Cl^- \rightarrow NaCl \text{ or } Na^+Cl^-$$

Similarly the formation of CaF_2 may be shown as:

$$\underset{[Ar]4s^2}{Ca} \rightarrow \underset{[Ar]}{Ca^{2+}} + 2e^-$$

$$\underset{[He]\,2s^2\,2p^5}{F + e^-} \rightarrow \underset{[He]\,2s^2\,2p^6 \text{ or } [Ne]}{F^-}$$

$$Ca^{2+} + 2F^- \rightarrow CaF_2 \text{ or } Ca^{2+}(F^-)_2$$

The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as

the electrovalent bond. The electrovalence is thus equal to the number of unit charge(s) on the ion. Thus, calcium is assigned a positive electrovalence of two, while chlorine a negative electrovalence of one.

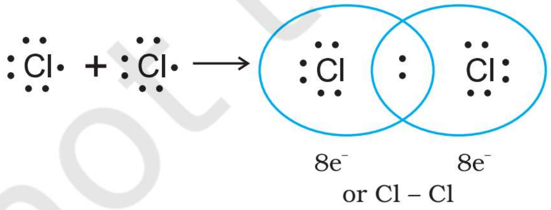
Kössel's postulations provide the basis for the modern concepts regarding ion-formation by electron transfer and the formation of ionic crystalline compounds. His views have proved to be of great value in the understanding and systematisation of the ionic compounds. At the same time he did recognise the fact that a large number of compounds did not fit into these concepts.

4.1.1 Octet Rule

Kössel and Lewis in 1916 developed an important theory of chemical combination between atoms known as **electronic theory** of **chemical bonding**. According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as **octet rule**.

4.1.2 Covalent Bond

Langmuir (1919) refined the Lewis postulations by abandoning the idea of the stationary cubical arrangement of the octet, and by introducing the term **covalent bond**. The Lewis-Langmuir theory can be understood by considering the formation of the chlorine molecule,Cl_2. The Cl atom with electronic configuration, $[Ne]3s^2\,3p^5$, is one electron short of the argon configuration. The formation of the Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon).



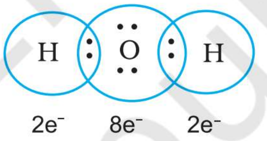
or Cl – Cl

Covalent bond between two Cl atoms

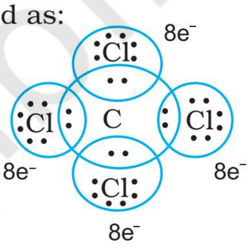
The dots represent electrons. Such structures are referred to as Lewis dot structures.

The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different. The important conditions being that:

- Each bond is formed as a result of sharing of an electron pair between the atoms.
- Each combining atom contributes at least one electron to the shared pair.
- The combining atoms attain the outer-shell noble gas configurations as a result of the sharing of electrons.
- Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as:

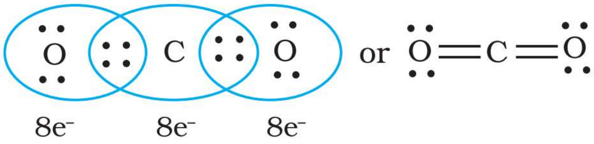


H atoms attain a duplet of electrons and O, the octet

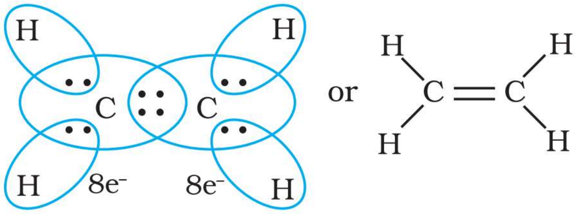


Each of the four Cl atoms along with the C atom attains octet of electrons

Thus, when two atoms share one electron pair they are said to be joined by a single covalent bond. In many compounds we have **multiple bonds** between atoms. The formation of multiple bonds envisages sharing of more than one electron pair between two atoms. **If two atoms share two pairs of electrons, the covalent bond between them is called a double bond.** For example, in the carbon dioxide molecule, we have two double bonds between the carbon and oxygen atoms. Similarly in ethene molecule the two carbon atoms are joined by a double bond.

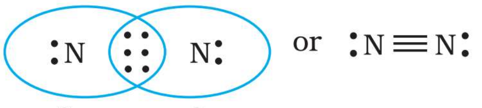


Double bonds in CO_2 molecule

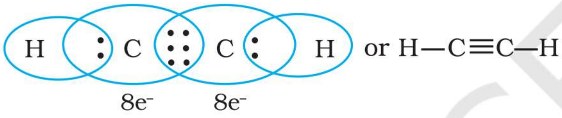


C_2H_4 *molecule*

When combining atoms share three electron pairs as in the case of two nitrogen atoms in the N_2 molecule and the two carbon atoms in the ethyne molecule, a triple bond is formed.



N_2 *molecule*



C_2H_2 *molecule*

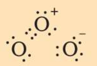
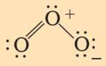
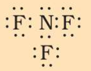
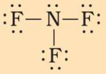
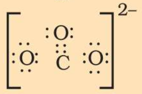
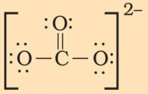
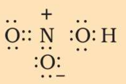
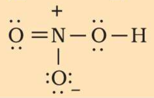
4.1.3 Lewis Representation of Simple Molecules (the Lewis Structures)

The Lewis dot structures provide a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule. While such a picture may not explain the bonding and behaviour of a molecule completely, it does help in understanding the formation and properties of a molecule to a large extent. Writing of Lewis dot structures of molecules is, therefore, very useful. The Lewis dot structures can be written by adopting the following steps:

- The total number of electrons required for writing the structures are obtained by adding the valence electrons of the combining atoms. For example, in the CH_4 molecule there are eight valence electrons available for bonding (4 from carbon and 4 from the four hydrogen atoms).
- For anions, each negative charge would mean addition of one electron. For cations, each positive charge would result in subtraction of one electron from the total number of valence electrons. For example, for the CO_3^{2-} ion, the two negative charges indicate that there are two additional electrons than those provided by the neutral atoms. For NH_4^+ ion, one positive charge indicates the loss of one electron from the group of neutral atoms.
- Knowing the chemical symbols of the combining atoms and having knowledge of the skeletal structure of the compound (known or guessed intelligently), it is easy to distribute the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.
- In general the least electronegative atom occupies the central position in the molecule/ion. For example in the NF_3 and CO_3^{2-}, nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions.
- After accounting for the shared pairs of electrons for single bonds, the remaining electron pairs are either utilized for multiple bonding or remain as the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons.

Lewis representations of a few molecules/ions are given in Table 4.1.

Table 4.1 The Lewis Representation of Some Molecules

Molecule/Ion		Lewis Representation
H_2	H : H*	H – H
O_2	:Ö::Ö:	:Ö=Ö:
O_3		
NF_3		
CO_3^{2-}		
HNO_3		

* Each H atom attains the configuration of helium (a duplet of electrons)

Problem 4.1

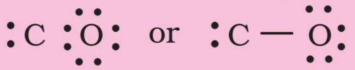
Write the Lewis dot structure of CO molecule.

Solution

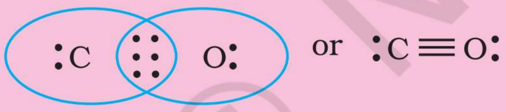
Step 1. Count the total number of valence electrons of carbon and oxygen atoms. The outer (valence) shell configurations of carbon and oxygen atoms are: $2s^2\ 2p^2$ and $2s^2\ 2p^4$, respectively. The valence electrons available are 4 + 6 =10.

Step 2. The skeletal structure of CO is written as: C O

Step 3. Draw a single bond (one shared electron pair) between C and O and complete the octet on O, the remaining two electrons are the lone pair on C.



This does not complete the octet on carbon and hence we have to resort to multiple bonding (in this case a triple bond) between C and O atoms. This satisfies the octet rule condition for both atoms.



Problem 4.2

Write the Lewis structure of the nitrite ion, NO_2^-.

Solution

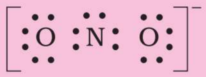
Step 1. Count the total number of valence electrons of the nitrogen atom, the oxygen atoms and the additional one negative charge (equal to one electron).

N($2s^2\ 2p^3$), O ($2s^2\ 2p^4$)

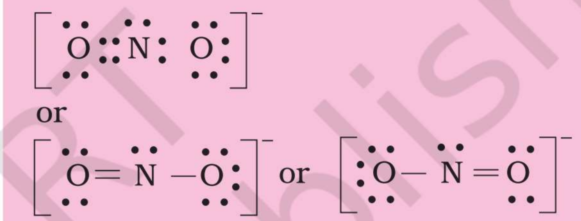
5 + (2 × 6) +1 = 18 electrons

Step 2. The skeletal structure of NO_2^- is written as : O N O

Step 3. Draw a single bond (one shared electron pair) between the nitrogen and each of the oxygen atoms completing the octets on oxygen atoms. This, however, does not complete the octet on nitrogen if the remaining two electrons constitute lone pair on it.



Hence we have to resort to multiple bonding between nitrogen and one of the oxygen atoms (in this case a double bond). This leads to the following Lewis dot structures.



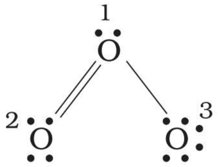
4.1.4 Formal Charge

Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as :

$$\text{Formal charge (F.C.) on an atom in a Lewis structure} = \left[\begin{array}{l}\text{total number of valence}\\ \text{electrons in the free}\\ \text{atom}\end{array}\right] - \left[\begin{array}{l}\text{total number of non}\\ \text{bonding (lone pair)}\\ \text{electrons}\end{array}\right] - (1/2)\left[\begin{array}{l}\text{total number of}\\ \text{bonding(shared)}\\ \text{electrons}\end{array}\right]$$

The counting is based on the assumption that the atom in the molecule owns one electron of each shared pair and both the electrons of a lone pair.

Let us consider the ozone molecule (O_3). The Lewis structure of O_3 may be drawn as :



The atoms have been numbered as 1, 2 and 3. The formal charge on:

- The central O atom marked 1

$$= 6 - 2 - \frac{1}{2}(6) = +1$$

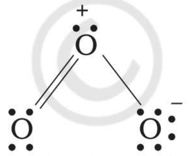
- The end O atom marked 2

$$= 6 - 4 - \frac{1}{2}(4) = 0$$

- The end O atom marked 3

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

Hence, we represent O_3 along with the formal charges as follows:



We must understand that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. **Generally the lowest energy structure is the one with the smallest formal charges on the atoms. The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.**

4.1.5 Limitations of the Octet Rule

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2 and BCl_3.

$$\text{Li}:\text{Cl} \qquad \text{H}:\text{Be}:\text{H} \qquad \text{Cl}:\overset{\text{Cl}}{\overset{\cdot\cdot}{\text{B}}}:\text{Cl}$$

Li, Be and B have 1,2 and 3 valence electrons only. Some other such compounds are $AlCl_3$ and BF_3.

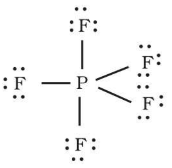
Odd-electron molecules

In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2, the octet rule is not satisfied for all the atoms

The expanded octet

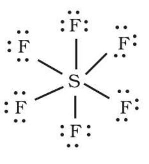
Elements in and beyond the third period of the periodic table have, apart from 3*s* and 3*p* orbitals, 3*d* orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

Some of the examples of such compounds are: PF_5, SF_6, H_2SO_4 and a number of coordination compounds.



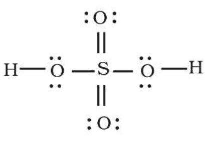
PF_5

10 electrons around the P atom



SF_6

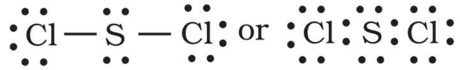
12 electrons around the S atom



H_2SO_4

12 electrons around the S atom

Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.



$$:\ddot{\underset{\cdot\cdot}{Cl}} - \ddot{\underset{\cdot\cdot}{S}} - \ddot{\underset{\cdot\cdot}{Cl}}: \text{ or } :\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{S}}:\ddot{\underset{\cdot\cdot}{Cl}}:$$

Other drawbacks of the octet theory

- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2, KrF_2, $XeOF_2$ etc.,
- This theory does not account for the shape of molecules.
- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

4.2 IONIC OR ELECTROVALENT BOND

From the Kössel and Lewis treatment of the formation of an ionic bond, it follows that the formation of ionic compounds would primarily depend upon:

- The ease of formation of the positive and negative ions from the respective neutral atoms;
- The arrangement of the positive and negative ions in the solid, that is, the lattice of the crystalline compound.

The formation of a positive ion involves ionization, i.e., removal of electron(s) from the neutral atom and that of the negative ion involves the addition of electron(s) to the neutral atom.

$M(g) \rightarrow M^+(g) + e^-$; Ionization enthalpy

$X(g) + e^- \rightarrow X^-(g)$; Electron gain enthalpy

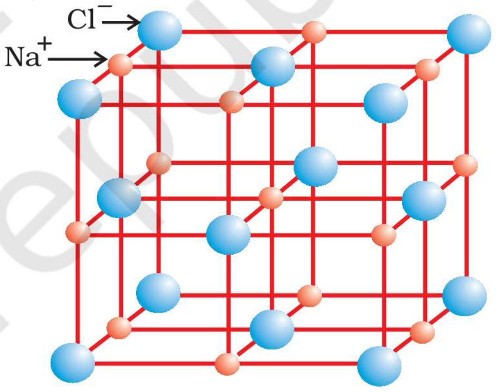
$M^+(g) + X^-(g) \rightarrow MX(s)$

The **electron gain enthalpy, $\Delta_{eg}H$,** is the enthalpy change (Unit 3), when a gas phase atom in its ground state gains an electron. The electron gain process may be exothermic or endothermic. The ionization, on the other hand, is always endothermic. Electron affinity, is the negative of the energy change accompanying electron gain.

Obviously ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively high negative value of electron gain enthalpy.

Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, NH_4^+ (made up of two non-metallic elements) is an exception. It forms the cation of a number of ionic compounds.

Ionic compounds in the crystalline state consist of orderly three-dimensional arrangements of cations and anions held together by coulombic interaction energies. These compounds crystallise in different crystal structures determined by the size of the ions, their packing arrangements and other factors. The crystal structure of sodium chloride, NaCl (rock salt), for example is shown below.



Rock salt structure

In ionic solids, the sum of the electron gain enthalpy and the ionization enthalpy may be positive but still the crystal structure gets stabilized due to the energy released in the formation of the crystal lattice. For example: the ionization enthalpy for $Na^+(g)$ formation from Na(g) is 495.8 kJ mol^{-1} ; while the electron gain enthalpy for the change $Cl(g) + e^- \rightarrow Cl^-(g)$ is, – 348.7 kJ mol^{-1} only. The sum of the two, 147.1 kJ mol^{-1} is more than compensated for by the enthalpy of lattice formation of NaCl(s) (–788 kJ mol^{-1}). Therefore, the energy released in the